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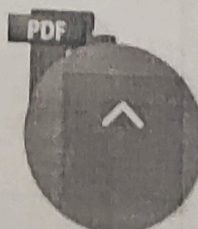
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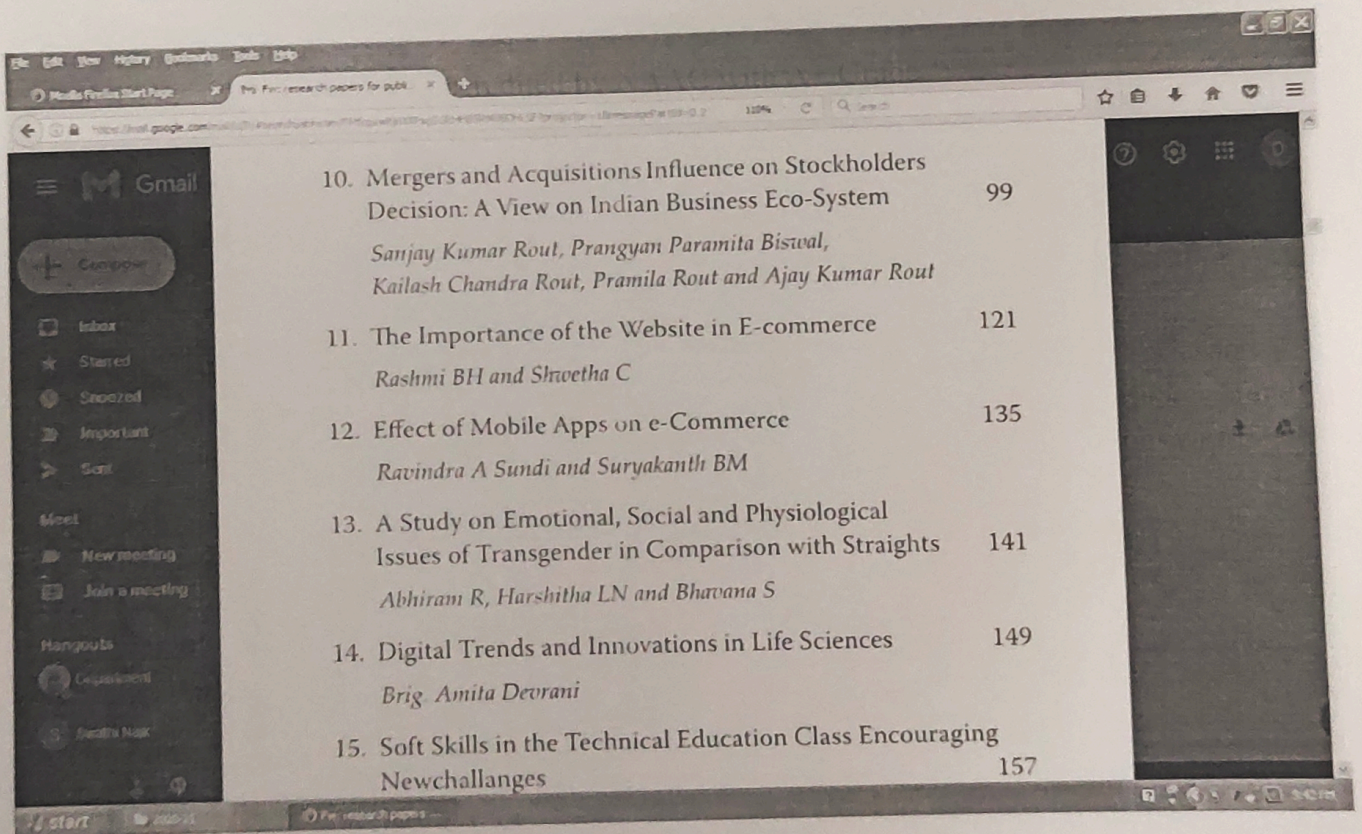
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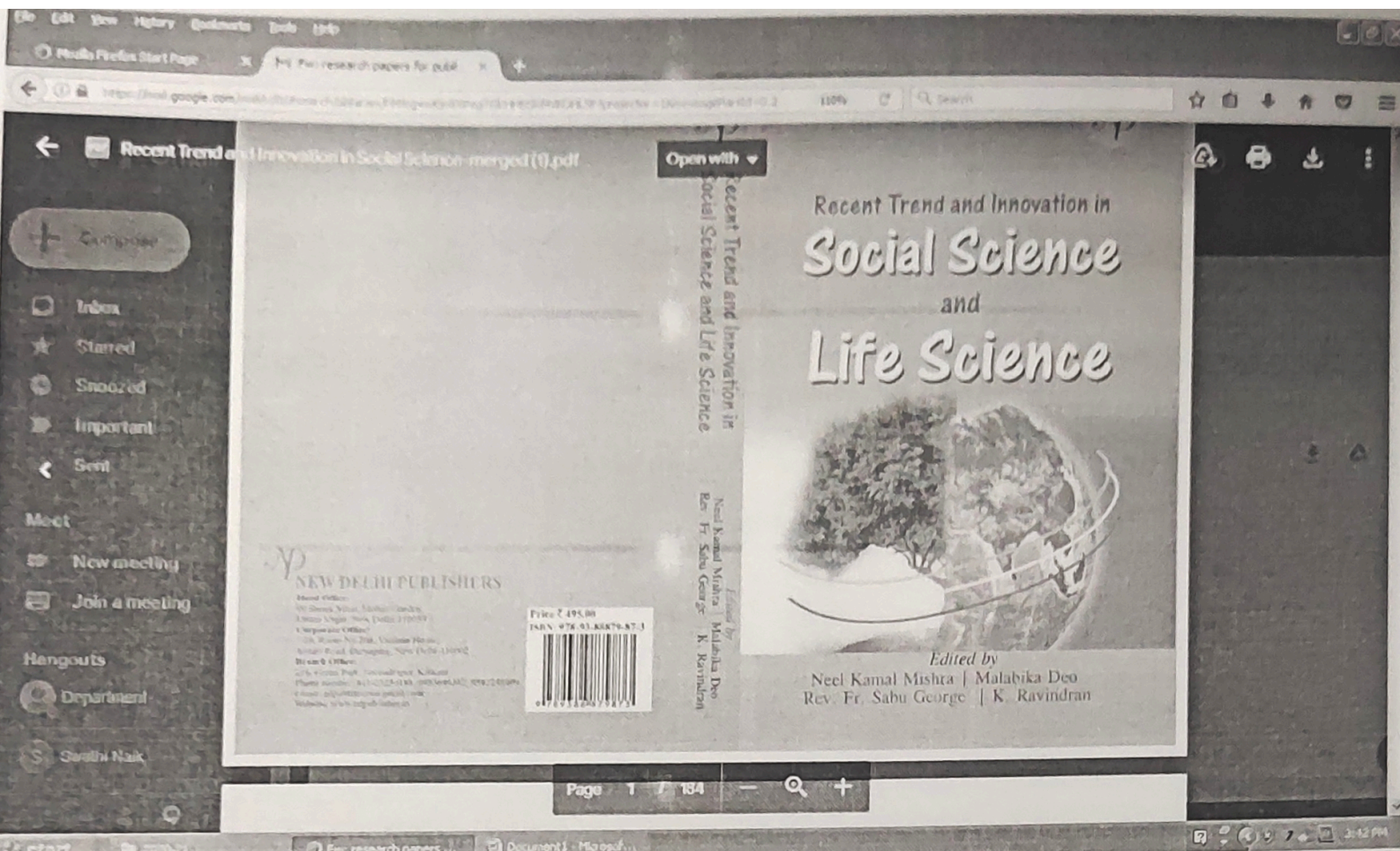
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**Dr. Jayaram Kanzal** M.Com., MBA, M.Phil, Ph.D.  
Visiting Professor to various B-Schools  
in and outside India, Bengaluru.

**Dr. B. M. Rama Murthy** MBA, M.Phil, Ph.D.  
Associate. Prof., Program Director,  
AIMS Institute, Bengaluru.

**Tabreez Pasha** M.Com., MBA, (Ph.D.)  
Asst. Prof., Department of Commerce and Management,  
Surana College, Bengaluru.



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## *Preface*

We have great pleasure in presenting the first edition “*Monetary System*” written for students of UG and PG courses. The subject matter is written in a simple and easily understandable language with sufficient support from real information.

The language of the book is simple and the coverage of various unit is exhaustive with examples. This work is prepared as a basic material for the learners to know fully about Monetary System. We have tried to make the book very useful for the students but still we will thankfully solicit and incorporate the suggestions of our readers. This title “Monetary System” provides them an opportunity to develop the skills necessary to meet the challenges.

This is an attempt to provide the students with thorough understanding of Practicals on Monetary System concepts. In writing this book we have benefited immensely from the studies of a number of books and the articles written by scholars spread over diversely.

We are sure this book will prove to be useful to students and teachers alike. The book would not have seen the light, but for the grace of God and the blessings and support of our family members and friends.

We offer our gratitude to Himalaya Publishing House Pvt. Ltd., who is leader in Commerce and Management publications. Our sincere regards to Mr. Niraj Pandey and Mr. Vijay Pandey for interest shown and for the best effort put forth in publishing this book.

Finally, we express our sincere thank to SPS, Bengaluru, for their excellent computer typesetting work and the printing.

Any suggestions regarding improvement of errors, if any, will gratefully be acknowledged.

*Bengaluru*  
*Feb., 2021*

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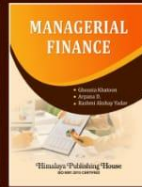
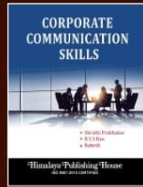
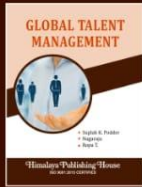
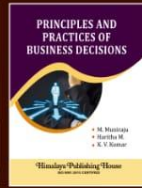
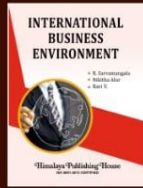
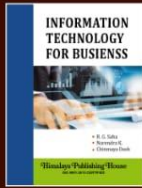
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# National Education Policy 2020: Vision for India's future Education

Editors

Dr. Riya Tiwari

Dr. S.G. Sharma

Dr. Yogita Jiwane

# **National Education Policy 2020: Vision for India's future Education**

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**Dr. S.G. Sharma**

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## Preface

*“The purpose of education is to make good human beings with skill and expertise. Enlightened human beings can be created by teachers.”*

**Dr. Kalam**

Education is essential for developing full human potential and promoting national development. Education must make a personality, enable learners to be ethical, rational, compassionate, and caring, while preparing them for gainful, fulfilling employment. As we all know, the humanity is undergoing fast transforms within the awareness landscape, with different remarkable technical and scientific advances, like the rise of massive data, appliance learning, and machines which will take over AI, many unskilled jobs worldwide. Simultaneously, the need for a trained labor pool, mainly connecting with data science and computer, together through multidisciplinary skills across the sciences, social sciences, and humanities, will be even more in more significant demand. With atmosphere change, rising toxic industrial waste, and depleting natural assets, there will be a significant shift in how we meet the world's force, water, food, and sanitation needs, again leading to the necessity for brand spanking new skillful labor, particularly in biology, chemistry, physics, agriculture, climate science, and science Education exposes the mind, expands it, and allows someone to enhance their lives in numerous ways.

The present edited book's theme supported National Education Policy 2020; authors from different specialization areas contributed their views on the new education policy. Through this book, the editor wants to form awareness and understanding of NEP 2020. As we all know that, after years of in-depth examination and discussion, the National Education Policy 2020 launched. It is already broadly discussed across the state. Citizens from different areas are participating in the discussion on an equivalent. After a comprehensive investigation and discussion, the National Education Policy launched and broadly talked about it across the country.

Our Prime Minister, Mr. Narendra Modi, also thrown light on NEP 2020, he said so far, we have been specializing in 'What to Think' in our education policy. Within the NEP, we specialize in 'How to think.' there is an avalanche of data during this digital era, and thus, we have tried to filter what is not needed. How can our Yonge generation think critically and innovate unless we ensure a purpose within the education system? The four-dimensional structure 5+3+3+4 - moving forward from 10+2 structure - may be a step during this direction." it is essential to form NEP 2020, so understanding new changes may be a must; this NEP2020. National Education Policy 2020 will set the inspiration for 21st century India. We have given extra impetus to the present national policy for ensuring that it makes Indians more empowered and only attractive to opportunities. During this new techno era, an individual must find new skills and not be to one profession all his life, get to update his/her self with new skills, re-skill, and up-skill. The formulation of national education policy predicated on this thought. This National Education Policy imagines a teaching-learning structure deep-rooted in the Indian culture that put in straight to reworking India. This NEP 2020 envisions an education system rooted in Indian ethos that contributes to transforming India, Bharat, sustainably an equitable and intellectual nation, by providing high-quality education to all or any, thereby making India a worldwide knowledge super power. The policy envisages that our institutions' curriculum and pedagogy must develop a deep sense of respect towards the primary Duties and Constitutional values, bonding with one's country, and conscious awareness of one's roles and responsibilities changing the world. The policy's vision is developing knowledge, skills, values, and dispositions that support responsible commitment to human rights, sustainable development and living, and global well-being, thereby reflecting a global citizen.

**Chief Editor**

Dr. S.G. Sharma

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# Growing Demand for Online Courses as a Tool for Academic Enhancement and Executive Development

**Savita Shastri<sup>#</sup>**

*<sup>#</sup>Assistant Professor, Department of MBA,  
Surana College, Bangalore University.*

*E-mail Id: savita.mba@suranacollege.edu.in*

## Abstract

The advent of computers, mobile phones, tablets and internet have brought in a revolution in many aspects of our life. Teaching and Learning is one of the most affected aspects of growing advancements in technology. Classroom Teaching has given way to online learning and books have been replaced with pen drives and e-books. E-Learning or Online Learning or Virtual Learning can be defined as a learning system which is based on formalized teaching with the help of electronic resources.

Online Learning was viewed as an impersonal medium of learning, but its usefulness in terms of reachability and cost effectiveness cannot be overlooked. The Online Education Market has seen rapid growth over the past decade. It was valued at INR 39 Billion in 2018 and is p to reach INR 360.3 Billion by the year 2024. This results in a CAGR of 43.85% between 2018–2024. The Online Higher Education Market valued at INR 5.03 Billion in 2018 is expected to reach INR 40.63 Billion by 2024.

The demand for online courses is growing rapidly among working professionals and students pursuing higher education. Online courses are being taken up my students as an add-on tool for Academic Enhancement and

working professionals view it as a source of Executive Development. The conventional education system has its limitations and is unable to cater to all, hence the popularity and effectiveness of online courses cannot be underestimated. The article here brings out various aspects of online courses and mentions in detail the many online learning platforms available to students and working professionals for academic enhancement and development. The article also looks at the progressive nature of National Education Policy 2020 in giving a boost to Online Education in India.

**Keywords:** Online Learning, E-Learning, Virtual Learning, Higher education, academic enhancement, NEP 2020

## **Introduction**

The Indian Education system has always been a target of criticism in terms of its obsolete curriculum, rote learning, quality of teaching and lack of infrastructure. These factors have paved the way for growth of online education in India. Online courses are largely accessible to anyone with an Internet connection and a computer or mobile device. This allows individuals, teams and friends to participate across the country or across the globe and enhance their knowledge and skill.

An online course is a way to learn a new skill or gain some new knowledge from the comfort of one's own home. These online courses can either be paid courses or offered for free. Some are offered by educational institutions, while others are delivered by experts in their field. Simplicity of learning, convenience, adaptability and a wide range of study materials are some of the features which draw people towards online courses. The most important thing for an online course to be popular and sought after is for it to be engaging and to deliver a clear outcome.

Being a country with growing young population, education as a sector seems to be on an acceleration mode. India's E-learning market is the second biggest after the US which is anticipated to develop by 15.64 percent and surpass \$48 billion by 2020. Online courses give wide and detailed knowledge directly to individuals in a convenient and flexible way. These online courses help to broaden the awareness and skill level of students pursuing higher education. Online Courses also help executives and professionals to develop their leadership and management skills or gain business insights through analytics.

## **Meaning & Definition**

The concept of Online Education is around 170 years old, when a correspondence course was offered in Great Britain wherein the instructor sent lessons and received assignments through mail. With this Distance Learning was born and modern Online Courses are a modern version of this.

An online course is a course that is focused on use of information and communications technology for learning. An online course does not require any face-to-face meetings in a physical location. In an online course 80% of the instruction and interaction between instructor and student happens online.

An online course refers to “a set of instructional experiences using the digital network for interaction, learning and dialogue.”

An online course is “the delivery of a series of lessons on a web browser or mobile device, which can be accessed anytime and anywhere.”

Online courses are designed as an online environment for convenient learning. Web-centric courses (also called hybrid or blended courses) are similar to online courses but require regular scheduled face-to-face classes or meetings.

## Types of Online Courses

Online courses with the help of technological innovations have become a viable option for both students as well as working professionals. Online courses were never made to be generic. They can be customized according to the end user. Following are some of the popular formats of online courses.

- **The Flipped Course:** This is the most common type of online course which is also one of the most effective medium of online learning. In this the instructor delivers the important points of the session consuming only 10% time, whereas the participants interact freely during the remaining 90% of the session time. These types of courses can be categorized as active learning environments.
- **The Hybrid Course:** This is a combination of a Flipped Course and a Face-to face course and is also known as a Blended course. In this the time given to participants for interaction is slightly more as compared to Face to face course. The instructor provides information and opens up the topic for discussion among learners.
- **Face to Face Course:** This involves a face to face interaction between the trainer /instructor and participants. This format is like a real-world classroom setting. Under this the instructor consumes more time and the participants ask questions when in doubt.
- **Web Based Course:** This is more of a passive learning course. In this the learning content is uploaded in the form of a document, video or pdf which can be accessed by the participants anytime, at their own convenience. This course allows flexibility and freedom to participants. Doubts and question can be posted online and will be addressed by the instructor later.
- **Peer Instruction Course:** A new concept from Harvard, this form of online course instruction is quite new and requires no interaction between instructor and students. In this the instructor posts the course syllabus on a virtual clipboard and it

will be the students themselves who will discuss for themselves regarding the details of the subject in a forum style medium. The absence of an authority figure can make students more comfortable.

- **Web Enhanced Course:** This is a combination of Web Based and face to face course format. The Web-enhanced format allows the instructor to meet the class at an allotted time and date to discuss the key points of a module .Like the face-to-face model, the instructor can remotely interact with the students by asking them questions and answering theirs in return. The students still have the option to finish the course at their own pace.
- **MOOC:** Massive Open Online Course is a platform which caters to large number of students. This is ideal for University professors who want to take a transition from traditional classroom to a Virtual classroom. MOOC is effective in delivering a session to large number of students.

## **Online Course Platforms**

Online courses have changed the style of learning and have upset conventional learning. Online Course Platforms are types of Learning Management Systems that provide users with access to digital classes. Today there are many platforms providing online courses for all categories of learners. There are specific courses for students as well as working professionals.

The online platforms offer free as well as paid courses. Learners have to take the online course of their choice, submit assignments and are eligible for a Course Completion Certificate. There are free courses also available which can be taken only for knowledge enhancement, but do not provide the learner with any certificate of recognition.

Majority of the candidates availing the online courses are in the age group of 18-34 years. Following are the 10 popular online course platforms delivering online education.



- **Swayam:** This is a program initiated by the Government of India and designed to achieve triple objectives of education, i.e. access, equity and quality. Swayam is a platform which brings courses starting from Class 9 to post graduation under one digital platform. All the courses are interactive and prepared by best teachers of the country. The current Swayam platform is developed by Ministry of Human Resource Development (MHRD) and NPTEL, IIT Madras with the help of Google Inc. and Persistent Systems Ltd.
- **NPTEL:** National Programme on Technology Enhanced Learning (NPTEL) is an initiative by Ministry of Human Resource Development to make learning accessible to all. The courses are structured and delivered by experts of Indian Institute of Technology and Indian Institute of Science. NPTEL offers 900 plus courses which are of 4 weeks to 8 weeks duration. These courses are designed for graduates, undergraduates and working professionals for enhancing their academic qualifications as well as giving them an edge at workplace.
- **Udemy:** Udemy, Inc is an American Online Learning Platform for students and professionals. It was founded in 2010 and currently has 35 million enrolments. It offers short term courses in 65 languages. Udemy is a platform that allows instructors to create online courses on their preferred and contemporary topics. This online platform offers 1,50,000 courses which comprises of both free and paid courses. Udemy is a part of growing MOOC movement and has been a recognized medium for online learning. The goal of Udemy is to disrupt and democratize the educational system.
- **Coursera:** This online course platform was founded in 2012 by professors of Stanford University and currently offers four week to twelve week courses. There are also on-demand courses wherein the users can take their own time in completing the course. Coursera works with universities and other organizations to offer courses, certifications and degrees in a wide variety of subjects. As on June 2020, Coursera

recorded 65 million users. More than 200 of the world's top universities and industry experts have partnered with Coursera for academic enhancement of their students and also development of their employees.

- **Saylor Academy:** The Saylor Academy was formerly known as the Saylor Foundation is a non-profit organization headquartered in Washington DC. Since its inception in 2008, it has been providing free online courses to students and working professionals. Saylor Academy offers 317 free college level courses which are taken up by students for their majors in college. The foundation works closely with university and college faculty and industry experts to design courses which would meet the changing dynamics of college education.
- **Skillshare:** This is yet another US based online learning platform which caters to people who want to learn from educational videos. The majority of the courses focus on interaction rather than lecturing, hence it is a participative medium. Skillshare has over 27,000 premium classes and more than 2,000 free courses available. The platform has introduced a “Groups” feature which allows members to connect and share their inputs with other creators. This takes the learning to a next level involving discussions and proactive engagement.
- **Edx:** This is an American MOOC provider launched in 2012 by Harvard University and MIT. Edx is one of the best providers of college level online courses. As of July 2020, edX has around 33 million students taking more than 3000 courses online. edX has weekly learning sequences which comprise of videos along with interactive exercises. Wherever applicable online laboratories are incorporated into the course. edX has partnered with many universities and organizations for delivery of their courses. It has an active presence in 196 countries worldwide.
- **Udacity:** Udacity is the definition of Innovation when it comes to online learning and education. Launched in 2012, Udacity is also an American MOOC provider. Originally, Udacity focussed on offering university style courses, it now focuses

more on vocational courses for professionals. It has presence in over 203 countries and has over 11.5 million users worldwide. It offers a wide variety of courses in computer science domain and caters to the changing industry demands. Udacity also offers executive programs for business leaders on aspects of Artificial Intelligence and other contemporary topics.

- **Futurelearn:** This is also an online education platform that offers hundreds of courses from the world's leading universities. Most courses include video and audio content, reading materials and short quizzes. Apart from free courses, Futurelearn offers premium courses for a fee. These 800 plus premium courses are in the field of IT, Business & Management, Teaching and Healthcare.
- **LinkedIn Learning Ex Lynda:** A few years ago, LinkedIn acquired one of the oldest e-learning sites called Lynda and transferred all its contents to LinkedIn Learning. The platform now offers thousands of courses for beginners as well as advanced learners across various disciplines. LinkedIn Learning is not accredited but most courses offer a certificate of completion which can be later added to ones LinkedIn profile. This especially is beneficial to working professionals to add stars to their career.
- **Master Class:** The uniqueness of MasterClass lies in the fact that the courses here are taught by world famous experts and celebrities. It offers courses on Business, Sports, Entertainment, Fashion, Photography, Politics, Science and Technology. Classes are delivered through high quality video lessons, assignments, workbooks and community activities. MasterClass is a good learning platform for creative people who are interested in personal development and seeking inspiration from the best in their field.

## Coparative Analysis of Online Course Platforms

Online Platforms	No. of Courses	No of Learners	No of Countries	Institution Tie-ups	Rating (Out of 5)
NPTEL	1,000	1.16 Million	160	200	4
Udemy	1,50,000	50 Million	195	190	4.4
Coursera	4,000	47 Million	29	213	4.5
Saylor Academy	25,000	20.2 Million	117	150	4.7
Skillshare	27,000	1 Million	150	250	3.9
EdX	3,600	18 Million	162	140	4.5
Udacity	17,000	1.6 Million	190	30	4.3
Future Learn	4,000	10 Million	140	175	4.4

Based on the data above, Udemy has the maximum number of courses on offer. As a result, the number of learners is highest on Udemy Online Course platform. When it comes to tie ups of these platforms with academic and other institutions, Skill share has over 250 tie-ups. Based on the user rating, Saylor Academy has received a rating of 4.7 out of 5.

### Benefits of Online Courses

In the past few years, online learning has drastically evolved as a parallel to conventional education system and has change the face of modern education. As online courses are cheaper and are more effective, more and more people are enrolling for these courses. The e-learning and online course market is soaring new heights and is estimated to be worth USD 325 Billion by the year 2025. The present COVID-19 pandemic has come as an opportunity for the

growth of online course platforms. Following are some of the benefits of online courses.

- The biggest advantage of online courses is that it is very convenient for the learner. He or she can access the online assignments, notes and material anytime and from anywhere.
- Online courses offer flexibility to the users as they offer wide variety of courses with varying duration which can be accessed by the user at his / her convenience.
- Online courses brings education to the learner's home, it also helps parents keep a track of their wards learning graph.
- Online courses offer more individual attention to the learner as there is no fear of face to face interaction and learner can confidently ask his doubts and queries.
- Online course also offer opportunity for learners to interact with a wide audience through chat rooms, bulletin boards and mailing lists.
- The courses offered through online platforms are updated and more contemporary as compared to conventional offline courses. These courses provide the learner with real world skills.
- Learning is a continuous and never ending process. Online courses work on this concept as the courses are available for everyone and for people of all age groups.
- Online courses have financial benefits. They are less expensive than offline education. In-fact some platforms also offer free online courses.
- Doing an online course makes the learner self-disciplined as there is no compulsion of attendance or time line. An online student is far more responsible than an offline student.
- Online courses also help in developing the technology skill of the users. Downloading videos, uploading assignments etc makes the person more computer savvy.
- Online courses help in broadening the scope and reach of education beyond boundaries.

## Limitations of Online Courses

In spite of having many advantages, online courses do have some limitations. Most students still prefer traditional learning mediums as compared to online learning mediums. On one hand there is limited face to face interaction and on the other hand there is more work and responsibility for the learner if he / she choose to take up an online course. Mentioned below are some of the drawbacks or limitations of online courses.

- Online courses require the learner to be more active and participative or else, the online course will neither be useful nor effective.
- Online course requires the learner to have good time management skill or else he / she will not be able to complete the course in time.
- Online course can be effective only when the learner shows seriousness and responsibility in taking the course.
- The freedom that the learner gets in online courses can be misused and the course may not result in the right outcome.
- As the instructor is readily available on online course platforms to interact and explain, this makes the learner become passive and disinterested to stay alert.
- Spending too much time on online courses results in excessive internet usage which could have cost implications.
- There are some courses which very strict timeline when it comes to assignment submissions, unlike offline courses; there is no extension of deadline in this case.
- If the online courses are not well accredited, they would be of no use to the learner. Frauds in accreditation could be one of the drawbacks of online courses.
- Online courses can have a negative impact on the mental health of the learner as it results in social isolation. There is no physical interaction among the instructor and learner or with co-learners. This could create a feeling of isolation among the learners.

## NEP and Online Education

The National Education Policy 2020 was unveiled by the Ministry of Human Resource Development after a period of 34 years. The policy would be fully operational from 2021. The policy aims at long overdue reforming of the education system in India in order to have holistic development of a student. The policy is revolutionary in nature amalgamating education and technology.

Over the last decade, India has transformed itself into an ‘information intensive society’ and there is a growing requirement to embrace the usage of technology in the field of education. In this regard, the NEP 2020 focuses on ‘extensive use of technology in teaching and learning, removing language barriers, increasing access as well as education planning and management’.

The NEP 2020 proposes to encourage online learning in India by providing good digital infrastructure, virtual labs and digital repositories across the country. Online education can reach out to all the sections of the society. The Policy envisages the creation of a dedicated unit for the purpose of devising the development of digital infrastructure, digital content and capacity building to supervise the e-education needs of both school and higher education. Following are proposals mentioned in NEP 2020 with regard to online education and e-learning.

- **Digital Infrastructure:** The current pandemic COVID-19 has exposed the dearth of digital infrastructure in India. Having 260 million school going population, it is imperative that we have adequate facilities to implement digital and online learning. The NEP 2020 focuses on developing adequate infrastructure across the country to promote e-learning. It is also encouraging the development of online courses which should reach out to the masses.
- **Virtual Labs:** The NEP 2020 aims at creation of more and more virtual labs which will help in providing students with experiment based learning. Use of technology in learning will

enhance the learning experience and also expose students towards modern and upcoming concepts. The focus of the new education policy is on experiential learning.

- **New Autonomous Body:** The new education policy creates a provision of creating an autonomous body 'National Educational Technology Forum (NETF)'. This autonomous body will oversee the capacity building, develop e-content and provide a platform for educational institutes and stakeholders to share best practices leveraging technology. This will help in bridging the digital divide and have a wider reach for online education in India.
- **Digital Literacy:** With the growing use of technology in all aspects of life, digital literacy has become imperative. The new education policy focuses on imparting knowledge on contemporary issues such as Artificial Intelligence, Big Data Analytics and Machine Learning at a young age. This will empower the youth to have desired skill sets that makes them employable globally.
- **Virtual Classrooms and E-Content:** NEP 2020 is very progressive and futuristic in nature and aims to make online learning and virtual classrooms accessible for every student. The smart classrooms will provide a strong platform to initiate interactivity through webinars and live discussions. It is also intended at preparing alternative modes of delivering education, which will be of immense benefit in times of crisis as the current pandemic.
- **Edtechs:** NEP 2020 has created wide range of opportunities in the Edtech sector. It aims to provide e-learning courses not only in English but also in many regional languages. . In addition to digital content, NEP also aims to provide learning apps, satellite-based TV channels, and teachers training to further strengthen online learning. The new education policy boosts India's vision towards creating an online pedagogy.



## Conclusion

Online learning is certainly the more effective option for students, but it's also better for the environment. It has been found that online courses equate to an average of 90% less energy and 85% fewer CO2 emissions per student than traditional in person courses. Online classes are no easier than classes offered in the traditional classroom setting and in some cases can be even be more difficult. Online courses require more self-motivation. It can be hard for some students to stay motivated when they'd rather be doing something else.

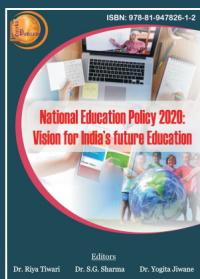
Online courses are an effective tool for academic enhancement in case of students and college goers. Along with a traditional offline certification, they can do a few online courses which will add value to their degree. In case of working professionals, online courses can help them to stay updated with latest trends and concepts on one hand, and on the other hand these online courses will aid their growth prospects in the organization. The additional skills that they acquire through online courses can help in negotiating a higher salary. Hence online courses have many benefits for both students as well as working professionals.

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## About the Book



The aim must be for India to have an education system by 2040 that is second to none, with equitable access to the highest-quality education for all learners regardless of social or economic background. This National Education Policy 2020 is the first education policy of the 21<sup>st</sup> century and aims to address the many growing developmental imperatives of our country. This Policy proposes the revision and revamping of all aspects of the education structure, including its regulation and governance, to create a new system that is aligned with the aspirational goals of 21<sup>st</sup> century education, including SDG4, while building upon India's traditions and value systems. The National Education Policy lays particular emphasis on the development of the creative potential of each individual. It is based on the principle that education must develop not only cognitive capacities both the 'foundational capacities' of literacy and numeracy and 'higher-order' cognitive capacities, such as critical thinking and problem solving-but also social, ethical, and emotional capacities and dispositions.

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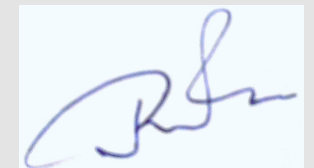
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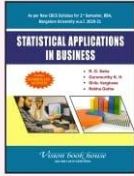
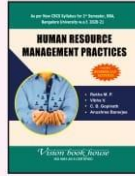
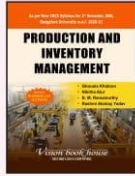
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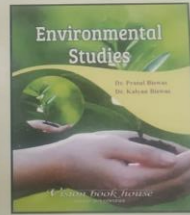
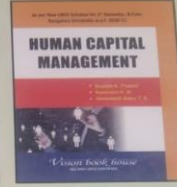
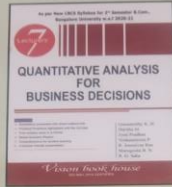
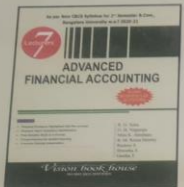
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Associate Prof., Sree Omkar Degree College,  
Founder, Archita Global Education, Bengaluru.

**Narendra K.** M.Com, M.Phil, PGDBA (Ph.D),  
Associate Prof., and Co-ordinator, PG Department of Commerce,  
Surana College, Bengaluru.

**Chinmaya Dash** MCA  
Asst. Prof., Department of Computer Science,  
St. Claret College, Bengaluru.

Co-Ordinator  
PG Department of Commerce (M.Com)  
SURANA COLLEGE  
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# *Preface*

We have great pleasure in presenting the first edition “*Information Technology for Business*” written for students of UG and PG courses. The subject matter is written in a simple and easily understandable language with sufficient support from real information.

The language of the book is simple and the coverage of various unit is exhaustive with examples. This work is prepared as a basic material for the learners to know fully about Information Technology for Business. We have tried to make the book very useful for the students but still we will thankfully solicit and incorporate the suggestions of our readers. This title “*Information Technology for Business*” provides them an opportunity to develop the skills necessary to meet the challenges.

This is an attempt to provide the students with thorough understanding of Practicals on Information Technology for Business concepts. In writing this book we have benefited immensely from the studies of a number of books and the articles written by scholars spread over diversely.

We are sure this book will prove to be useful to students and teachers alike. The book would not have seen the light, but for the grace of God and the blessings and support of our family members and friends.

We offer our gratitude to Himalaya Publishing House Pvt. Ltd., who is leader in Commerce and Management publications. Our sincere regards to Mr. Niraj Pandey and Mr. Vijay Pandey for interest shown and for the best effort put forth in publishing this book.

Finally, we express our sincere thank to SPS, Bengaluru, for their excellent computer typesetting work and the printing.

Any suggestions regarding improvement of errors, if any, will gratefully be acknowledged.

***Bengaluru***

**Authors**

***Feb., 2021***

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# 1 MODULE

## INTRODUCTION TO E-COMMERCE

### *Learning Objectives*

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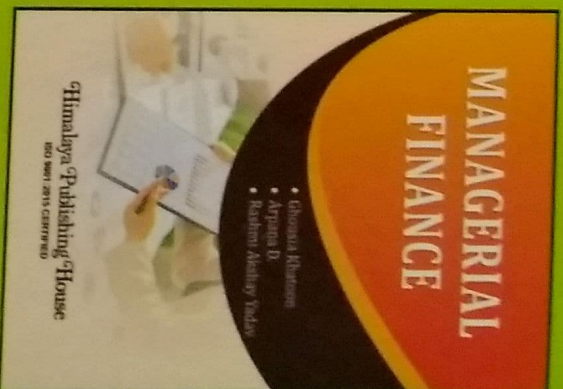
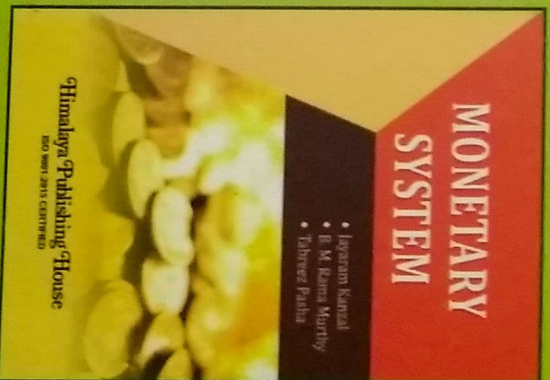
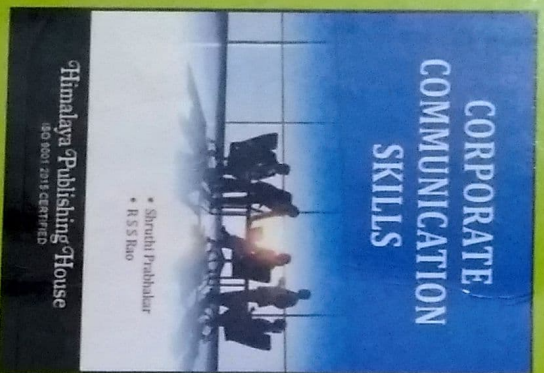
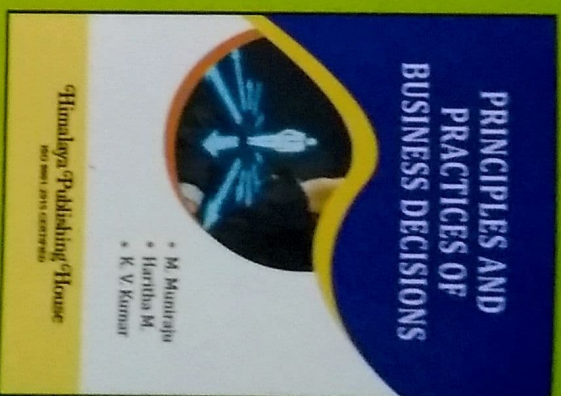
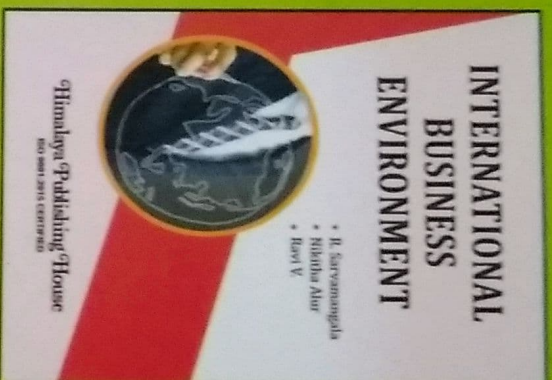
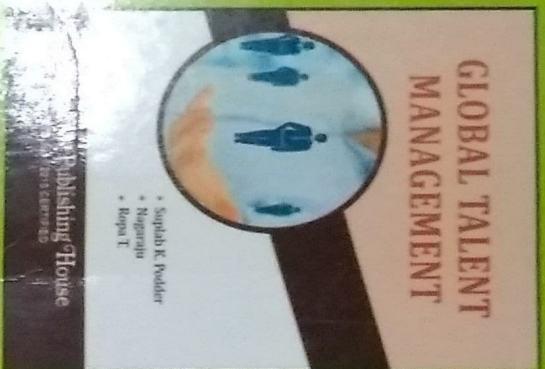
# ELECTRONIC DATA INTERCHANGE (EDI)

### *Learning Objectives*

- Meaning of EDI
- Definition of EDI
- History of EDI
- Evolution of EDI
- Uses of EDI
- EDI Standards
- EDI Working Concept
- Implementation Difficulties of EDI
- Financial EDI
- EDI
- Internet
- EDI Services
- ANSI X12
- EDI/FACT



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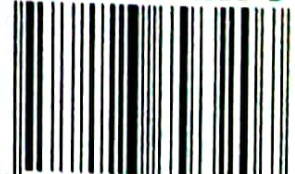
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आङ्ग्लकन्नडादिक्षेत्रे ख्यातनामधेया च । तया  
उपन्यास-प्रवासकथन-तन्त्रज्ञानप्रतिपादन-  
अनुभवकथनरूपाः अनेकाः कृतयः रचिताः ।  
प्रायः सर्वाः अपि कृतयः विविधाभिः भाषाभिः  
अनूदिताः । स्तम्भलेखिकात्वेन अपि तया कार्यं  
कृतम् । समाजसेवाकार्येषु आत्मानम् आधिक्येन  
योजितवती मान्या सुधामूर्तिवर्या उच्चस्थानस्था  
अपि सरलव्यवहारा सौजन्यपूर्णहृदया च ।  
अनेकाभिः प्रशस्तिभिः पुरस्कृता सा साहित्यक्षेत्रे  
प्रकाशमानतारायते ।



संस्कृतभारत्याः कार्यकर्त्री  
साहित्यशास्त्रे विदुषी

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जागृत' 'गोमन्तकम्' 'मनः तत्प्रशमनं च'

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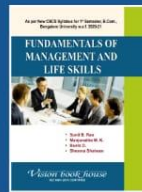
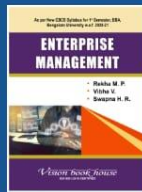
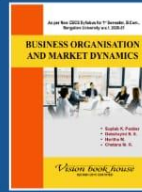
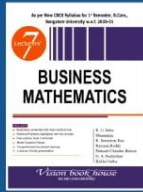
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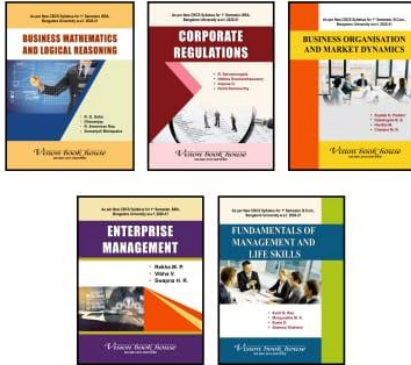
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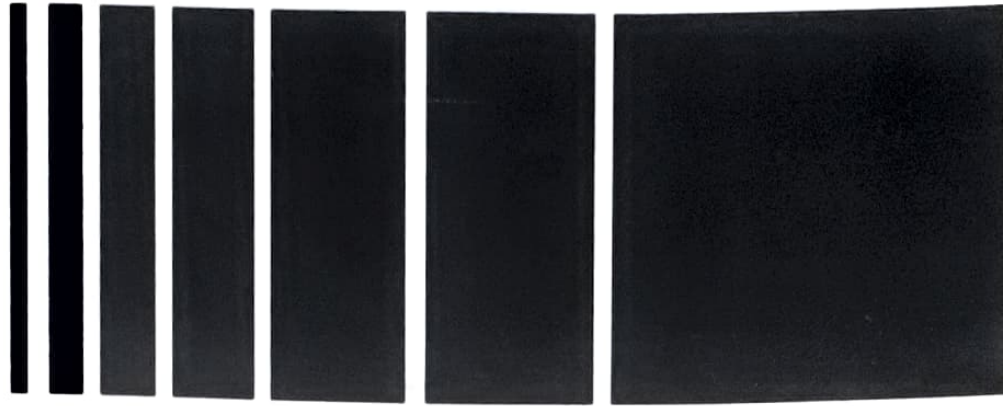
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**Dr. Haritha M.** MBA, M.Com., B.Ed, M.Phil, Ph.D  
Asst. Professor & Program Manager, PG Department of Commerce,  
Acharya Institute of Management and Science, Bengaluru.

**Dr. Jyoti Pradhan** BE, MBA, Ph.D  
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Christ Academy Institute for Advanced Studies, Bengaluru.

**Venkatalaxmi P.** M.Com., MBA, M.Phil, (Ph.D)  
Associate Prof., Department of Commerce & Management,  
Seshadripuram First Grade College, Yelahanka, Bengaluru.

**R. Sreenivas Rao** M.Sc (Com.) M.Sc.(Maths)  
Asst. Prof. and HOD, Department of Computer Science,  
Surana College, Bengaluru.

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Asst. Prof. and HOD, (B.Com),  
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## Syllabus

### Unit 1: Introduction to Statistics

Introduction, Meaning, Definitions, Features, Objectives, Functions, Importance and Limitations of Statistics, Important Terminologies in Statistics, Data, Raw Data, Primary Data, Secondary Data, Population, Census, Survey, Sample Survey, Sampling, Parameter, Unit, Variable, Attribute, Frequency, Seriation, Individual, Discrete and Continuous. Classification of Data. Requisites of Good Classification of Data. Types of Classification, Quantitative and Qualitative Classification (simple Illustrations).

### Unit 2: Tabulation and Presentation of Data

Types of Presentation of Data, Textual Presentation, Tabular Presentation, One-way Table, Two-way Table, Important Terminologies, Variable, Quantitative Variable, Qualitative Variable, Discrete Variable, Continuous Variable, Dependent Variable, Independent Variable, Frequency, Class Interval, Tally Bar, Diagrammatic and Graphical Presentation, Rules for Construction of Diagrams and Graphs. Types of Diagrams, One Dimensional Simple Bar Diagram, Sub-divided Bar Diagram, Multiple Bar Diagram, Percentage Bar Diagram, Two Dimensional Diagram, Pie Chart, Graphs, Histogram, Frequency Polygon, Ogives, Curve, Simple Problems on Tabulation, Diagrams and Histogram Only.

### Unit-3: Measures of Central Tendency

Meaning and Objectives of Measures of Tendency, Requisites of an Ideal Average, Types of Averages, Arithmetic Mean, Median and Mode, Problems on Calculation of Arithmetic Mean, Median and Mode Direct Method Only (Including problems involving empirical relationship between Mean, Median and Mode).

### Unit 4: Measures of Dispersion and Skewness

Meaning and Objectives of Measures of Dispersion, Requisites of Good Measure of Dispersion, Types of Measures of Dispersion, Range, Quartile Deviation, Mean Deviation, Standard Deviation and their Co-efficient Problems on Direct Method only. Measures of Skewness, Meaning, Absolute and Relative Measures, Karl Pearson's Coefficient of Skewness and Bowley's Coefficient of Skewness, Problems.

### Unit 5: Correlation, Regression and Time Series Analysis

Meaning and Types of Correlation, Karl Pearson's Coefficient of Correlation, Spearman's Rank Correlation Coefficient, Correlation Coefficient through Regression Coefficient Meaning of Regression, Regression Lines, Regression Coefficients, Regression Equations, Problems, Meaning and Components of Time Series, Analysis of Time Series by Moving Averages and Least Squares Method.

### Business Lab Activities

1. Collect data from at least 5 friends about their monthly expenditure on Mobile Recharge, Cosmetics, Chats and Other Expenses and present the same in a Tabular Form
2. Collect data from at least 5 friends about the percentage of marks obtained in SSLC and PUC and present the same in a Bar Diagram Form
3. Collect data from at least 10 friends about the pocket money they receive in a month and present the same in the form of a frequency distribution with class interval of Rs. 25, 50 etc
4. Collect data about marks scored in English subject in PUC from at least 30 students of your class and calculate Arithmetic Mean
5. Collect the data about the age of at least 10 married couples and compute correlation coefficient

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 Frequency Polygon  
 Ogives  
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 Practical Problems *with Answer*

Introduction  
 Meaning of Measures of Tendency  
 Objectives of Measures of Tendency  
 Requisites of an Ideal Average  
 Types of Averages  
 Arithmetic Mean  
 Median and Mode  
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# COMPUTER ORGANIZATION

As per New CBCS Syllabus for Students of I Semester BCA, Bangalore Central University w.e.f.2018 - 2020



Rashmi Estwar  
Sara Kutty T.K





**NEW PARADIGMS IN BUSINESS MANAGEMENT PRACTICES**  
**Volume-3**

**SRUTHI. S**

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**Volume-3**

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## MANAGING AND LEADING CHANGE IN ORGANIZATIONS: A COMPETITIVE DIFFERENTIATOR

**SAVITA SHASTRI**

Assistant Professor

Department of MBA, Surana College, Bangalore University

9900213214

[savita.mba@suranacollege.edu.in](mailto:savita.mba@suranacollege.edu.in)

193/28, BSM Layout II Stage, K S Town, Bengaluru – 560060

### ABSTRACT

Change, an inevitable reality in today's competitive business world has threatened the existence of many organizations. It has become imperative for people and organizations to predict, manage and adapt to changing environment. Change impacts both internal as well as external environment of an organization. People are at the forefront of managing change. Transformational Leadership is the need of the hour, wherein the top brass anticipates and imbibes change in their DNA.

Change Management is a term which depicts organizational preparedness for change. HR managers play a vital role in understanding the reasons for change and effectively managing the change process. All organizations are exposed to similar challenges and threats, the difference rests in the way they handle the challenges and survive the change. Management of change and effective leadership can bring competitive advantage to the organization.

This paper attempts to bring out the impact of managing change effectively in organizations and how it can prove to be a competitive differentiator and make the organization stay on top of the pyramid.

**Keywords:** Organizational Change, Change Management, Competitive Advantage, Transformational Leadership, Competitive Differentiator

### INTRODUCTION

The pace of change in the 21<sup>st</sup> century has taken everyone by surprise. The year 2020 has created ripples and cracks in many organizations which cease to exist now. The preparedness to face and tackle change has assumed prime importance in organizations. The role of leaders has never been this important, and today most organizations are trying to improve and enhance their capabilities to change, both human as well as material capabilities.

Change has an influence on both internal as well as external environment of an organization. Every organization makes a strategy to manage change, however the implementation of this strategy is what separates the good organizations from the great ones. The timely anticipation of change and efficiency with which the organization reacts to change provides a competitive advantage.

Managing and leading change can prove to be a competitive differentiator and give the organization edge over others. People are at the forefront of managing and leading change in organizations. Transformational Leadership is the need of the hour, wherein the top brass anticipates and imbibes change in their DNA.

### **THEORITICAL BACKGROUND**

Due to Globalization and technological advancements, today's organizations are operating in an extremely dynamic and competitive business environment. Resilience to change is being seen as a key success factor in the present scenario. Change Management as a concept has emerged as early as 1960's, when Everett Rogers proposed descriptive adopter groups of how people respond to change. He classified them as Innovators, Early Adopters, Early Majority, Late Majority and Laggards.

In 1980's the Change Management Model proposed by Julien Phillips, a consultant with Mckinsey & Company was very well received. In the 90's, Daryl Conner stressed on the human performance and adoption technique that would be of help in managing and adapting to technological innovations effectively. The next decade saw the focus shift towards human side of change. Linda Ackerman Andersen in her work has highlighted the role of change leader in managing change successfully. The current decade recognizes change management as a formal vocation and applies Lean and Agile principles to the field of Change Management.

Different Change Management models have emerged from time to time which has varied success ratio. The most famous model is the Plan-Do-Check-Act (PDCA) Cycle suggested by Quality Management Guru, W Edwards Deming. Jeff Hiatt has proposed a Prosci ADKAR Model which focuses on individual change. ADKAR represents the five building blocks for successful change in an individual. 'A' stands for awareness of the need for change, 'D' stands for desire to participate and support the change, 'K' stands for knowledge of what to do during and after change, 'A' stands for ability to realize and implement the change, and 'R' stands for reinforcement to ensure results of the change continue.

The most commonly accepted Change Management model developed by Change Management Foundation comprises of four simple steps. The first step is to determine the need for change, the second step is to prepare and plan for change, the third step is to implement the change and the final step is to sustain the change and prepared to face any new change.



## **REVIEW OF LITERATURE**

Many researchers have dealt with the topic of organizational change, change management and role of HR managers in managing change. Most researchers have consented to the challenges of change management and have suggested strategies to have effective transition and transformation. Following are some of related research work that highlights the aspect of change management.

(Ricardo & Arianna, 2018) The researcher deals with the impact of training, development and innovation on bringing and managing change in organizations. Human factor plays an important role in accepting and emulating organizational change. The focus of the article is Organizational Innovation as a way by which companies, business entities and organizations manage change in the multi-dimensional perspective of survival, competitiveness, growth and development.

(Motab, 2016) Managing change is a core challenge for HR professionals as people working in the organization are impacted by change. Effective change management can result in greater productivity, better work life quality and better readiness for future changes. Organizational change is a very complex process which can have a negative or positive outcome on the organization. Successful change management is dependent on understanding the role of technology, role of customers and improving communication within the organization.

(Sirkin, Perry, & Alan, 2005) The authors believe that managing change is tough as there is very less agreement on what factors most influence transformation initiatives. In recent years, many management gurus have based the success of change on soft aspects such as culture, leadership and motivation. The writers suggest a DICE Framework that can adopted to bring organizational change. This framework comprises of four factors which are Duration, Integrity, Commitment and Effort.

(Jalagat, 2016) The researcher has critically evaluated the impact of change and change management in achieving the organizational goals and objectives. Leaders and managers play an effective role in bringing and managing change in the organization. The researcher concludes that, in order to bring successful change, the management and organization must ensure that any change initiative must be aligned with the goals and objectives of organization.

(Gill, 2010) The researcher identifies the importance of leadership in managing and implementing change. The researcher proposes an integrative model of leadership for change which reflects the cognitive, emotional, spiritual and behavioural dimensions and requirements. The model takes into considerations parameters such as vision, values, strategy, empowerment, motivation and inspiration.

## **RESEARCH OBJECTIVES**

The present research identifies the following three objectives:

- To understand the various aspects of change in organization
- To identify the challenges in managing and leading change in organizations
- To suggest strategies for making change management as a competitive differentiator

## **RESEARCH METHODOLOGY**

The research design is exploratory in nature, wherein the researcher tries to understand and study an aspect in detail. The research is based on secondary sources of information. Information available in newspapers, research articles, blogs, and websites is the source of data for this research. The researcher has done extensive study about the forces that bring about change in organizations and the coping mechanisms.

## **DISCUSSION AND ANALYSIS**

The business environment is experiencing rapid changes at both local as well as global level. Due to new emerging technologies, the change is reflected more in exterior innovations as compared to internal factors. The organizations that recognize, react and adapt to these changes quickest are the ones that would have a competitive advantage over the rest.

**Aspects of Change:** In order to make change management a competitive differentiator, it is important to understand the various aspects of change in organizations. Change is essential for organizations to grow, develop and innovate. Dynamic business leaders have realized that successful management of change can bring them competitive advantage.

Change can be seen in the various technological innovations that are taking place all over the world. Organizations need to constantly upgrade themselves in order to stay in line with the changing technology. The next big change can be viewed in the customer attitude and demands. Customer is exposed to vast information through social media and other sources, as a result of which the awareness levels as well as expectation levels have soared very high. This puts immense pressure on the organizations to understand market demand and make necessary modifications to their products and services.

Changing attitude and expectations of employees is yet another important aspect of change. Today's workforce is multidimensional, their voice is stronger and they are well aware of their rights.

Commitment and loyalty is a rare attribute in the current breed of employees. They are constantly looking for better opportunities and have very limited involvement with their organization. In such situation, a company which has the ability to win the buy in of their employees on the change will survive and succeed. HR Managers have to constantly upgrade their styles of managing workforce. There are many more aspects of change such as government policies, global economic environment, natural calamities, etc, that could affect the existence of organizations. It is important to have right systems in place to anticipate changes taking place in both the external as well as the internal environment. Timely anticipation can help in preparing to face and manage the changing elements effectively.

**Challenges in managing and leading change:** The human component plays a crucial role in the process of managing and leading change in organizations. Leading the change process is paramount

and winning the support of employees through persuasiveness can prove to be a game changer. The biggest challenge that organizations face in managing change is the integration and alignment between social, technical and strategic components. Change management requires collaboration from entry level to top level hence change has to be viewed as all pervasive.

Human factors pose a big challenge in managing and implementing change. People's natural tendency for inertia can be a big hindrance in the change management process. Proactive communication and counselling can help in preparing employees to accept the change and prepare themselves to manage the change. Employee empowerment and flexibility can also aid the process of managing change. Leaders and managers play a critical role in managing change; they act as role models, change agents and champions for change. Employees look to their leaders for clarity, connection and accountability. Having such dynamic and transformational leaders is a big challenge faced by any organization. Lots of leaders talk about change and want it to happen, but only a select few take the initiative and make it happen.

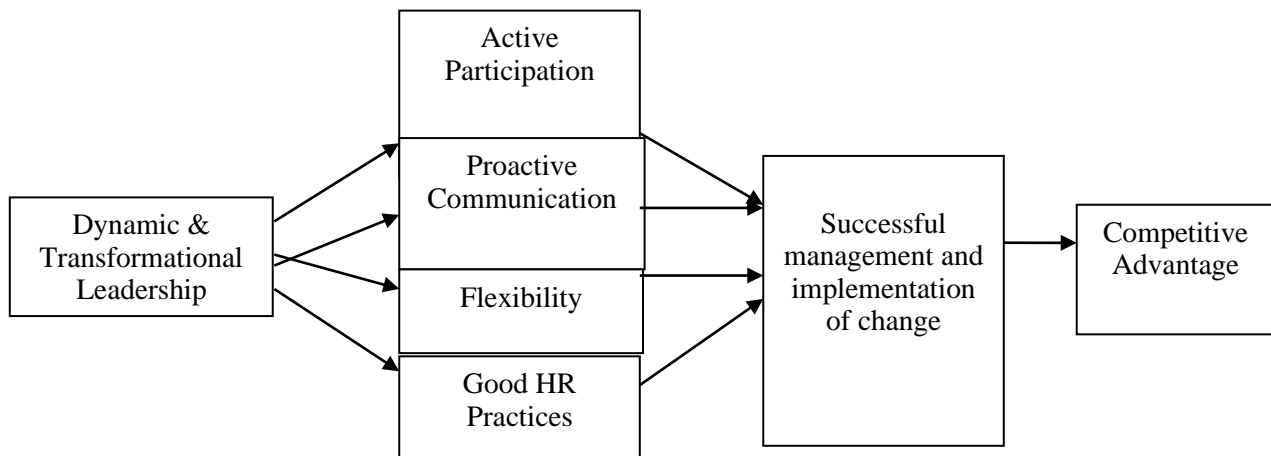
***Strategies for making change management a competitive differentiator:*** The pace of change in the 21<sup>st</sup> century is forcing all organizations to focus on and improve their capabilities to change. Following are the strategic initiatives that can be take to make the process of managing change effective, which in turn can become a source of competitive advantage for an organization.

- Constant and accurate environmental scanning can go a long way in timely prediction of change. This could help the leaders to prepare their team to adapt and accept change.
- Great organisations use change as an opportunity to develop and engage the workforce. The goal of people development is to create an integrated “change-enabled” organisation in which every person is equipped to detect and act on opportunities to improve organisational performance.
- Change Management will become a competitive differentiator only when it is imbibed in the DNA of its people. Hence, the organization needs to institutionalize the process of change management.
- The approach towards managing change must be collaborative instead of being directive. Under collaborative approach, leaders and employees work together to understand, prepare and undergo a change.

- The role of leadership in managing change requires care, communication and commitment. Leaders act as the bridge between the organization and envisioned change. Transparency and effective communication can prove to be assets in implementing change in organizations.
- Organizational change is a journey that requires a strategy at three stages, one would be in the pre-change stage, and the second would be during the change and third strategy for the post change stage. There must be adequate focus on the skill development and participation of employees at every stage of the change.

The overall effectiveness of these strategies is strongly dependent on the people who are leading the change process. Organisations great at strategic organisational change are able to transform themselves into systems optimised for detecting, creating, and accomplishing the changes needed to maintain their position as industry leaders.

The model presented below identifies a linkage between leadership and its impact on the organization. Dynamic and transformational leadership can result in active participation, proactive communication, flexibility and Good HR Practices. These factors will help in successful management and implementation of change. As a result of this, an organization can have a strategic position in the market and have competitive advantage over others.



**Chart 1: Change Management: A Competitive Differentiator**

## CONCLUSION

In 21<sup>st</sup> century the ability of an organization to optimise its performance is strongly related to its proficiency to change. The source of competitive advantage would depend on the organization's ability to change faster, better and with fewer resources than their competitors. The organizations must strive to build a robust change capability. This would mean the ability to constantly learn and improve, the ability to engage people proactively, and the ability to view change as an opportunity and imbibe it in the culture and DNA of the organization.

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# OPERATION RESEARCH

As per New CBCS Syllabus for IV Semester BCA, Bangalore University

· K. Balaji



## ABOUT THE AUTHOR



K. Balaji, is currently serving as Assistant Professor in the department of computer applications - SURANA COLLEGE, Bangalore. He has over 11 years of rich experience in teaching post graduate students. His subject area expertise includes Operations Research, Data Mining, Database Management Systems, Network Information Security, Computer Graphics and many more.

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# An insight into the superior performance of ZnO@PEG nanocatalyst for the synthesis of 1,4-dihydropyrano[2,3-*c*]pyrazoles under ultrasound

Sumaiya Tabassum<sup>a</sup>, Sunaja Devi K.R.<sup>b</sup>, Santhosh Govindaraju<sup>c,\*</sup><sup>a</sup> Department of Chemistry, Surana College, South End Road, Basavanagudi, Bengaluru 560004, India<sup>b</sup> Department of Chemistry, CHRIST (Deemed to be University), Bengaluru 560029, India<sup>c</sup> Department of Sciences and Humanities, School of Engineering and Technology, CHRIST (Deemed to be University), Kumbalagodu, Mysore Road, Bengaluru 560074, India

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## ABSTRACT

The investigation presents a straightforward synthesis of fifteen 1,4-dihydropyrano[2,3-*c*]pyrazoles using ZnO@PEG nanocatalyst in ethanol via Multicomponent approach under the influence of ultrasound. The present methodology successively tolerates a variety of functional groups and offers several advantages such as excellent yields without chromatographic purification, milder reaction conditions, shorter reaction times, and the use of an environmentally benign reusable catalyst. Ecstatically, the reaction was successfully scaled to gram level ascertaining the wider applicability of ZnO@PEG nanoparticles in multicomponent reactions.

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## 1. Introduction

The synthesis of heterocyclic compounds possessing 4-*H* pyran ring has attracted synthetic organic chemists in recent years as they are imperative in the field of medicinal chemistry. Pyrano [2,3-*c*]pyrazoles are one among such heterocycles that have known to display a wide range of biological activities such as anticancer [1], antimicrobial [2], anti-inflammatory [3], analgesics [4]. They also act as a versatile reaction intermediate [5] and as biodegradable agrochemicals [6].

Multicomponent reactions (MCRs) [7] are one-pot reactions that offer operational simplicity and diversity as they can successfully amalgamate most of the atoms in the reactants into products. MCRs are attractive and environmentally benign [8] as they are highly atom efficient [9], use less hazardous chemicals, produce minimum side products, generate higher yields in shorter reaction time thereby saving energy, time, raw materials, and solvents required for the reaction.

The acceleration of the reaction rates was reported by Richards and Loomis in the year 1927 set forth a new channel by providing an alternate methodology in conventional organic synthesis. Ultrasonication creates a remarkable change in a chemical reaction due

to the phenomenon of cavitation which results in creating immense temperature, pressure variations. The sudden gush of the reaction media on the surface of the catalyst increases the mass transfer [10] resulting in the upsurge of the chemical reactivities by nearly a million-folds [11].

Heterogeneous/Homogeneous catalysts supported on inert substrates such as polyethylene glycol (PEG) [12] have garnered much attention in recent years and are widely used in the field of synthetic organic chemistry for the development of clean and greener protocols [13]. PEGs are commercially available, non-toxic and show unique properties (negligible vapor pressure, thermally stable) which makes them environmentally-friendly [14]. Recently, polymer-supported catalysts [15] have emerged as viable alternatives to homogeneous catalysts as they are inert, inexpensive, easy to prepare, and most importantly they are recyclable. The PEG capped nanocatalysts are a valuable addition to sustainable methodologies as the demand for benign nanocatalysts in organic synthesis is on the rise.

Recently, pyrano[2,3-*c*]pyrazoles have been synthesized by the use of catalysts [16–19] under varied reaction conditions. However, the reported protocols suffer from drawbacks such as harsher reaction conditions, less yield, use of toxic solvents, and prolonged reaction times. Thus, in this regard, the development of a new eco-friendly protocol for the synthesis of pyrano[2,3-*c*]pyrazoles which

\* Corresponding author.

E-mail address: [santhosh87org@gmail.com](mailto:santhosh87org@gmail.com) (S. Govindaraju).



are more effective and rapid is of significant interest to chemists all over the world.

A rigorous literature survey reveals that 1,4-dihydropyrano[2,3-c]pyrazoles skeleton has not been prepared using nanocatalysts. Moreover, our research team has recently prepared, characterized (XRD, FTIR, UV-DRS, SEM, EDAX) and successfully used ZnO@PEG [20] in photocatalytic degradation of malachite green dye. Additionally, Lewis acid catalysts such as ZnO [21], Al<sub>2</sub>O<sub>3</sub> [22] and CuO [23] are widely used in MCRs. These observations initiated us to explore the applicability of ZnO@PEG in the synthesis of pyrano[2,3-c]pyrazole via MCR approach and we have successfully reported its synthesis under sonication as shown in Scheme 1.

## 2. Materials and methodology

### 2.1. Experimental section

Reagents and solvents were purchased from Sigma Aldrich. All materials were of commercial reagent grade. Melting points were determined using Thiele's apparatus (con. H<sub>2</sub>SO<sub>4</sub>) with a calibrated thermometer. The progress of the reaction and the purity of the compounds was monitored by TLC [analytical silica gel plates (Merck60 F<sub>254</sub>)]. Infrared (IR) spectra were recorded using an Agilent Cary 630 FT-IR spectrophotometer. <sup>1</sup>H NMR spectra were recorded using an Avance Bruker instrument operating at 400 MHz and <sup>13</sup>C NMR spectra were recorded at 100 MHz in DMSO *d*<sub>6</sub>. Chemical shifts are reported in ppm. Mass spectra were recorded using a Q-TOF or Waters micro mass LCT Premier mass spectrometer using an electrospray ionization technique. Sonication was performed using a SIDILU Indian make sonic bath operated at 35 kHz (constant frequency, 80 W) maintained at 25 °C by circulating water.

### 2.2. General procedure for the synthesis of 1,4-dihydropyrano[2,3-c]pyrazoles using ZnO@PEG nanoparticles

A 50 mL flask was charged with a substituted aldehyde (1, 1 mmol), 4-nitro phenylacetonitrile (2, 1 mmol), ethyl acetoacetate (3, 1 mmol), hydrazine hydrate (4, 1 mmol) and 0.1 g of ZnO@PEG in ethanol (3 mL). The mixture was sonicated (35 kHz, constant frequency) at 25 °C for 15 min. After completion of the reaction [monitored by TLC, using EtOAc: Hexane (9:1) as the eluent], the reaction mixture was treated with EtOAc (5 mL) to dissolve the product formed, and filtered through a pre-weighed sintered glass crucible. The solid (ZnO@PEG nanoparticles) present in the sintered glass crucible was repeatedly washed with water and dried in a hot air oven, the crucible was weighed, the solid was collected and kept aside for reuse. The filtrate was then taken into a separating funnel, the organic layer was separated, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to get the crude compound which was then recrystallized from ethanol to get the pure product. The structures of all the products were confirmed by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS analyses.

### 2.3. Spectral data

3-methyl-5-(4-nitrophenyl)-4-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5a):

Pale yellow powder; Yield 97%; mp 212–213 °C; IR (ATR cm<sup>-1</sup>): ν 3315, 3244, 2960, 1543, 1506, 1315, 920, 610; <sup>1</sup>H NMR (400 MHz, DMSO *d*<sub>6</sub>): δ 1.92 (s, 3H, -CH<sub>3</sub>), 4.54 (1H, s, -CH), 6.94 (s, 2H, -NH<sub>2</sub>), 7.24–8.28 (m, 9H, Ar-H), 12.47 (s, 1H, -NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO *d*<sub>6</sub>): δ 12.5, 31.6, 88.8, 103.7, 122.4, 123.9, 127.4, 128.6, 129.8, 134.8, 138.5, 144.3, 146.4, 150.6, 162.3 ppm; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub> 349.1301, found 349.1305.

4-(4-chlorophenyl)-3-methyl-5-(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5b):

Buff powder, Yield 95%; mp 200–201 °C; IR (ATR cm<sup>-1</sup>): ν 3345, 3256, 2968, 1512, 1332, 920; <sup>1</sup>H NMR (400 MHz, DMSO *d*<sub>6</sub>) δ (ppm): 1.99 (s, 3H, -CH<sub>3</sub>), 4.53 (s, 1H, -CH), 6.95 (s, 2H, -NH<sub>2</sub>), 7.14–8.33 (m, 8H, Ar-H), 12.24 (s, 1H, -NH); <sup>13</sup>C NMR (100 MHz, DMSO *d*<sub>6</sub>) δ (ppm): 13.76, 32.84, 89.01, 110.83, 122.32, 125.09, 129.53, 129.81, 131.14, 133.01, 139.26, 145.16, 147.43, 150.72, 161.88; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub>ClN<sub>4</sub>O<sub>2</sub> 383.0911, found 383.0907.

4-(4-bromophenyl)-3-methyl-5-(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5c):

Pale yellow solid, Yield 92%; m.p 226–227 °C; IR (ATR cm<sup>-1</sup>): ν 3321, 3240, 2960, 1501, 1372, 913; <sup>1</sup>H NMR (400 MHz, DMSO *d*<sub>6</sub>): δ 2.10 (s, 3H, -CH<sub>3</sub>), 4.79 (s, 1H, -CH), 6.87 (s, 2H, -NH<sub>2</sub>), 7.22–8.33 (m, 8H, Ar-H), 12.67 (s, 1H, -NH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO *d*<sub>6</sub>): δ 13.7, 32.8, 88.9, 111.7, 120.7, 122.4, 125.2, 125.9, 128.8, 129.5, 129.9, 132.7, 139.4, 144.5, 147.3, 151.9, 161.7 ppm; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>15</sub>BrN<sub>4</sub>O<sub>3</sub> 449.0225, found 449.0221.

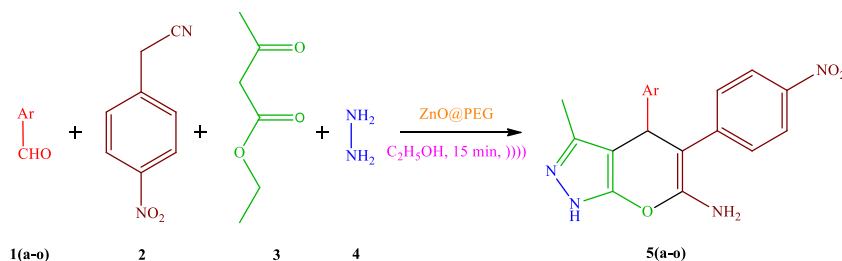
3-methyl-4,5-bis(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5d):

Yellow powder, Yield 94%; mp 230–231 °C; IR (ATR cm<sup>-1</sup>): ν 3334, 3213, 2963, 1565, 1315, 956; <sup>1</sup>H NMR (400 MHz, DMSO *d*<sub>6</sub>) δ (ppm): 1.97 (s, 3H, -CH<sub>3</sub>), 4.69 (s, 1H, -CH), 6.80 (s, 2H, -NH<sub>2</sub>), 7.45–8.29 (s, 8H, Ar-H), 12.40 (s, 1H, -NH); <sup>13</sup>C NMR (100 MHz, DMSO *d*<sub>6</sub>) δ (ppm): 13.10, 32.14, 89.09, 112.26, 122.52, 122.79, 129.57, 129.95, 138.84, 140.62, 143.41, 144.16, 147.53, 150.29, 162.48; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub>N<sub>5</sub>O<sub>5</sub> 394.1151, found 394.1148.

4-(6-amino-3-methyl-5-(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazol-4-yl)phenol (5e):

Yellow powder, Yield 91%; mp 245–246 °C; IR (ATR cm<sup>-1</sup>): ν 3321, 3346, 3136, 2954, 1561, 1314, 966; <sup>1</sup>H NMR (400 MHz, DMSO *d*<sub>6</sub>) δ (ppm): 2.03 (s, 3H, -CH<sub>3</sub>), 4.69 (s, 1H, -CH), 6.86 (s, 2H, -NH<sub>2</sub>), 6.99–8.29 (m, 8H, Ar-H), 11.60 (s, 1H, -OH), 12.52 (s, 1H, -NH);

<sup>13</sup>C NMR (100 MHz, DMSO *d*<sub>6</sub>) δ (ppm): 12.50, 32.31, 89.63, 102.86, 105.69, 113.24, 122.86, 124.35, 126.81, 129.16, 129.41, 139.79, 144.50, 145.62, 156.21, 163.59; HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>17</sub>N<sub>4</sub>O<sub>4</sub> 365.1250, found 366.1248.



Scheme 1. Synthesis of 1,4-dihydropyrano[2,3-c]pyrazoles.

3-methyl-5-(4-nitrophenyl)-4-p-tolyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5f):

Yellow solid, Yield 87%; mp 236–237 °C; IR (ATR  $\text{cm}^{-1}$ ):  $\nu$  3339, 3217, 2931, 1548, 1526, 1301, 936, 610;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ ):  $\delta$  2.04 (s, 3H,  $-\text{CH}_3$ ), 2.34 (s, 3H,  $-\text{CH}_3$ ), 4.92 (s, 1H,  $-\text{CH}$ ), 6.62 (s, 2H,  $-\text{NH}_2$ ), 7.15–8.32 (m, 8H, Ar-H), 12.66 (s, 1H,  $-\text{NH}$ ) ppm;

$^{13}\text{C}$  NMR (100 MHz, DMSO  $d_6$ ):  $\delta$  13.5, 21.7, 32.4, 89.5, 112.7, 122.7, 124.0, 129.2, 130.5, 131.1, 133.8, 138.8, 145.4, 147.1, 150.9, 162.4 ppm; HRMS (ESI):  $m/z$  [M + K] $^+$  calcd for  $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_3$  401.1016, found 401.1012.

4-(6-amino-3-methyl-5-(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazol-4-yl)-2-methoxyphenol (5g):

Yellow powder, Yield 91%; mp 208–209 °C; IR (ATR  $\text{cm}^{-1}$ ):  $\nu$  3321, 3346, 3150, 2943, 1544, 1375, 909;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ )  $\delta$  (ppm): 2.09 (s, 3H,  $-\text{CH}_3$ ), 3.64 (s, 3H,  $-\text{OCH}_3$ ), 4.87 (s, 1H,  $-\text{CH}$ ), 6.80 (s, 2H,  $-\text{NH}_2$ ), 6.66–8.36 (m, 7H, Ar-H), 11.23 (s, 1H,  $-\text{OH}$ ), 12.55 (s, 1H,  $-\text{NH}$ );  $^{13}\text{C}$  NMR (100 MHz, DMSO  $d_6$ )  $\delta$  (ppm): 12.74, 32.42, 56.51, 89.19, 112.33, 112.61, 114.98, 122.36, 123.71, 125.18, 130.05, 138.84, 145.16, 146.12, 147.39, 148.21, 148.95, 162.58; HRMS (ESI):  $m/z$  [M + H] $^+$  calcd for  $\text{C}_{20}\text{H}_{19}\text{N}_4\text{O}_5$  395.1355, found 395.1351.

4-(3,4-dimethoxyphenyl)-3-methyl-5-(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5h):

Pale yellow powder, Yield 95% mp 220–221 °C; IR (ATR  $\text{cm}^{-1}$ ):  $\nu$  3362, 3254, 2956, 1555, 1321, 933;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ )  $\delta$  (ppm): 2.05 (s, 3H,  $-\text{CH}_3$ ), 3.73 (s, 3H,  $-\text{OCH}_3$ ), 3.87 (s, 3H,  $-\text{OCH}_3$ ), 4.69 (s, 1H,  $-\text{CH}$ ), 6.61 (s, 2H,  $-\text{NH}_2$ ), 6.59–8.35 (m, 7H, Ar-H), 12.23 (s, 1H,  $-\text{NH}$ );  $^{13}\text{C}$  NMR (100 MHz, DMSO  $d_6$ )  $\delta$  (ppm): 12.47, 31.99, 55.62, 89.42, 112.38, 112.57, 113.49, 123.34, 124.10, 129.14, 131.96, 139.00, 144.69, 145.47, 146.53, 148.62, 150.56, 162.09; HRMS (ESI):  $m/z$  [M + H] $^+$  calcd for  $\text{C}_{21}\text{H}_{21}\text{N}_4\text{O}_5$  409.1512, found 409.1510.

3-methyl-5-(4-nitrophenyl)-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5i):

Pale Yellow powder, Yield 95%; mp 238–240 °C; IR (ATR  $\text{cm}^{-1}$ ):  $\nu$  3327, 3219, 2947, 1568, 1339, 910;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ )  $\delta$  (ppm): 1.97 (s, 3H,  $-\text{CH}_3$ ), 3.60 (s, 6H,  $-\text{OCH}_3$ ), 3.68 (s, 3H,  $-\text{OCH}_3$ ), 4.67 (s, 1H,  $-\text{CH}$ ), 6.85 (s, 2H,  $-\text{NH}_2$ ), 6.59–8.30 (m, 6H, Ar-H), 12.28 (s, 1H,  $-\text{NH}$ );  $^{13}\text{C}$  NMR (100 MHz, DMSO  $d_6$ )  $\delta$  (ppm): 12.32, 31.85, 57.05, 60.35, 89.36, 104.53, 112.34, 123.55, 128.67, 129.79, 137.41, 139.56, 144.27, 146.39, 149.60, 152.01, 162.23; HRMS (ESI):  $m/z$  [M + H] $^+$  calcd for  $\text{C}_{22}\text{H}_{23}\text{N}_4\text{O}_6$  439.1618, found 439.1614.

3,4-dimethyl-5-(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5j):

Yellow solid, Yield 93%; mp 242–243 °C; IR (ATR  $\text{cm}^{-1}$ ):  $\nu$  3350, 3263, 2924, 1569, 1367, 914;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ ):  $\delta$  1.69 (s, 3H,  $-\text{CH}_3$ ), 1.99 (s, 3H,  $-\text{CH}_3$ ), 4.54 (s, 1H,  $-\text{CH}$ ), 6.93 (s, 2H,  $-\text{NH}_2$ ), 7.66–8.33 (m, 4H, Ar-H), 12.23 (s, 1H,  $-\text{NH}$ ) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO  $d_6$ ):  $\delta$  12.5, 18.6, 28.5, 89.5, 113.4, 123.5, 129.1, 139.9, 144.4, 145.7, 149.1, 163.6 ppm. HRMS (ESI):  $m/z$  [M + Na] $^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_3$  309.0964, found 309.0960.

3-methyl-5-(4-nitrophenyl)-4-(pyridin-4-yl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5k):

Yellow solid, Yield 90%; mp 248–249 °C; IR (ATR  $\text{cm}^{-1}$ ):  $\nu$  3354, 3210, 2921, 1526, 1350, 934;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ ):  $\delta$  2.03 (s, 3H,  $-\text{CH}_3$ ), 4.69 (s, 1H,  $-\text{CH}$ ), 6.86 (s, 2H,  $-\text{NH}_2$ ), 7.19–8.61 (s, 8H, Ar-H), 12.52 (s, 1H,  $-\text{NH}$ ) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO  $d_6$ ):  $\delta$  13.1, 32.1, 89.1, 112.3, 122.5, 122.8, 129.6, 138.8, 140.6, 143.4, 147.5, 148.5, 150.3, 162.5 ppm; HRMS (ESI):  $m/z$  [M + H] $^+$  calcd for  $\text{C}_{18}\text{H}_{15}\text{N}_5\text{O}_3$  350.1253, found 350.1250.

3-methyl-5-(4-nitrophenyl)-4-(thiophen-2-yl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5l):

Yellow solid, Yield 95%; mp 246–247 °C; IR (ATR  $\text{cm}^{-1}$ ):  $\nu$  3361, 3264, 2908, 1587, 1331, 929;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ ):  $\delta$  1.97

(s, 3H,  $-\text{CH}_3$ ), 4.69 (s, 1H,  $-\text{CH}$ ), 6.80 (s, 2H,  $-\text{NH}_2$ ), 6.90–8.28 (m, 7H, Ar-H), 12.40 (s, 1H,  $-\text{NH}$ ) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO  $d_6$ ):  $\delta$  12.3, 31.9, 55.1, 60.4, 89.4, 112.3, 123.6, 125.6, 127.3, 128.7, 129.8, 137.4, 139.6, 146.4, 149.6, 152.0, 162.2 ppm; HRMS (ESI):  $m/z$  [M + Na] $^+$  calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_3\text{S}$  377.0684, found 377.0681.

3-methyl-4-(2-methylpyridin-4-yl)-5-(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5m):

Pale Yellow powder, Yield 90%; mp 218–219 °C; IR (ATR  $\text{cm}^{-1}$ ):  $\nu$  3345, 3276, 2900, 1567, 1330, 945;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ ):  $\delta$  2.01 (s, 3H,  $-\text{CH}_3$ ), 2.23 (s, 3H,  $-\text{CH}_3$ ), 4.68 (s, 1H,  $-\text{CH}$ ), 6.80 (s, 2H,  $-\text{NH}_2$ ), 7.18–8.58 (s, 7H, Ar-H), 12.47 (s, 1H,  $-\text{NH}$ ) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO  $d_6$ ):  $\delta$  13.54, 28.41, 32.27, 88.50, 112.38, 122.67, 123.84, 132.43, 138.19, 140.74, 143.99, 147.70, 151.33, 157.12, 161.25 ppm; HRMS (ESI):  $m/z$  [M + H] $^+$  calcd for  $\text{C}_{19}\text{H}_{18}\text{N}_5\text{O}_3$  364.1410, found 364.1409.

3-methyl-4-(3-methylthiophen-2-yl)-5-(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (5n):

Yellow powder, Yield 91%; mp 230–231 °C; IR (ATR  $\text{cm}^{-1}$ ):  $\nu$  3356, 3260, 2954, 1579, 1367, 956;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ ):  $\delta$  1.98 (s, 3H,  $-\text{CH}_3$ ), 2.12 (s, 3H,  $-\text{CH}_3$ ), 4.69 (s, 1H,  $-\text{CH}$ ), 6.82 (s, 2H,  $-\text{NH}_2$ ), 6.53–8.29 (m, 6H, Ar-H), 12.38 (s, 1H,  $-\text{NH}$ ) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO  $d_6$ ):  $\delta$  12.34, 13.47, 30.43, 88.79, 113.69, 123.58, 125.70, 127.35, 130.57, 133.42, 136.61, 138.64, 146.13, 150.21, 152.77, 161.48 ppm; HRMS (ESI):  $m/z$  [M + H] $^+$  calcd for  $\text{C}_{18}\text{H}_{17}\text{N}_4\text{O}_3\text{S}$  369.1020, found 369.1021.

2-(6-amino-3-methyl-5-(4-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazol-4-yl)-5-nitrophenol (5o):

Yellow powder, Yield 90%; mp 227–229 °C; IR (ATR  $\text{cm}^{-1}$ ):  $\nu$  3335, 3245, 2932, 1534, 1345, 932;  $^1\text{H}$  NMR (400 MHz, DMSO  $d_6$ ):  $\delta$  2.04 (s, 3H,  $-\text{CH}_3$ ), 4.69 (s, 1H,  $-\text{CH}$ ), 6.83 (s, 2H,  $-\text{NH}_2$ ), 7.13–8.36 (m, 7H, Ar-H), 11.61 (s, 1H,  $-\text{OH}$ ), 12.23 (s, 1H,  $-\text{NH}$ ) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO  $d_6$ ):  $\delta$  12.49, 31.86, 89.42, 111.21, 112.45, 114.30, 122.03, 124.11, 129.14, 131.91, 139.08, 143.43, 145.47, 145.79, 148.67, 156.38, 161.25 ppm; HRMS (ESI):  $m/z$  [M + H] $^+$  calcd for  $\text{C}_{19}\text{H}_{16}\text{N}_5\text{O}_6$  410.1101, found 410.1009.

### 3. Results and discussion

To explore the feasibility and generality of ZnO@PEG nanoparticles catalyzed sonicated MCR, the reaction variables such as the energy efficiency, catalyst, solvent, and feed ratio of catalyst were optimized to observe their roles in enhancing the rates and yield of the products. Benzaldehyde, 4-nitro phenylacetoneitrile, ethyl acetoacetate and hydrazine hydrate were chosen as model substrates.

A variety of catalysts were explored under different reaction conditions (reflux temperature, microwave, and ultrasonic irradiation) and the results are presented in Table 1. To rationalize the influence of the catalyst, a control reaction was first carried out in the absence of catalyst wherein a maximum yield of only 25% was obtained and most of the starting materials were recovered (Table 1, Entry 1). Later, a cluster of catalysts (Lewis acids, *N*-containing bases, metal oxides) (Table 1, Entries 2–9) under various reaction conditions were examined and a maximum yield of 55% was obtained. Switching the reaction only with PEG afforded only 70% of the maximum yield (Table 1, entry 10). However, after incorporating PEG to ZnO and when ZnO@PEG nanocatalyst is used as a catalyst, to our delight, the yield of the reaction increased to 95% (Table 1, Entry 11). Hence, ZnO@PEG nanoparticles under ultrasonic irradiation were preferred for our further studies.

We then began to assess the effect of various solvents (nonpolar, polar aprotic, and polar protic solvents) on the model reaction to substantiate the best choice and the results of the findings are listed in Table 2. We initially probed this experiment under the solvent-free condition on sonication gave the maximum yield

**Table 1**  
Optimization of the catalyst for the synthesis of **5a**<sup>a</sup>.

Entry	Catalyst	Reflux (80 °C)		MW (250 W)		US	
		Time (min)	Yield (%) <sup>b</sup>	Time (min)	Yield (%) <sup>b</sup>	Time (min)	Yield (%) <sup>b</sup>
1	No Catalyst	600	15	30	10	15	25
2	CuSO <sub>4</sub> ·5H <sub>2</sub> O	600	35	30	15	15	35
3	Ln(OTf) <sub>3</sub>	600	25	30	20	15	40
4	Pyridine	600	80	30	45	15	60
5	Piperidine	600	86	30	50	15	50
6	Fe <sub>2</sub> O <sub>3</sub>	600	30	30	30	15	40
7	CuO	600	30	30	35	15	50
8	Al <sub>2</sub> O <sub>3</sub>	600	35	30	40	15	50
9	ZnO	600	62	30	45	15	75
10	PEG	600	50	30	65	15	70
11	ZnO@PEG	600	75	30	60	15	95

<sup>a</sup> Reaction conditions: benzaldehyde (1 mmol), 4-nitro phenylacetone nitrile (1 mmol), ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol) and 0.1 g of ZnO@PEG in ethanol (3 mL).

<sup>b</sup> Isolated yields.

**Table 2**  
Optimization of the solvent for the synthesis of **5a**<sup>a</sup>.

Entry	Catalyst	Reflux (80 °C)		MW (250 W)		US	
		Time (min)	Yield (%) <sup>b</sup>	Time (min)	Yield (%) <sup>b</sup>	Time (min)	Yield (%) <sup>b</sup>
1	No Solvent	600	17	30	15	15	15
2	Toluene	600	15	30	25	15	25
3	<i>n</i> -Hexane	600	20	30	25	15	30
4	DCM	600	30	30	25	15	30
5	THF	600	35	30	30	15	40
6	DMSO	600	35	30	30	15	30
7	CH <sub>3</sub> CN	600	40	30	50	15	55
8	DMF	600	50	30	50	15	70
9	H <sub>2</sub> O	600	60	30	60	15	60
10	H <sub>2</sub> O	1200	65	60	60	45	70
11	Ethanol	600	65	30	70	15	95

<sup>a</sup> Reaction conditions: benzaldehyde (1 mmol), 4-nitro phenylacetone nitrile (1 mmol), ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol) and 0.1 g of ZnO@PEG in solvent (3 mL).

<sup>b</sup> Isolated yields.

(15%) of **5a** whereas unsatisfactory yields were obtained under other conditions even after the prolonged time (Table 2, Entries 2–9). The yield of the product increased incrementally when water is used as a solvent for an extended time (Table 2, Entry 10).

Furthermore, when the reaction was performed in the presence of ethanol within a short period (Table 2, Entry 10) yield of 95% was obtained. Hence, it is clear that the best solvent is ethanol and for further studies, ethanol was chosen as the reaction solvent.

With the prospect to reduce the reaction time and to maximize the product yield, the amount of catalyst required to promote this successful transformation under ultrasonication was ascertained and the results are summarized in Table 3. Consequently, the best result was obtained by using the 0.1 g of catalyst (Table 3, Entry 2). When the reaction was carried out using 0.05 g of the catalyst, the

**Table 3**  
Optimization of the amount of ZnO@PEG for the synthesis of **5a**<sup>a</sup>.

Entry	Amount of ZnO@PEG (g)	Time (min)	Yield <sup>b</sup> (%)
1	0.05	15	40
2	0.1	15	95
3	0.15	15	95
4	0.2	15	95
5 <sup>c</sup>	1	15	95

<sup>a</sup> Reaction conditions: benzaldehyde (1 mmol), 4-nitro phenylacetone nitrile (1 mmol), ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol) and ZnO@PEG in ethanol (3 mL).

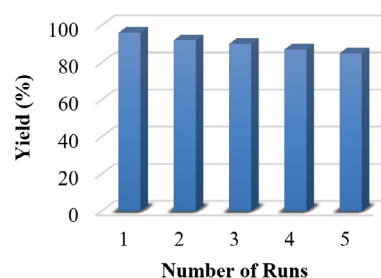
<sup>b</sup> Isolated yield.

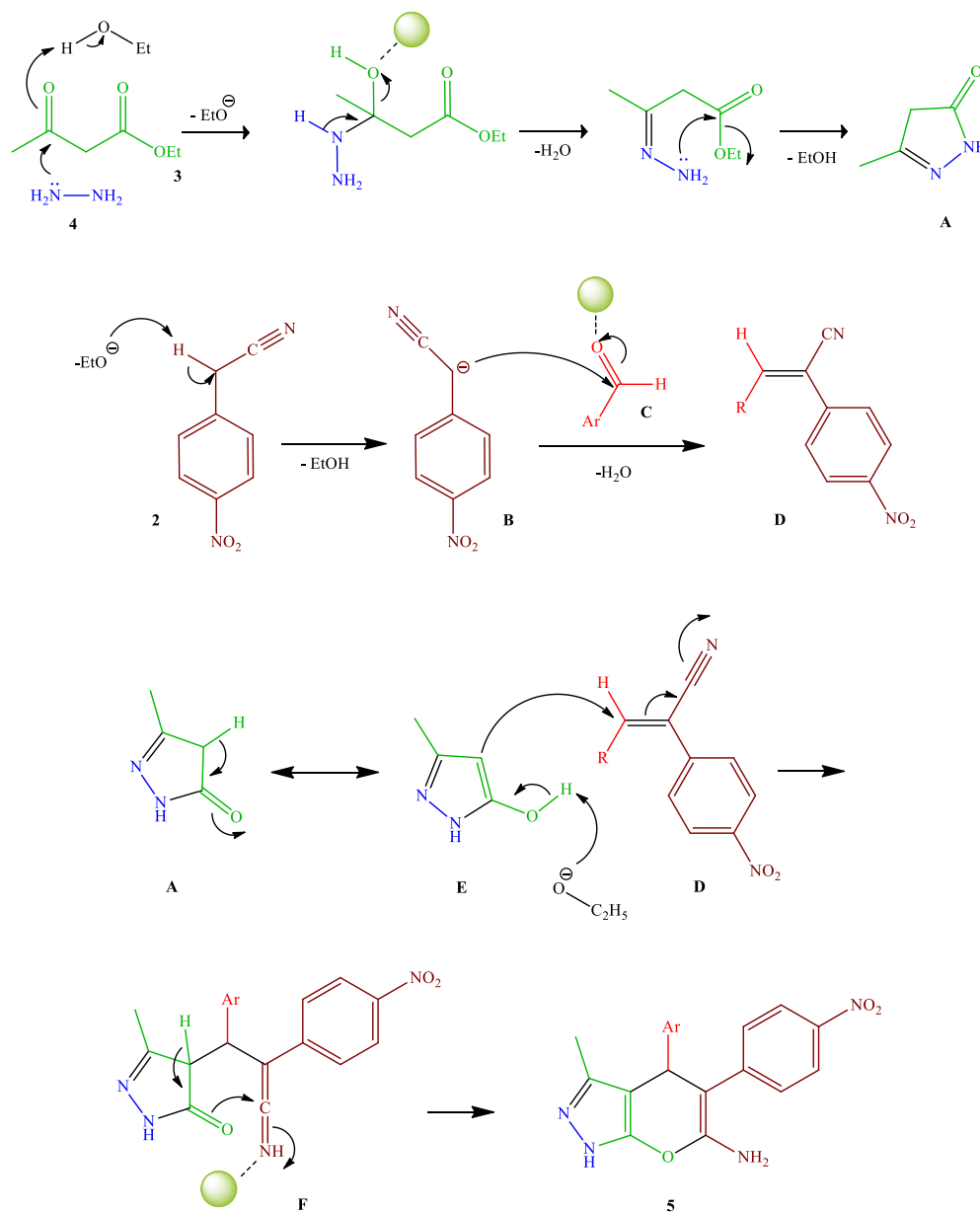
<sup>c</sup> The reaction was carried out in 10 mmol scale.

reaction progressed steadily to give moderate yield (Table 3, Entry 1). Consequently, the best result was obtained by using the 0.1 g of catalyst (Table 3, Entry 2). Further increment in the quantity of the catalyst did not show any significant enhancement in the yield of the desired product (Table 3, Entries 3,4). Later, a scale-up of the model reaction to 10 mmol scales was performed and as anticipated, the desired product was obtained in 95% yield (15 min, Table 3, Entry 5).

Later, the possibility of recycling the catalyst was investigated by performing model reaction and it was observed that the ZnO@PEG nanoparticles could be reused for five consecutive cycles with almost the same catalytic activity giving 95%, 92%, 90%, 87%, and 85% yields (Fig. 1).

To demonstrate the reliability and practicability of our new protocol the substituted aldehydes, 4-nitro phenylacetone nitrile, ethyl acetoacetate, hydrazine hydrate was subjected to the optimized

**Fig. 1.** Reusability of ZnO@PEG in the synthesis of **5(a-o)**.



**Scheme 2.** A plausible mechanism for the synthesis of 1,4-dihydropyran[2,3-c]pyrazoles.

**Table 4**  
Synthesis of 1,4-dihydropyran[2,3-c]pyrazoles.

Entry	R	Product	Time (min)	Yield (%) <sup>a</sup>	m.p. (°C)
1	4-Phenyl	5a	15	97	212–213
2	4-Chlorophenyl	5b	15	95 <sup>†</sup>	200–201
3	4-Bromophenyl	5c	15	92	226–227
4	4-Nitrophenyl	5d	15	94 <sup>†</sup>	230–231
5	4-Hydroxyphenyl	5e	15	91 <sup>†</sup>	245–246
6	4-Tolyl	5f	15	87	236–237
7	3-Methoxy 4-hydroxyphenyl	5 g	15	91 <sup>†</sup>	208–209
8	3,4-Dimethoxyphenyl	5 h	15	95 <sup>†</sup>	220–221
9	3,4,5-Trimethoxyphenyl	5i	15	95 <sup>†</sup>	238–240
10	Methyl	5j	15	93	242–243
11	Pyridin-4-yl	5k	15	90	248–249
12	Thiophen-2-yl	5l	15	95	246–247
13	3-Methylpyridin-4-yl	5m	15	90 <sup>†</sup>	218–219
14	3-Methylthiophen-2-yl	5n	15	91 <sup>†</sup>	230–231
15	2-Hydroxy 4-nitrophenyl	5o	15	90 <sup>†</sup>	227–229

<sup>a</sup> Isolated yield.

<sup>†</sup> Novel compound.

condition and successfully synthesized fifteen 1,4-dihydropyranopyrazoles **5(a – o)** in excellent yields under sonication. The results of this study are presented in Table 4.

It was also observed that in all cases the four substrates congregated successfully to afford the desired product in good to excellent yields in short reaction times (Table 4, Entries 1–15). It is seen that the presence of electron-donating and withdrawing groups tethered on the aromatic ring, did not have any substantial effect on the efficacy of the reaction and product yield.

A plausible mechanism for the formation of the substituted 1,4-dihydropyranopyrazoles catalyzed by ZnO@PEG is envisaged. The initial step may involve the intermolecular cyclization between ethyl acetoacetate (**3**) and hydrazine hydrate (**4**) catalyzed by ZnO@PEG to give the cyclized product (**A**). Also, the hydroxyl groups present on PEG may play a vital role in enhancing the electrophilicity of aldehyde by activating the carbonyl group of the aldehyde (**C**) through hydrogen bonds. This may further lead to a decrease in the energy of transition state which enables the nucleophilic attack of the activated phenyl acetonitrile (**B**) (stabilized by the nitro group of the aryl ring) to give a Knoevenagel adduct (**D**). The enol form (**E**) of the ketone (**A**) may react by a Michael type addition reaction with **D** to give a highly unstable intermediate **F** which on intermolecular cyclization results in the formation of substituted 1,4-dihydropyranopyrazoles (**5**) as depicted in the Scheme 2.

#### 4. Conclusions

We have described a facile, versatile, environmentally benign, rapid and economical protocol for the synthesis of 1,4-dihydropyranopyrazoles under ultrasonic irradiation. The effect of ZnO@PEG nanoparticles as a catalyst along with the use of benevolent processes like ultrasound is significant for the preparation of 1,4-dihydropyranopyrazoles in excellent yield. Cost-effective recovery, reusability of the catalyst without appreciable loss of activity, avoidance of laborious column purification steps, straightforwardness, reliability, broad substrate scope, absence of hazardous organic solvents, and rapid reaction rate are the additional advantages of the current method.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Green methods and sustainable materials

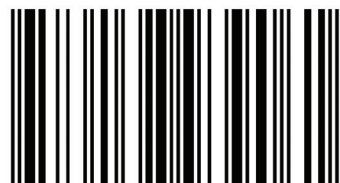
Green methods focuses on designing and development of materials that minimize the generation or use of hazardous substances. The area has gained much attention and significance because of increasing environmental concerns. Every material in our life carries an embedded energetic and environmental footprint, determined in large part by its design, component materials, manufacture, and reuse. The knowledge regarding these sustainable materials is fundamental to fabricate quality products and process design. To synthesize materials that use benign rather than toxic compounds, easier to undertake, lesser energy and time consuming, with reusable reagents, will contribute to the economic feasibility of new green materials over the full life cycle of products. The book discusses the scope of practically useful materials via scientific discovery and engineering development with an eye towards commercial implementation.

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**Dr.P.Nikhil Chandra**, Assistant Professor of Chemistry, Sree Narayana College, Kollam, Kerala, 691001 India

**Dr.Mothi Krishna Mohan**, Assistant Professor of Chemistry, Kerala Department of Sciences and Humanities, Christ University Faculty of Engineering, Bangalore, Karnataka, 560074 India



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# Green methods and sustainable materials

Edited by

**Dr. P. Nikhil Chandra MSc (Chem.), MSc (Env.Sci.), Ph.D.**

(P.G. and Research Department of Chemistry, Sree Narayana College, Kollam,  
Kerala, 691001, India)

**Dr. Mothi Krishna Mohan, Ph.D.**

(Kerala Department of Sciences and Humanities, Christ University Faculty of Engineering,  
Bangalore, Karnataka, 560074, India)

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## *Preface*

The book presents various recent developments, state of the art methods and progresses in the field of energy and sustainable materials. The efforts and way that is under development to improve the usability of energy systems, reducing their environmental impact were discussed. Discussions in the book mainly aims at providing researchers, academics, engineers and advanced students information and points of discussion, a platform for current scenario and future perspectives in green energy. Both theoretical and applied aspects are treated in this book with sufficient examples. Different chapters are contributing to the increasing interest in reducing the environmental impact of many types of energy efficient sustainable materials that led to green methods.

First chapter deals with advanced and modern types of surface modifications that convert ordinary membranes to advanced membrane types and its industrial applications. Second chapter discusses the fabrication of high quality thin films for various applications have got immense significance in the area of science and technology especially in the area of electronic devices and voltaic cells. Third chapter deals with various aspects of sustainable photo catalytic degradation of ciprofloxacin using new generation  $\text{CeO}_2\text{-La}_2\text{O}_3$  nano composites. Fourth chapter deals with innovative and green metal organic framework capable of gas sensing applications. Fifth chapter deals with the vast world of polymeric membranes, its application, modification and future aspects. The last chapter, the sixth one discuss about green, rapid and an efficient one pot protocol for pyrimidine derivatives in which the methodology is environmentally benign, catalyst-free, excellent yields, broader substrate scope, high conversion rate, operational simplicity, excellent functional group tolerance, shorter reaction time, and use of a green solvent.

Green methods focuses on designing and development of materials that minimize the generation or use of hazardous substances. The area has gained much attention and significance because of increasing environmental concerns. Every material in our life carries an embedded energetic and environmental footprint, determined in large part by its design, component materials, manufacture, and reuse. The knowledge regarding these sustainable materials is fundamental to fabricate quality products and process design. To synthesize materials that use benign rather than toxic compounds, easier to undertake, lesser energy and time consuming, with reusable reagents, will contribute to the economic feasibility of new green materials over the full lifecycle of

products. The book discusses the scope of practically useful materials via scientific discovery and engineering development with an eye towards commercial implementation.

This book discusses areas from different visions on reducing the impact of energy on the environment (green methods) and sustainable materials to choose in a broad manner, not all areas or methods are discussed. Different chapters in this book show that many researchers are investigating the efficient use of energy whilst looking for ways to decrease its impact on the environment. This shows the importance of such research and development to be followed for the future of mother earth.

**Dr.P.Nikhil Chandra**

**Dr.Mothi Krishna Mohan**

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(<sup>1</sup> Department of Sciences and Humanities, School of Engineering and Technology, CHRIST (Deemed to be University), Kumbalagodu, Mysore Road, Bengaluru 560074. India.

<sup>2</sup> Department of Chemistry, Surana College, South End Road, Basavanagudi, Bengaluru 560004. India.)

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## Chapter 1

### Green approach of surface modified polymer membranes in filtration/purification applications

Dr. P. Nikhil Chandra <sup>a, b \*</sup>

<sup>a</sup> P.G. and Research Department of Chemistry, Sree Narayana College, Kollam, Kerala, 691001, India

<sup>b</sup>Advanced Centre of Environmental Studies and Sustainable Development (ACESSD), Mahatma Gandhi University, Kottayam, Kerala, 686560 India

\*e-mail: pnikhilchandra@gmail.com

#### Abstract

The greatest challenges we are facing today involves sustainable supplies of two interrelated resources, clean water and energy at an affordable economical way. Membrane technology is expected to be energy efficient and green approach for purifying water, but most filtrations suffer from fouling during filtration. Thus, the need and development of improved membranes that have higher flux, which are more selective, are less prone to fouling, and which are more resistant is important. This article summarizes various types of membrane methods, its surface modification methods to mitigate membrane fouling and rejection efficiency that helps to maintain high levels of filtration productivity with special reference to water purification. Common membrane surface modification techniques are reviewed, including layer by layer (LbL), surface coating, grafting, and various treatment techniques such as chemical treatment, UV irradiation, and plasma treatment, among others.

#### 1.1 Backgrounds

A membrane is an inter phase between two adjacent phases which is permeable or semi-permeable barrier, often a thin polymeric solid, which restricts the motion of “certain” species and allow the passage of other components through it. Membranes are thus a type of phase that act as a barrier to prevent mass movement but allows restricted and/or regulated passage of one or more species through it. Hence, a membrane can be solid, liquid or gas or a combination of all these. The performance of a membrane is usually explained between two factors, flux and selectivity. Ideally a membrane with a high selectivity and flux is preferred for filtration and separation processes.

Membrane processes are currently used in several ways to filtration especially to purify water with desalination by reverse osmosis (RO) or nano filtration (NF) being the most common types,

but not the only, example. Being energy efficient with high efficiency, more technical support is required for these methods. Advanced surface coating techniques can play a large role in confining low cost microfiltration membranes get upgraded to RO or NF levels. The application of surface modified hollow fiber UF membrane for the removal of certain organic micro pollutants is now reported (M.T.Jain et al, 2017). The growing need to purify more and more water represents a growth opportunity for membrane technology. Advanced membranes are needed to meet these challenges. As most of the commercially used membranes are polymeric, this scenario creates a good opportunity for polymer science.

During eighteenth century when the world faces World War II, the water scarcity in Europe triggered the development of membrane based filters for water purification. However, due to lack of research and technology, slow operation, reduced selectivity and elevated costs, these membrane filters could not be widely exploited. The history of membranes and its applications started with the scientist Abb'é Nollet (19 November 1700 – 25 April 1770), a French clergyman and physicist. He used the word 'osmosis' to describe permeation of water through a semipermeable membrane in 1748. In 1855 Adlof Fick (3 September 1829 – 21 August 1901) who was a German-born physician and physiologist published his laws of diffusion, which are still used today to describe diffusion through membranes. In same year, the first man-made plastic, nitrocellulose (branded Parkesine, patented in 1862), was created by Alexander Parkes from cellulose treated with nitric acid and a solvent. Later in 1867, Moritz Traube also prepared artificial membranes with his several discoveries. In 1877, Wilhelm Pfeffer, a German botanist and plant physiologist successfully manufactured membrane by precipitating copper ferrocyanide in the pores of porcelain.

Rapid development of theories of thermodynamics of solution (van't Hoff's and Gibbs theory) during 1870-1920 lead to the development of relationship between osmotic pressure and other thermodynamic properties. Different types of membranes become commercially available during this period. Membrane technology then triggered its expansion to more versatile polymers, mainly cellulose acetate. Membranes found their first significant application in the testing of drinking water at the end of World War II. Until 1945, membranes were used primarily for the removal of microorganism and removing particles from liquid and gaseous streams. With the development of microfiltration membrane during 1950's the technology was widely used for



water purification, sea water purification, desalination etc. Major defects like low permeation rate and flux make them practically inapplicable.

Sourirajan and Loeb in 1958 modified the commercially available cellulose acetate membrane by heat treatments. They developed membranes of a single membrane material, but the porosity and pore size change in different layers of the membrane. Anisotropic membranes made by other techniques and used on a large scale often consist of layers of different materials which serve different functions. The flux of these membranes was 10 times higher than that of any membrane then available. This discovery made reverse osmosis a potentially practical method for desalination and softening of water. Between 1960-80, several experiments based on the original Loeb–Sourirajan technique, other membrane formation processes, including interfacial polymerization and multilayer composite casting and coating were developed for making high performance membranes. In the late 1970s, an important mile stone happened in the history of membranes with the development of the second generation of membranes known as composite membranes. Significant progress has been made in the mid-1980 with deployment of large plants installed worldwide using microfiltration, ultrafiltration, reverse osmosis and electro dialysis processes. Another major development in the 1980s was the emergence of industrial membrane for gas separation processes. New areas of applications of membrane related technologies are explored mainly in pharmaceutical and chemical fields. A wide range of applications including drug delivery, gas concentration sensors, catalysis and nanotechnology applications are exploring the advantageous of membrane technology.

## **1.2 Membrane Separation Techniques**

Membrane separation is the most advanced and effective filtration technology utilized to clarify, concentrate and separate continuously molecular or ionic compounds from their solution state. This process is potentially interesting for water processing, in particular in the treatment or recycling of water polluted by micron, submicron and/or ionic species. There is a number of membrane based separation techniques, varying in the driving forces employed. These forces include concentration gradient, applied pressure and electrical potential. Filtration membrane processes are effective separation techniques with a wide variety of applications, from the food/beverage/pharmaceutical/medical industries to water purification. During operation, water constituent mixtures(source) are pumped against the active side of the membrane surface, producing permeate and retentate. Due to the size exclusion and electrostatic

repulsion effects of the membrane, different components in the feed stream pass through the membrane at different speeds. The more permeable/small species will be dominant in the permeate, while the less permeable/large particles get rejected and go into the retentate.

The various membrane separation processes are osmosis, dialysis, pervaporation, electro dialysis, micro filtration, ultrafiltration, reverse osmosis and nanofiltration. Among membrane separation processes, the distinction between various processes is somewhat arbitrary. The membrane separation processes can be broadly classified in to two, pressure driven and non pressure driven processes.

Four main types of pressure driven filtration membranes exist include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). They are classified based on their distinctive pore size and ability to reject different sized matter. Microfiltration (MF) membranes have pores on the order of 1  $\mu\text{m}$  and have the largest pore size with an average of  $\sim 100$  nm. They are generally used to reject relatively large particles, sediments and also useful for removing large colloids, algae, bacteria, microbes, cells, and viruses etc. UF membranes are tighter and have smaller pores than MF membranes. Their average pore size of  $\sim 10$  nm makes them great candidates for small colloids and protein rejection. MF and UF membranes accomplish separation essentially by size exclusion; solutes larger than the membrane pore size are rejected, while solutes smaller than the membrane pore size, including water, flow through the pore structure. They can be used in food processing, blood dialysis and the pharmaceutical industry for purifying and concentrating solutions of macromolecules such as proteins, polysaccharides and drugs. NF membranes have pore sizes of only 1 nm or less and are normally positively or negatively charged, making them suitable for softening water by rejecting divalent ions. As they have exceptionally small pores, it is used for transport of salt and water through their selective layers are described using a combination of diffusive, convective, and electrostatic models. RO membranes are considered nonporous and used to reject monovalent salts such as NaCl. They are dense (non-porous) membranes and water transport through RO membranes occurs via a solution-diffusion mechanism They are used in the desalination process, which produces freshwater from sea water as well as specific inorganic contaminants (arsenic, fluoride, nitrate, nitrite, selenium and synthetic organics) removal.

Membrane Separation	Membrane Type	Driving Force	Applications
Osmosis	Symmetric microporous	Chemical potential	Separation of solutes from water
Dialysis	Symmetric Microporous	Concentration Gradient	Separation of micro-solutes and salts from macromolecular solutions
Microfiltration	Symmetric and Asymmetric composite	Hydrostatic pressure	Purification, sterile filtration
Ultrafiltration	Asymmetric composite	Hydrostatic pressure	Separation of macromolecular solutions
Nanofiltration	Asymmetric microporous, composite	Hydrostatic pressure	Separation of small organic compounds and selected salts from solutions
Reverse osmosis	Asymmetric, Composite	Hydrostatic pressure	Separation of micro-solutes and salts from solutions
Gas permeation	Asymmetric, Composite	Hydrostatic pressure Concentration Gradient	Separation of gas mixtures
Pervaporation	Asymmetric, Composite	Concentration Gradient, vapour pressure	Separation of mixtures of volatile liquids
Membrane distillation	Microporous	Temperature	Separation of water from non volatile solutes
Electrodialysis	Ion exchange, homogeneous or microporous	Electrical potential	Separation of ions from water and non-ionic solutes

**Table1.** Major types of membrane filtration and its distinctions

The additional advantage of membrane separations includes their relatively low energy requirement, economical and non involvement of phase transitions, unlike conventional processes such as distillation, extraction and crystallization. Membrane separation processes have several advantages like a) low energy alternative to evaporation in concentrating a dilute feed, b) the chemical and mechanical stresses on the product are minimal with modest energy requirement, c) single step product concentration and purification and d) possibility of scale up. Membrane separation processes achieve separation through a combination of sieving, hindered

transport through the narrow membrane pores and other specific interactions between the components and the membrane material such as adsorption, hydrophobic and electrostatic interactions.

### **1.3 Water Filtration Membranes**

Technical advancement and cost reductions helped many membrane systems now capable of decontaminating non-saline waters or treated wastewaters in single-step processes. Membrane technologies are now emerged as alternatives to conventional water treatment and as a means of polishing treated wastewater effluent for reuse applications and are more energy intensive also. Future of low pressure systems that significantly reduce energy use, operation and maintenance costs is surely a good sign and give it some edge than high pressure filtration methods like RO and NF. Membranes are commonly used for the removal of dissolved solids, color and hardness in drinking water. In wastewater reclamation and reuse, water quality requirements may call for reductions in suspended solids, total dissolved solids, and selected constituents such as nitrates, chlorides and natural and synthetic organic compounds. Membrane treatment, applied to the end of conventional wastewater treatment systems, is a viable method of achieving desired effluent quality levels at reasonable costs. Oily waste water, stillage from biomethanol plant, laundry waste water, effluent from textile and paper industry are generally subjected to membrane treatment before disposed to water streams. The above specified processes have energy costs which are only one-half or one-tenth of the sophisticated membrane methods without surface modification.

Most commonly used process for the production of drinking water are RO and NF as a viable alternative to conventional water treatment because it can operate at lower pressures and higher recovery rates than RO systems. NF can be made more cost effective by surface modifications in many groundwater softening applications where the incoming turbidity is low. Efficiency of another method, electrodialysis (ED) shows decreased flux rapidly with the increase in the feed concentration. So the process is best utilized for the purification of saline water containing less than 5000 ppm of total dissolved solids. Water at the low concentration end of the brackish scale is generally subjected for the electrodialysis treatment for better results. Another method called Electrodialysis reversal (EDR) is an improvement over the original electrodialysis process. In EDR, the direct-current driving force is periodically reversed to prevent scaling and fouling of the membrane surface. Methods of effluent decolonization like membrane filtration technology

has the ability to clarify, concentrate and separate dye content. The limitations of these methods caused it not to be used in classical waste water treatment process.

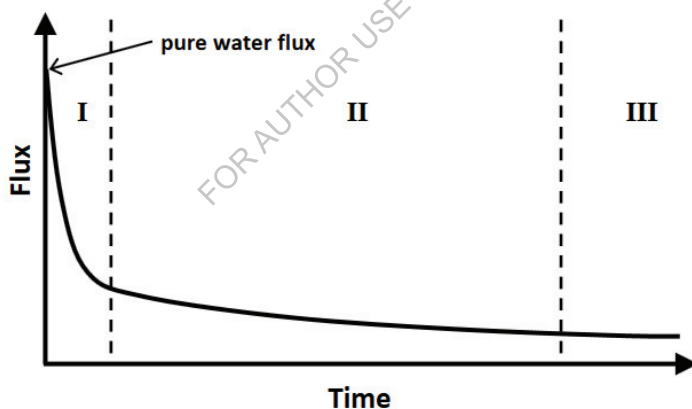
The mechanical properties, ease of processing, thermal stability, and chemical resistance are important considerations for water purification membrane materials. Many polymers, such as polysulfone (PSf), poly(ether sulfone) (PES), poly(vinylidene fluoride) (PVDF), cellulose acetate (CA), polypropylene (PP), poly(acrylonitrile) (PAN), and polyamides, have appropriate materials property sets. Additionally, these polymers are available in large quantities at reasonable cost, which contributes to their selection in the manufacture of water purification membranes.

Polymer	Chemical structure	Membrane type
Polypropylene		MF
Poly(vinylidene fluoride)		MF
Polysulfone		UF
Poly(ether sulfone)		UF
Poly(acrylonitrile)		UF
Crosslinked Aromatic Polyamide		NF/RO
Cellulose acetate		RO

**Table 2.** Membrane materials used for water purification

## 1.4 Membrane Fouling

One of the basic problems in membrane separation is permeation fouling, which is the undesirable accumulation of solutes either externally on the membrane surface or, in the case of a porous membrane, internally within the pores, or both. As foulant builds up on the membrane surface or in the pores, the mass transfer resistance of the membrane to water transports increases, decreasing the membrane productivity. Often, fouling is characterized in terms of flux decline at a fixed transmembrane pressure, as shown in Figure 1. In pure water filtration, the only mass transfer resistance to water passage through the membrane is that of the membrane itself. However, if foulant accumulates on the membrane surface, an additional resistance is imposed on water passage, and the flux is lower than during pure water filtration. This decrease in flux typically occurs very rapidly when a membrane is first challenged with a fouling feed solution. The flux then typically decreases gradually before reaching a steady state value.



**Figure 1.** Flux decline curve in membrane filtration showing (I) rapid decrease in flux when the membrane is challenged with a fouling feed solution, (II) a long term gradual decrease in flux, and (III) steady state flux.

The many factors contributing to membrane fouling and the mechanisms by which foulant accumulation proceeds are extensively reviewed elsewhere. Fouling is exacerbated by concentration polarization, which is the accumulation of solute near the membrane surface due to

the rejection of the solute by the membrane as water permeates through the membrane. A high concentration of solutes near the membrane surface facilitates solute deposition onto the membrane. In UF, concentration polarization can be severe enough to cause precipitation of solutes, forming a gel layer on the membrane surface. In RO and NF, such precipitation results in the formation of mineral scale. Hydrophobicity, surface charge and many other properties also appear to contribute to membrane fouling. For this reason, many surface modifications focus on hydrophilizing a hydrophobic membrane surface. Surface roughness has been implicated as a significant determinant of membrane fouling susceptibility in several studies. Several studies have suggested that surface roughness, which arises from the interfacial polymerization procedure used to fabricate the membrane, may contribute to membrane fouling susceptibility.

### **1.5 Membrane Development and Surface Modification**

The earliest surface modification was done by W. Pfeffer in 1877. He is interested in mimicking the semipermeable nature of plant cell walls; Pfeffer used these membranes to study osmosis following the observations of Nollet, Graham, and others. He prepared copper ferrocyanide membranes by saturating porous porcelain with copper sulfate solution, then contacting one face of the porcelain with a solution of potassium ferrocyanide. Another modification was in 1896 by C. J. Martin, who reported the modification of ceramic Pasteur-Chamerland water filters with gelatin or silicic acid. To modify filters with gelatin, a 10% solution of hot gelatin was fed through a filter under a pressure of 10 atmospheres until it cooled, forming a solid film within the filter pores. Preparation of membranes by coating a porous structure continued into the 20th century. A series of papers published in 1907 and 1908 by Bechhold (who coined the term “ultrafiltration”) reported fabricated membranes by impregnating filter paper with solutions of collodion, glacial acetic acid-collodion, and gelatin. Later on, fabrication techniques for membranes was developed by Bechhold, which were tuned by others, including Elford, Krueger, and Ritter, who produced flat sheet membranes of uniform thickness in a variety of pore sizes. Membrane technology becomes more attractive for industrial use due to its advancement. A patented method was developed by Duclaux for the production of UF membranes in large quantity by impregnating cloth with solutions of cellulose acetate.

The theory of fouling mitigation first appears in a 1923 publication by Brinkman and Szent-Gyorgyi. The filtration of a solution of hemoglobin through a collodion sac membrane was attempted, only water was observed to permeate through the membrane. Elford in 1933, reported

the effect of sodium oleate on the passage of dye through collodion ultrafilters. The study discussed the addition of sodium oleate to a dye solution facilitated passage of the dye through a collodion membrane due to the preferential adsorption of the oleate over dye at the collodion/water interface. Several early studies on filtration of biological solutes such as proteins and viruses using collodion ultrafilters were based on these types of membranes. Reports by Ward and Tang (1929) and by Galloway and Elford (1931) both described an increase in passage of viruses through membranes when the viruses were suspended in biological broth instead of water. Galloway and Elford compared this change in virus filterability to a type of modification of the surface properties of virus and filter owing to adsorption of certain surface active constituents of the broth. The advancement of synthetic polymer industry accelerated membrane development throughout the late 1950's and 1960's. Practical RO membranes became a reality when Loeb and Sourirajan (L-S) fabricated asymmetric RO membranes by phase inversion of cellulose acetate from acetone solution in 1960, later described in his 1963 publication. Various surface active cationic, anionic, non-ionic, and amphoteric active agents were also tested over L-S RO membranes by Vos and Burris in 1969. In this work, the authors were studying the effects of various adsorbents, including nonionic materials and various commercial anionic and cationic surfactants, on the drying of cellulose acetate membranes.

A modern type RO membrane was created in the late 1970's by Cadotte developed the thin film composite polyamide membrane. This membrane was the product of work begun in 1967, when porous support membranes were fabricated from polyether sulfone (PSf) by phase inversion. The so synthesized membranes have small (20 nm) pores on one side and much larger (400 nm) pores on the other with many properties like high flux, high salt rejection. The ultrathin barrier layer was formed atop the small pores on one face of the UF support membrane. Different techniques used to fabricate modern membranes had been developed by the early 1980's. Different types of polymers were successfully being used to fabricate MF, UF, and RO membranes. Lonsdale in 1982 published a review describing developments in membrane technology and its modifications. This later helped the membrane research which gave a focus on improvement of the properties of these basic membrane architectures, and surface modifications.

## **1.6 Significance and strategies of surface modifications**

Additive blending is a common method where one or more surface-modifying components are incorporated into a polymer used to form the membrane. This technique is not a clear



modification of a preformed membrane, but the surface modifying reagents typically preferentially partition to the surface of the polymer membrane. Thus forming a membrane that has different surface and bulk properties can also be considered as a modification. Surface modifying compounds may also be applied to the surface of preformed membranes. Simple modification involves use of hydrophilic macromolecules, which are adsorbed to the surface of the membrane. In order to improve the durability of these surface modifications, the macromolecules or polyelectrolytes may be coated onto the membrane surface and subsequently cured by cross linking to get a stable material. A variety of surface treatment techniques are available including chemical treatment, plasma treatment, UV irradiation, and other related techniques. These approaches may be used alone or in association with other methodologies.

The US origin Millipore Corporation has a long history of research in surface coatings for increased permeation flux for membranes. In 1986, Steuk was granted a patent for water purification membrane surface treatment, which describes the preparation of a composite membrane consisting of a microporous membrane coated with a cross linked layer of hydrophilic polymer. The modification is applied to both the top surface of the membrane and inside the pore walls, relies on no intermediate binding agent and makes the membrane surface hydrophilic. Millipore continued to develop different surface coating technology with a number of their patents describe various polymeric coatings, including crosslinked hydrophilic coatings, crosslinked hydrophobic coatings, crosslinked charged coatings, multilayered coatings, and perfluorocarbon copolymer coatings, for various industrial applications. A US based industry Dow has also reported the mitigation of membrane biofouling through surface modification. Tang and co-workers published a series of reports describing membrane surface modifications and characteristics of 17 commercial RO and NF membranes by four different manufacturers, including Dow Filmtec, Hydranautics, GE Osmonics, and Saehan Industries.

Low pressure filtrations like UF and MF are also extended to the quality level of RO and NF for effective removal of low molecular weight compounds and ions with surface modification. Usually, the low pressure filtrations are preferred at base level municipal and industrial applications as the investments are low. As these low pressure systems are mostly restricted at the pretreatment level and require further improvement with respect to flux and other filtration properties. These also find application in potable filtration units, where the primary target is mainly pathogens, turbidity etc. It is worthwhile if such membranes also remove low molecular

weight pollutants that are found in water matrix lately. Advanced surface coating techniques can play an important role in confining such separation surfaces to the conventional membranes.

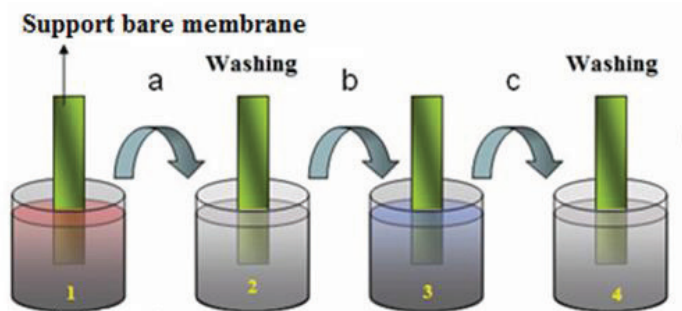
### **1.6.1 LB and SAM methods**

Surface coating can be very interesting, provided it has molecular level control and ability to upscale at industrial level. Molecular level control is very much attained through Langmuir–Blodgett (LB) and self-assembled monolayers (SAMs). LB technique is a way of making short range order supra molecular assembly in ultrathin films with a layered structure and crystal parameter, which have many applications for optical and molecular electronic devices as well as signal processing and transformation. LB technique can be one of the best methods to provide a scope to realize the molecular electronics in reality. Feng X et al (2020) reported the LB modification for incorporating nano materials into lipid bilayer system for bio-sensing applications. Song Y et al (2019) also showed the ability of LB and SAM for tuning ion conductivity behaviour. SAMs are an important element of modern nanotechnology, which can be used for the fabrication of monomolecular insulator films of well defined thickness in the nanometer range to provide an alternative to commonly used oxide dielectrics in future, nano scale electronic and spintronic devices, and also in organic electronics assembles. They offer unique opportunities to increase fundamental understanding of self organization, structure property relationship and various interfacial relationships. But both have certain limitations with respect to substrates. Most of the coatings which can be applied at macroscopic scale have drawbacks, as they do not have control at molecular level.

### **1.6.2 Layer by layer (LbL) method/Absorbed coatings**

Method of incorporating a material into the casting solution is also a type of modification like preferentially migrate to the surface during membrane formation; the membrane may be directly coated, after formation, with another material that imparts desirable characteristics to the surface. These coatings may consist of material that is simply adsorbed to the membrane surface via secondary interactions (e.g., van der Waals or electrostatic interactions) or materials that are cured (e.g., crosslinked) in situ on the membrane surface to afford enhanced stability. The strength of these secondary interactions depends upon the nature of the polymer surface and of the surface modifier. LbL is a new generation 2D layering method which is regarded high since it combines both the properties of LB and SAM. It carries an important advantage of bottom up control over the fabricated assembly with various surface properties. LbL is more convenient

with respect to the simplicity of application and potential to apply to various substrates of different geometries. Fabrication of composite membranes by coating skin layers on MF/UF membrane by LbL method is an economical and aqueous based cleaner technology. The method involves alternative immersion of membranes on oppositely charged aqueous polyelectrolyte at room temperature. The primarily driven force in LbL is pure electrostatic attraction and sometimes could also involve hydrogen bonding, hydrophobic, covalent bonding, charge transfer, biological recognition etc. Due to these types of interactions in the multilayer, the resulting polyelectrolyte multilayers (PEMs) are highly stable to severe conditions. The substrate versatility and material flexibility also increases the popularity of LbL assembly. The application includes a wide range such as water purification, gas separation, fuel cells, controlled drug delivery, biosensing, implantable materials, photocatalysis, and metal organic frame works. These modified membranes also find their way to the removal of biological contaminants. The ability to tune the thickness of PEMs from few angstroms to micrometers is yet another property suitable for industrial applications. Most important property over other surface modification methods is the decreased water flux of hydraulic resistance layer, the LbL method improves the water flux by weakening the hydraulic layer. Nikhil C P et al (2018) showed the use of LbL for heavy metal removal. Usha K et al (2007) showed the use of LbL as biosensor, Disha V.J. (2012) reported its use as phosphate recovery, Chandra N P et al (2020) reported its use for selective ion transport. Thus, a wide range of publications with a variety of applications were reported for surface modified LbL membranes proved that modification has a great role in membrane technology.



**Figure 2.** LbL method for PEM membrane fabrication

### 1.6.3 Grafting

Grafting is a popular surface modification technique mainly used for many organic and inorganic substrates. Grafting generally refer to the attachment of macromolecules to a bare membrane surface. It has got wide application in biomaterials, where synthetic polymers, proteins, polysaccharides, and other macromolecules have been applied to surfaces of biomaterials to reduce thrombogenic response upon implantation. Again, grafting of hydrophilic polymers has also been used to improve the fouling resistance of membranes. The process of grafting involves a) tethering a synthetic or natural polymer chain to the membrane surface, b) growing a polymer chain from the membrane surface. In the initial type method, an end-functionalized polymer is covalently bound to a membrane surface containing an appropriate reactive group. Thus, these polymers may be synthesized by anionic, cationic, living free radical, group transfer, or ring-opening metathesis polymerizations, which permit fine control over the structure and properties of the polymer prepared typically result in relatively low graft densities. Sometimes special coupling reactions may be required between the membrane surface and the grafted polymers. A wide variety of grafting densities may be accessible with polymers obtained by later type method. Immobilization of appropriate initiators is generally possible via several techniques, such as plasma, corona discharge, or chemical treatment. Porter C J et al (2020) reported a grafted modification of cellulosic membranes used for selective layer filtration. Vatanpour V et al (2020) reported a surface modification of reverse osmosis membranes by grafting of

polyamidoamine dendrimer containing graphene oxide nanosheets for desalination improvement. Bao X et al (2019) reported a polyamidoamine dendrimer grafted forward osmosis membrane with superior ammonia selectivity and robust antifouling capacity for domestic wastewater concentration.

#### **1.6.4 Blending with additives**

Membrane surface modification can be achieved by incorporating a surface modifying additive (hydrophilic material) into the membrane casting solution before membrane fabrication. Different porous water purification membranes of UF and MF applications are formed via phase inversion, in which a cast solution is made from a solvent to form a film and subsequently immersed in a non-solvent for the polymer to solidify. The so fabricated membrane polymer is often hydrophobic and dissolved in a water miscible organic solvent. Usually a hydrophilic material in the casting solution will tend to migrate to the membrane bulk and to the pore wall surfaces during phase inversion. Thus a membrane largely comprised of a hydrophobic polymer, but with a hydrophilic surface, is formed. Membranes containing surface modification macromolecules generally showed improved flux compared with unmodified when filtering crude contaminated water or oil/water emulsions. Jiang et al. (2005) incorporated a PPO-PEO-PPO triblock copolymer into PES UF membranes. These membranes incorporating the triblock copolymer showed reduced fouling relative to PES control membranes during oil/water emulsion fouling experiments. Deng Y et al (2019) fabricated superhydrophilic and underwater superoleophobic membranes via an in situ crosslinking blend strategy for highly efficient oil/water emulsion separation. Arahman N et al (2019) reported an improving water permeability of hydrophilic PVDF membrane prepared via blending with organic and inorganic additives for humic acid separation.

#### **1.6.5 Chemical treatment methods**

Another important surface modification includes chemical treatment which increases coating durability, covalently coupling the agents to the membrane polymer. These agents may be either small molecules or, more commonly, polymers. By different pathways through which covalent coupling to the membrane surface may be achieved. Different reagents were used to introduce desired chemical moieties on a membrane surface. By sulfonation, it is possible to introduce hydrophilic groups on hydrophobic polymers such as poly(aryl sulfone)s (e.g., PSf and PES), which are often used in water purification membranes. Sulfonation of surface would also result

in substantial increases in hydrophilicity and T<sub>g</sub> relative to the unsulfonated polymer. Another way to introduce sulfonate groups into polymer membranes has also been explored. Higuchi and his co-workers modified the surface sulfonation of PSf hollow fibers by propane sultone with Friedel-Crafts catalysts. A common method to introduce aryl sulfonic acid groups to poly(arylsulfone)s is through direct contact of membrane surface with chlorosulfonic acid. After neutralization, it yields membranes with highly hydrophilic sulfonate groups directly connected to the aromatic rings of the polymer backbone. It is also possible by chain cleavage and subsequent branching or crosslinking. The hydrophilization of commercial thin film composite polyamide RO membranes was described by Gill et al.(1981). The surfaces of ceramic membranes have also been chemically modified and studied. Zirconia and titania UF membranes were treated by immersion in solutions of phosphoric or alkyl phosphoric acid to evaluate effects of charge and hydrophobicity on protein adsorption, protein rejection, and water flux.

Membrane surface natively contains some functional groups which can also be utilized for grafting. Polyamide RO and NF membranes typically have residual free carboxylic acids and primary amines. These groups can be utilized for the interfacial polymerization used to prepare the polyamide membrane. Freeman et al. (2011) grafted poly(ethylene glycol) diglycidyl ethers to these free moieties to create fouling-resistant RO and NF membranes. The resultant grafted PEG chains generally decreased the membrane pure water permeation by about 30-50%, depending upon the membrane type used and the molecular weight (MW) of PEG taken. The reports also showed that the coating of RO membranes increased their salt rejection from 99.1% to 99.3-99.5%, and coating NF membranes increased their salt rejection from 97.8% to 98.7%. If suitable functional groups are not natively present on the membrane surface, additional reagents may be used to prepare the surface for grafting. Xu et al. (2003) showed that PEG chains were tethered to poly(acrylonitrile-co-maleic acid) membranes by after refluxing the membrane with acetic anhydride, which converted carboxyl moieties on the membrane surface to anhydrides. Surface modification can be extended to bulk of polymeric membranes also. For example, Xu et al. (2002) grafted poly(acrylic acid) to microporous hollow fiber polypropylene (PP) membranes by using a benzoyl peroxide initiator in the presence of acrylic acid monomer. Acrylic acid was grafted to the outside of the fibers from a toluene solution. The poly(acrylic acid) formed a thin, dense layer at top of the PP membrane. Reports of inorganic membrane surfaces are also available. For example, Cohen, Castro, and Monbouquette (2001) successfully grafted PVP to the

surface of porous silica membrane. Cohen and Faibish (2001) also grafted PVP to zirconia membranes. All these modified membranes exhibited improved oil rejection, which was attributed to narrowing of defects in the membrane.

#### **1.6.6 Spin coating method**

Spin coating method for surface modification has got high industrial application since it allows the deposit of smooth films of polymer, thicker than those obtained by LB technique. Benz et al. (2002) prepared 2- $\mu\text{m}$  films using solutions of PVDF diluted in DMF and acetone, and tuning the relative humidity. It has got wide application in micro lithographic processes for producing photo resists in the microelectronics industry. Spin coating process involves the unique spraying of an excess of polymer solution to the surface of a horizontal membrane substrate, which is then rotated or spun at high and controlled speed. The rotation may range from several hundred to thousands of revolutions per minute. The centrifugal force causes the solution to spread in a thin film from which the solvent rapidly evaporates to yield a uniform solid polymer coating on the membrane. The thin film formation mechanism can be described as follows. (1) deposition of excess polymer solution which covers the membrane surface, (2) rapid radial displacement of the bulk of the deposited solution due to centrifugal forces resulting from the rapidly spinning the membrane, (3) laminar radial flow of the liquid layer of uniform thickness left on the membrane surface, and (4) removal of excess solvent by evaporation until the film stops flowing radially and eventually dries. Thus, generally speaking, the spin coating is performed in four steps, deposition, spin up, spin off, and evaporation. Main advantages of spin coating are to produce very fine, thin, and uniform coating, but the disadvantage includes the difficulty with large area samples. The thickness of film can be changed by changing spin speed or switching to different modes. Despite being laboratory friendly, it has demerit of incapable for large substrate, lack of material efficiency, and cost of disposal. The inability to create multilayers, presence of containments are also some drawbacks of spin coating.

Zhang et al (2008) reported a Mg-Al layered double hydroxide (LDH) film by spincoating a nano dispersed MgAl-LDH sol on an alloy substrate. Xu et al (2012) fabricated transparent and robust super hydrophobic surfaces by spin coating silica nanoparticles on various substrates. He and Wang (2011) also reported a super hydrophobic ZnO nano rods on zinc foil substrate by electrochemical deposition, which involves spin coating. This finds application as anti contamination, antifouling, and self-cleaning films etc.

### **1.6.7 Spray coating surface modification**

Another technique where solution of materials to be coated is sprayed on the membrane by help of a spray gun. By electrical or chemical means coating precursor is prepared. Major advantages of this method are, it is simple, high availability, automated, quick, cost effective, repairable, and nontoxic. This technique can also be applied on different substrates. But the wastage of the material compared to other processes is high in this case. Other demerits include high consumption of material, over spray, difficult to produce thick coatings, low degree of adhesion on small substrate, and extremely difficult for the substrate with small curvature.

Lathe and Rao (2012) reported single-step spray coating method to achieve super hydrophobic coating on glass surface. Kim and Cho (2015) also used spray coating for fabricating polystyrene (PS) and multi walled carbon nanotubes (MWCNTs) on cover glass. Zhang et al (2014) synthesized super hydrophobic aluminum by single-step spray coating.

### **1.6.8 Electrochemical deposition technique**

Inducing chemical reactions in an aqueous electrolyte solution with the help of applied voltage is the basis of electrochemical deposition. The method helps to positioning arbitrary a 3 D geometry is a great advantage. This low energy process is thus uniquely suited for dealing with modification of soft matters. It also offers unique spatial selectivity and is flexible and cheap process. The method is also combatable with of nano, bio, and micro technologies. This can also be applied to grow functional material through complex 3D masks. Another advantage is that it works near room temperature from water based electrolytes. It can be scaled down very low to high dimensions. Disadvantages of electrochemical deposition are in size and strength of modification. It is only suitable for selected size and poor strength of structures. It also requires high temperature during deposition and has less control in growth. This method can contribute for the fabrication of super hydrophobic metal coatings industrially. Liu et al (2014) synthesized controlled adhesion super-hydrophobic coating on copper surface by this method. Cao et al (2014) reported super hydrophobic surface by single step methods. Zhao et al (2011) changed the wettability of stainless steel surface to super hydrophobic by this type of deposition.

### **1.6.9 Hydrothermal synthesis**

This method is usually used for the synthesis of super hydrophobic and super liquiphobic surface coating. Method involves the production of crystalline substances from hot aqueous solution at high vapor pressure. The process shall creating roughness on the surface of substrate by using



high temperature and high pressure. During the process, the crystals are grown in an autoclave where materials along with water are supplied. Temperature gradient is set in between the opposite ends of autoclave chamber. Materials dissolve at hotter end and they are deposited on the seed crystals at cooler atmosphere results in crystals grow. Substrates which have high vapor pressure at or near their melting points can be grown by this method. It has the ability to synthesize large crystals of high quality. This process has thus found large application in industry. Hao et al (2015) created the roughness on the surface of zinc by this method with HCl followed by hydrothermal treatment with ammonium hydroxide. Shen et al (2014) also created different nanostructures by using different techniques on micro structured titanium alloy surface. Hu et al (2013) developed and reported super hydrophobic glass surface with high adhesive force using this type of method.

#### **1.6.10 Lithography technique**

Lithography employs simple chemical processes to create an image on substrate surfaces. It produces two components with water repelling positive part and water retaining negative part. Photolithography uses a mask of carrying the requisite pattern information and mask pattern that is to be transferred on the substrate by using some optical technique. This method is found mainly in integrated circuit manufacturing. Electron beam lithography is another type of technique for creating surface roughness by electron beam bombardment on the surface. The bombarding electron beam changes the solubility of resist, enabling selective removal of either the exposed/non exposed regions of the resist by immersing it in solvent. This method is mainly used to produce super hydrophobic surface where no mask is needed, thus eliminating costs and time delay. Another advanced nano imprint lithographic technique combines the speed of optical lithography with the resolution of electron beam lithography to make nanostructures on the substrate surface. It creates coating by pressing and heating a thin film between a patterned template and surface. The patterned film adheres to the substrate due to heating. This technique can produce features at very small resolutions ~10nm, which cover a large area with a high throughput. Interference lithography or holographic lithography is a technique for creating arrays of fine features on the substrate without the use of complex optical systems or photo masks. Method uses two or more coherent light waves with interference pattern between them are set up and are recorded in photo resist. These interference patterns produced have both intensity of maxima and minima and after exposing of surface to photolithographic processing, a pattern of

periodic intensity emergences on the surface based on the photo resist. Berendsen et al (2009) fabricated a type of super hydrophobic thermoplastic polymer surface by thermal imprint method followed by plasma polymerization of hexafluoro propene layer.

#### **1.6.11 Sol-gel process**

This is a common method to synthesis super hydrophobic coating on different substrate surface including membranes. In this method, the colloidal particles with different sizes ranging from 1 to 100nm are dispersed in gels that have interconnectivity with very low pore size and polymeric chains of average length of less than  $1\mu\text{m}$ . The conversion of monomer to colloidal solution (sol) would act an initiator for gel formation. The surface scale ranging to nano scale can be controlled at early stage of this process. This method is mainly used for biological fabrications. This technique is highly useful for surfaces with homogenous coating as compared to traditional ceramic method. This coating technique shows some drawbacks like large volume shrinkage, crack formation while drying, increase in carbon content while using organic reagents during preparative step, densification during sintering and need for continuous monitoring. Several studies have been reported in synthesis of super hydrophobic coating on substrates using sol-gel method. For instance, Laksmi et al (2012) spray coated the sol-gel composite of silica and a copolymer in a hybrid sol-gel matrix. Fan et al (2012) developed super hydrophobic copper wafer with water contact angle of  $155^\circ$ . Wang et al (2014) prepared a super hydrophobic sol-gel of modified silica particles.

#### **1.6.12 Chemical vapor deposition**

CVD technique is mainly used in materials processing technology in which, the precursor is heated into gas form at high temperature and it then deposited on the surface of the substrate due to reaction with the hot surface and thus forms a thin film layer on the surface. The method is for bulk materials and powders with high purity, deposition of materials on surface, and development of composite material via infiltration techniques. It is also used in fields of semiconductor and producing synthetic diamonds. Rezaei et al (2014) synthesized super hydrophobic coating on glass, aluminum, and silicon slides using this method. Huang et al (2005) created aligned carbon nanotubes on modified silicon substrate using CVD technique.

#### **1.6.13 Plasma treatment of membrane surfaces**

Plasma treatment bags large application in polymer surface modification. Plasma is an ionized gas produced by a strong electrical discharge in a low pressure environment is treated with

membrane surfaces. These interactions can induce electronically excited states in the polymer atoms, resulting in homolytic bond cleavage and leading to formation of free radicals and unsaturated bonds. Thus crosslinking within the polymer substrate or reactions with other molecules brought into close proximity to the polymer surface are facilitated. The aim of plasma treatment is typically to improve membrane fouling resistance and selective resistance. Plasma treatment has been used as an activation technique for grafting from the backbone. Exposure of membranes like PAN, PSf, and PES, UF to air or water vapor following treatment with helium or helium/water plasma resulted in a significant increase in their hydrophilicity due to formation of peroxides and further oxidation products on the membrane surface. Because of the complexity of functionalizable surface moieties in surface, the mechanisms governing plasma surface modification are not fully understood mainly for those used in water purification. Plasma treatment is employed in many of the commercial available polymer membranes. The Pall Corporation has used plasma treatment to hydrophilize many of its casted membranes for processing biological fluids.

Plasma treatment may sometimes be used to surface modify a membrane with a cross linked polymer. When plasma is applied for activation, the interaction of ionized gas molecules with the membrane surfaces induces hydrophilic or reactive moieties to the surface of substrate. When the plasma is comprised of monomers or low molecular weight polymer chains, there is chance for molecules to recombine on the membrane surface, forming a robust coating of highly crosslinked polymer. Sometimes, plasma activation can induce grafting of vinyl monomers to the membrane surface. Plasmas may induce peroxides on the membrane surface, which are then undergoing thermolysis to form radicals that trigger polymerization processes. Plasma may also be used to modify variable types of membranes other than flat sheets. For example,  $\alpha$ -allyl glucoside was grafted from the surfaces of polypropylene MF hollow fiber membranes. Such carbohydrates are highly hydrophilic and may be useful monomers for membrane modification. Majority of membrane surface modification studies focus on improving hydrophilicity, some reports describe the influence of other characteristics, such as surface geometry, on fouling mitigation. For example, thin film composite RO membranes were activated by contact with H<sub>2</sub>/He plasma and then exposed to oxygen to stimulate peroxide formation on the membrane surface. Corona discharge treatment or glow discharge treatment is closely related to plasma treatment. It has been used as a surface activation technique for subsequent grafting to polymer

surfaces. In this method, the electrodes that induce ionization of oxygen near the membrane, resulting in the formation of hydroxyl and peroxide groups on its surface. The corona discharge treatment alone can be applied to induce membrane surface hydrophilic, which may improve fouling resistance.

#### **1.6.14 Irradiation**

Different forms of energy radiation, including both ultraviolet and higher energy radiation, have been successfully employed in surface modification. Radiation can be used alone or to induce grafting of polymers or to the membrane surface. Nyström M et al (1991) studied modification of PSf UF membranes by UV irradiation showed an increase (six times) in pure water flux after UV exposure in aqueous media. Reports showed that photosensitizers or photoinitiators are frequently required to induce radical formation in polymers via UV exposure, but PSf and PES membranes were photoactive on their own. The irradiation over PES will result in decreased molecular weight with time, and the chain scission would probably occur at the phenoxyphenyl sulfone groups in the backbone of both PSf and PES. Plasma and corona discharge induced grafting requires substantiate conditions for plasma formation. But, the surface activation by UV irradiation works with or without a photoinitiator, has therefore gained substantial interest. UV irradiation involves relatively mild reaction conditions including ambient temperature and pressure and relatively light equipment making the process relatively low cost. Photo-grafting by UV irradiation is a robust technique which can be applied to a variety of vinyl monomers. Acrylic acid is probably the most frequently employed monomer for surface modification by this technique because of its hydrophilicity. Other monomers like methacrylic acid, hydroxyethyl methacrylate, various poly(ethylene glycol) methacrylates and a lot others can also be applied. Photografting methods can also be used to create functional membrane surfaces. Some type of advanced “smart” polymers respond to external stimuli such as changes in temperature or pH, may be grafted to a membrane surface to induce a change in separation characteristics. Ulbricht et al (2005) created pH responsive coatings on polypropylene and polyethylene terephthalate MF membranes by photografting method.

Radiations other than UV irradiation were also been tested and used to induce grafting to many polymer surfaces. Use of radiation graft polymerization to prepare membranes, materials used in medical applications, and sorbents has been reviewed by V. Y. Kabanov et al (2003) and M. M. Nasef et al (2004). Different high energy radiations like  $\gamma$  rays, X rays, or electron beams were

employed for this purpose. These high energy radiations requires high quality radiation source and can induce graft polymerization at a wide range of conditions, including low temperature and in the solid state, and the degree of grafting may be controlled by appropriate selection of irradiation conditions. These high energy radiations tend to penetrate more deeply into the polymer substrate than former discussed methods. Therefore, grafting can be accomplished within the bulk of the substrate to produce a more nearly homogeneously-modified membrane. The high energy radiation grafting is the preparation of ion exchange membranes with grafted ion containing polymers throughout the membrane matrix by M. M. Nasef et al (2004) is a good example. Reports showed that  $\gamma$  ray and electron beam irradiation have been used to surface modify porous water purification membranes. For example, Lee et al (2001) irradiated porous polypropylene membranes with  $\gamma$  rays from a cobalt source to form peroxides on its surface. Electron beams have been used to treat PE hollow fibers in a series of publications by Saito et al (1991, 1997, and 2000). When come to industry, the Pall Corporation describes the use of ionizing radiation to graft several polymers to membrane surfaces (D. B. Pall et al (1989), P. J. Degen (1990, 1992, 1994, and 1998). Membranes for modification included PVDF MF, polyamide MF, and PSf UF membranes which are incorporated into filtration systems targeted to remove leucocytes from platelet concentrates, particularly viruses, from pharmaceutical solutions, removal of proteinaceous material from fluid mixtures, removal of impurities from ultrapure water for microelectronics applications, or removal of impurities.

## **1.7 Conclusions**

Surface coating has intense applications in a wide range of field including self cleaning, antifogging, anti bacteria, sensing, drug delivery, anti rusting and environmental remediations. These surfaces can be considered like biomimicng from the nature like lotus leaf, butterfly wings, skin of shark, etc. In this chapter, idea regarding the possible methods of surface coating of membranes or any substrates for filtration or any type of applications has been discussed. It also provides the ideas about the different models with applications for superhydrophobic/hydrophilic surface are discussed. Different techniques for synthesis of artificial coatings would certainly upgrade the application to a new level.

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## Chapter 2

### **Pristine and Modified MWCNTs based high quality thin films as transparent conducting electrodes (TCEs)**

**Dr. Mothi Krishna Mohan**

*Kerala Department of Sciences and Humanities, Christ University Faculty of Engineering,  
Bangalore, Karnataka, 560074, India*

#### **Abstract**

The fabrication of high quality thin films for various applications has got immense significance in the area of science and technology. Thin films are materials having size ranges from few nanometers to micrometers. Generally, these are 2-dimensional materials with tunable properties. These are produced by condensing molecular/atomic/ionic species of matter or by direct solution based techniques. Thin films are used to enhance and modify the properties and functionalities of bulk materials or substrates. In general, thin film technology is used to make materials with unique and excellent properties. Sometimes, properties of thin films are mostly similar to that of the bulk materials, but sometimes it may end up with entirely different properties. The methods used for fabrication, reaction parameters, and nature of the materials is keen to get thin films with superior properties. Structure, geometry and thickness are the three important parameters to be monitored while fabricating thin films for specific applications [1,2]. Thin films are considered as the link between monolayer and bulk structure of a material. Varieties of techniques are available for thin film fabrication and the properties mainly depends on methods of fabrication and kinetics of crystal growth [3,4]. Thin films have enormous application in the area of electronic devices. Transparent conducting films (TCFs) are the important components of various devices such as photovoltaics, LCDs, OLEDs, transistors etc. Highly transparent and conducting films of pristine and modified MWCNTs through solution based processing techniques are environmentally benign, which would be competent enough to replace commercially available Indium doped tin oxide (ITO) and fluorine doped tin oxide (FTO). The chapter discusses the specific application of MWCNTs based thin films as transparent conducting electrodes.

**Keywords:** MWCNT, ITO, FTO, Transparent Conducting Electrodes

## 2.1 Introduction:

Materials having at least one dimension less than 100 nm are generally considered as nano materials [5]. Base material of carbon nanotubes (CNTs) are graphene sheets, which are bent into cylindrical shape and exist either as single walled carbon nanotubes (SWCNTs) or multi walled carbon nanotubes (MWCNTs). It can be either semiconducting or metallic depending upon the chirality along the graphene sheet [5, 6]. Carbon nanotube thin films are believed to have a 2D network with randomly oriented carbon nanotubes. Basically, CNTs contain semiconducting as well as metallic tubes and because of that it shows a semiconductor-metallic transition when the film thickness increases [5,7,8]. CNT thin films with density close to percolation threshold exhibit semiconductor nature and can be suitable for transistor applications [9,10]. Films with thickness up to 100 nm show good transparency and electrical conductivity, which can be used as an alternative for indium-tin-oxide (ITO electrodes) [11,12]. CNT thin films can be fabricated using vapor based or liquid based techniques. All the methods have its own advantages and pit falls. While fabricating thin films, horizontal as well as vertical alignment is possible with respect to the substrate [5]. Solution based techniques became more interesting due to several advantages. It is a low temperature process, does not need vacuum conditions, cost effective and produce uniform films on large areas. CNTs have high aspect ratio and independent CNTs stick together results in the formation of large bundles. This is the major challenging factor and while fabricating a thin film, one should separate the tubes without using harsh conditions, which would reduce the conductivity [5]. CNTs dispersion can be made by using various strategies. The major methods are as follows 1) surfactant dispersion aids 2) polymers as dispersion aids 3) direct dispersion of bare CNTs in different solvent systems, and 4) dispersion aids as protein and starch. The used dispersion aids have to be removed after the thin film fabrication; otherwise the conductivity would be lowered drastically due to their insulating nature. Direct dispersion in different solvents avoids the separation of dispersion aids, but it may result in extensive bundling [5]. Most of the optoelectronic devices such as LCDs, OLEDs and photovoltaics require transparent conducting electrodes as the base material [13,14]. Generally used TCFs are transparent and highly conductive modified metal oxide semiconductors. Among various materials, the well studied and efficient TCO is ITO which is combination of  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ . ITO has excellent transparency and low sheet resistance, which make it a good candidate for most of the devices. The major drawbacks of ITO are 1) scarcity and cost of indium 2) brittle



nature under low strain and 3) degradation of performance due to cyclic bending [15-21]. In order to overcome the instability and brittleness, ITO has been coated on a flexible polymer substrate and controlled the ratio of indium and tin by various researchers. But the result was an expensive film with poor optoelectronic properties [14,22]. Other factors such as reduced life time under certain conditions and the degradation of performance due to the diffusion of indium into the active layers of electronic devices and corrosion of ITO by small quantity of adhesives and acids in the environment also compels researchers to think about some alternatives [23-25]. In order to overcome the limitations of ITO, conducting polymers have been applied as TCFs in early 1980s. These TCFs were found to be superior to ITO in some aspects such as flexibility and ease of production. But electrical instability was one of the major constraints [26-28]. Metallic structures were investigated as another good option for TCFs. But its hazy appearance limits its display applications, but these films were successfully applied to photovoltaics [29-33]. So many materials have been developed for TCFs applications, but none of them were ideal for large scale, long term commercial fabrications. Compared to TCOs and other options developed, carbon nanotubes (CNTs) have got a lot of advantages, which include abundance of raw material (carbon), high mechanical strength, excellent electrical properties with high flexibility, ease of solution-based processing at room temperature, chemical stability, and a wide spectral range of transmittance with a neutral color [14,34]. Recently, researchers have developed optically transparent and highly conductive single walled carbon nanotube thin films, which were found to be highly transparent to infrared radiation. These films with sheet resistance of around 200 ohm/sq exhibited an average transmittance greater than 90% [35]. Another work demonstrated the fabrication of highly flexible, flat conductive thin film composed from a hybrid network containing silver nanowires and single walled carbon nanotubes and both were embedded in a cured resin [36]. One group has successfully fabricated graphene constructed carbon films (TGFs) for solar cell applications [37]. Highly transparent and conductive thin films of carbon-welded isolated single walled carbon nanotubes were prepared by Jiang et al and his coworkers [38]. Recently, highly conducting films of multi walled carbon nanotubes with different lengths were fabricated on glass substrate by spin coating technique [39]. The purification and preparation of semiconducting carbon nanotubes thin films for flexible electronic application was carried out and the results were found to be promising [40]. L. et al. and coworkers fabricated uniform carbon nanotube films on large area and successfully designed high

performance transistors out of that [41]. The fabrication of thin films can be carried out using vapor based or solution based techniques. Commonly used vapor based techniques are chemical vapor deposition and physical vapor deposition, while the important solution based techniques are spray coating and spin coating techniques. Solution based techniques are cost effective, environmentally benign, and requires simple reaction conditions compared to vapor based techniques. The thin films of low dimensional carbon based materials with superior physical and chemical properties can have the ability to act as alternatives for commercially available ones.

## **2.2 Scope and Significance**

Optically transparent and electrically conductive thin films have great significance in device applications. TCFs are the base materials for widely used devices such as LCDs, OLEDs and photovoltaics. Varieties of materials and methods have been developed for the last three four decades to fabricate thin films with superior physical and chemical properties. But none of the materials were ideal for long term, large area commercial applications. The base materials for most of the devices are either Indium doped tin oxide (ITO) or fluorine doped tin oxide (FTO). ITO is the most dominant material with excellent transparency and good electrical conductivity. The major drawbacks of ITO are 1) scarcity and cost of indium 2) brittle nature under low strain and 3) degradation of performance due to cyclic bending. Also, diffusion of indium into the active layers of electronic devices and corrosion of ITO by small quantity of adhesives and acids in the environment are other constraints for its application. So many materials have been developed as alternatives for ITO, but none of them were suitable for long term, large area commercial applications. Developing cost effective, stable and efficient TCFs as base material is of great interest in device fabrication field. Multi walled carbon nanotubes and its modified forms based thin films are thought of as good alternatives for ITO material. High quality films can be obtained by optimizing the reaction parameters and also through proper characterization. These films with superior properties can be fabricated without the use of expensive and highly sophisticated gaseous based film fabrication techniques, rather the films can be processed by solution based cost effective techniques under ambient conditions. Among the materials, low dimensional carbon materials have got immense significance such as abundance of raw material (carbon), high mechanical strength, excellent electrical properties with high flexibility, ease of solution-based processing at room temperature, and chemical stability.

## **2.3 Interdisciplinary relevance**

Thin film technology is a hot research area due to its applications in diverse fields. The scope of this area not only limits in materials science but has applications in various engineering and science disciplines. Thin film processing and its fabrication on suitable substrates are based on chemistry principles, but it has applications in corrosion science, non-linear optics, LCDs, OLEDs, photovoltaics, self cleaning surfaces etc. This area is very significant in physics, chemistry, materials science, mechanical engineering and electronics and communication engineering.

## **2.4 International and national status**

Thin film technology plays an important role in optoelectronic devices. Nobody can imagine a world without electronic devices. The LCD industry is the large consumers of TCFs for years with sales of approximately USD 1.5 billion in 2014 [42]. The commercial market in TCFs applied in touch panels was almost USD 1 billion in 2012, and the number will approximately be about USD 5 billion by 2019 [43]. The Solar cell industry based on thin films is expected sales over USD 16.3 billion by 2017 and the number will be even more bigger in future [44]. The whole world is suffering from energy crisis due to the scarcity of fossil fuels. The future energy source is renewable photovoltaics. The base material for the photovoltaic device is a transparent conducting electrode and the above said statistics unambiguously proved the importance of TCFs in a global scenario. Our nation is also moving more towards the use of solar energy. This topic has a lot of significance in international as well as national points of view.

## **2.5 Challenges for MWCNTs**

- 1) Synthesis of high quality MWCNTs under ambient conditions
- 2) Optimize the reaction parameters to get MWCNTs with high purity
- 3) Study the structure and properties of the synthesized materials by using various physico-chemical characterization techniques.
- 4) Optimize the reaction parameters to get highly conductive and transparent thin films
- 5) Characterize the thin films using various sophisticated techniques

6) Compare the properties of the prepared films with commercial ITO and FTO materials

## 2.6 Conclusion

Optoelectronic devices are inevitable part of our life. Cost effective, efficient and environmentally benign materials have got immense significance nowadays. The scientific community needs sustainable materials, which can be synthesized through green protocols for energy and environmental applications. The base structure of most of the electronic devices is either ITO or FTO with superior physical and chemical properties. The above mentioned materials are efficient and durable; however some limitations are also associated with them. So many materials have been developed in the past with an intention to overcome the drawbacks of the widely used materials. The developed materials were further modified to improve the properties, but none could effectively replace the commercial ones. Among the materials developed, low dimensional carbon materials have got great attention. These materials possess excellent properties and it can be synthesized under ambient conditions. These materials are cost effective as it can be obtained from the abundant source, carbon. Powdered forms of carbon based materials have been synthesized effectively through various solution as well as gaseous based techniques. The major challenge of this field is to prepare these materials with high purity. Preparation methods were not discussed in this chapter, but the aids used to prepare good dispersions of CNTs for high quality thin film fabrication was mentioned briefly. Commonly used low dimensional carbon materials are graphene, MWCNTs, SWCNTs. Carbon dots etc. The properties of graphene and CNTs are comparable. CNTs and graphene were found to be very effective for energy as well as environmental applications. Environmental pollution is a serious matter of concern nowadays and the development of cheap and efficient systems add some value to this point. Among the carbon based materials, MWCNTs are widely used due to its high efficiency, cost effectiveness, ease of preparation and benign nature. The aim of this chapter was to give some insights on the specific application of MWCNTs as transparent conducting electrodes. Various reaction parameters have to be optimized while fabricating thin films. The chapter briefed about the significant developments happened in the area of MWCNTs based thin films as transparent conducting electrodes. The scope, significance, international and national status, interdisciplinary relevance and challenges of CNTs based research were concisely

discussed. The importance of solution based film processing techniques and its comparison with gaseous based techniques were also explained.

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## Chapter 3

### Sustainable photocatalytic degradation of Ciprofloxacin using CeO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub> Nanocomposite

**Dephan Pinheiro, Sunaja Devi K R\***

*Department of Chemistry, CHRIST (Deemed to be University), Bangalore, Karnataka- 560029,  
India.*

\* E-mail: [sunajadevi.kr@christuniversity.in](mailto:sunajadevi.kr@christuniversity.in), <https://orcid.org/0000-0001-7826-1620>

#### **Abstract**

Ceria-lanthana nanocomposite was synthesized using an environmentally benign phytochemical synthesis using leaf extract from the plant *Spinacia oleracea*. The catalyst was characterized using techniques such as XRD, FTIR, UV-DRS, TGA and SEM-EDAX. Incorporating 15 wt % of lanthana into ceria led to an increase in the lattice defects on ceria which in turn improved the photocatalytic efficiency of the catalyst. This was evidenced from its ability to degrade ciprofloxacin drug, an antibiotic extensively polluting water bodies, in the presence of UV light. Conditions required for the maximum degradation were evaluated. Ceria-lanthana nanocomposite was able to degrade upto 68 % of the drug. The catalyst also was recyclable up to 5 cycles further bolstering the catalysts' green credentials besides its utility in pollution abatement.

**Keywords:** Green synthesis; pollution abatement; ceria-lanthana; ciprofloxacin; photodegradation.

#### **3.1 Introduction**

Antibiotic pollution is a major reason for bacteria to develop resistance to antibiotics thus rendering a lot of drugs useless. All major rivers in the world are polluted with a high amount of antibiotics. The rise in antibiotic resistance has already been recognized by the UN as a global health emergency that could kill about 10 million by the year 2050. These antibiotics reach the water bodies mainly through three ways, from the effluents of wastewater treatment plants, chemical and pharmaceutical industries and from aquaculture and animal husbandry activities [1, 2]. Ciprofloxacin (CIP) is an extensively used fluoroquinolone-based antibiotic used on human beings and livestock [3]. While many ways of removing CIP from wastewater like sedimentation, sorption on soil and advanced oxidation processes are available, these methods come with disadvantages of a high cost, long duration and being harmful to the environment [4].

The fluoroquinolone units of CIP have chromophore groups that can absorb solar radiation [5, 6]. Hence, degrading CIP from the wastewater using UV light aided by a suitable photocatalyst is an attractive proposition, especially if the photocatalyst is cheap, since the other requirement is sunlight that is readily available [7]. Thus, in this photocatalytic degradation process, sustainable renewable energy is used to mitigate a serious water pollution problem.

Ceria, an abundantly available and inexpensive rare earth oxide, has attracted a lot of attention in the last few decades as a good heterogeneous catalyst for a large number of applications. The versatility of ceria is mainly due to its oxygen storage capacity (OSC), made possible due to its ability to switch between its two oxidation states +3 and +4. Because of its semiconductor properties, ceria has also been explored for its photocatalytic applications. However, a large band gap of 3 eV, fast electron-hole recombination rates and poor electronic conductivity are its major drawbacks. The vacancies present in the fluorite structure of ceria play a big role in the ability of ceria to accept and release oxygen[8]. This property can be tuned for maximum oxygen storage capacity by various methods. While the size, shape and morphology of the nanoparticle play major roles, doping ceria with metal ions can also be a method of enhancing the desirable properties. Studies have shown that doping ceria with cations of low valency like  $Gd^{3+}$ ,  $Y^{3+}$ ,  $La^{3+}$ , etc. are known to create oxygen vacancies in its lattice, leading to a huge enhancement in the ionic conductivity and thereby an increase in its reactivity [9]. This has been attributed to the difference in the ionic radii between the  $Ce^{4+}$  and  $La^{3+}$  ions which are 0.097 and 0.110 nm respectively[10]. Similar incorporation of rare earth oxides into the widely used photocatalyst, titania, has also shown improvement in its photocatalytic efficiency[11]. While several methods of synthesizing ceria-lanthana composites such as sol-gel [12], co-precipitation[13], hydrothermal[14] and hydrolyzing oxidizing Ce-La carbide alloys[10] are available, we report here the preparation of Ce-La composites through an environmentally benign process using the leaves of *Spinacia oleracea*. This catalyst was used effectively to degrade CIP using a sustainable process using UV radiations, which are present in natural sunlight.

## 3.2 Experimental

### 3.2.1 Materials

Cerium nitrate hexahydrate was procured from Indian Rare Earth Ltd., (A Govt of India Undertaking, based in Kerala, India). Lanthanum nitrate was purchased from *S.D.Fine Chemicals*. Ciprofloxacin was taken from the drug named CIPLOX, eye drops manufactured by

Cipla Ltd. which contains 0.3% w/v of ciprofloxacin with 0.01% w/v Benzalkonium chloride as preservatives and was used to prepare a stock solution. Fresh leaves of *Spinaciaolearacea* were purchased from the local vendors in Bengaluru, Karnataka, India.

### 3.2.2 Preparation of catalyst

In a typical procedure, 2 g of the leaves were added to 10 mL of water in an RB flask after washing and shredding them and refluxed for 30 minutes. The solution is filtered, 2.146 g of cerium nitrate and 0.398 g of lanthanum nitrate were added and stirred for 30 minutes to get a mole percentage of  $\text{CeO}_2$ :  $\text{La}_2\text{O}_3$  in the ratio 85:15. The solution is then progressively heated to 400 °C using a muffle furnace and held at that temperature for 5 h. The powder obtained was designated as CeLa. Fig. 1 gives the schematic representation of the preparation of CeLa catalyst.



Figure 1. Schematic representation of the preparation of CeLa

### 3.2.3 Characterization

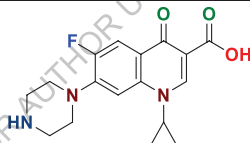
The  $\text{CeO}_2$  and Modified  $\text{CeO}_2$  were characterized using XRD, FTIR, UV-DRS, TGA and SEM-EDAX. XRD was recorded using Bruker AXS Kappa Apex X-ray diffractometer with  $\text{CuK}\alpha$  ( $\lambda=1.5406 \text{ \AA}$ ) radiation in the  $2\theta$  range of 5 - 90°. FTIR Prestige 21 (Shimadzu) was used to record FTIR spectra in the wavenumber range of 400-4000  $\text{cm}^{-1}$ . Shimadzu MPC3600 was used to measure the diffuse reflectance in the wavelength range of 200 - 800 nm using  $\text{BaSO}_4$  as standard. The morphological analysis was carried out using FEI Inspect S50-Scanning electron microscope (SEM) with EDAX detector. Perkin Elmer STA8000 was used for thermal studies at a heating rate of 20°C/min in the temperature range of 25 to 800 °C. The degradation intermediate

of CIP was identified using LC-MS (Agilent with PDA/MS, APCI+MODE and APCI-MODE) instrument.

### 3.2.4 Photo degradation of Ciprofloxacin

A stock solution of ciprofloxacin was prepared from the drug sample directly. The drug sample was suitably diluted to obtain a working sample of 10 mg L<sup>-1</sup>. The absorbance of this solution was noted using a UV visible spectrophotometer (Shimadzu UV-1201). The drug solution was mixed with the catalyst and stirred for about 30 min to attain absorption desorption equilibrium between the drug and catalyst. This solution was kept under a UV light source (high-pressure mercury lamp) with a power consumption of 30 W, for 4 h with stirring, at room temperature. A definite volume of the solution was drawn out, centrifuged to remove the photocatalyst and then placed in the UV-vis spectrophotometer to record the absorbance at  $\lambda_{\text{max}} = 276$  nm. The absorbance of the solution after regular intervals was noted to study the kinetics of photodegradation. The characteristics of CIP are given in Table 1.

**Table 1.** Properties of Ciprofloxacin

Structure	
Chemical name	1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid
Chemical formula	C <sub>17</sub> H <sub>18</sub> FN <sub>3</sub> O <sub>3</sub>
Molecular weight (g)	331.35
$\lambda_{\text{max}}$ (nm)	276
Common use	Antibiotic
Class of drug	Fluoroquinolone

## 3.3 Results and Discussion

### 3.3.1 Characterization

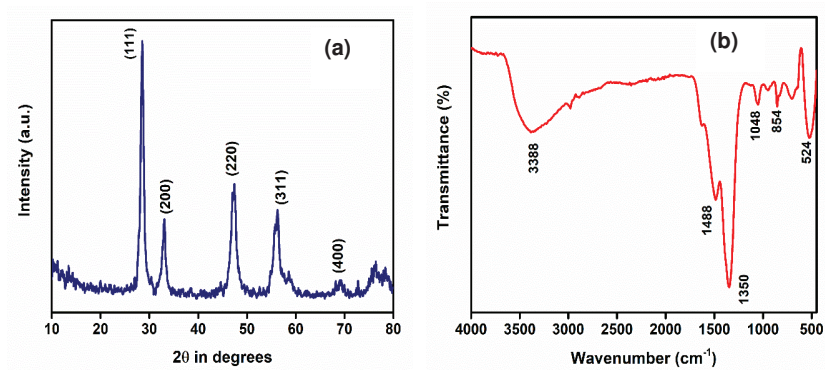
The XRD profile obtained for CeLa nanoparticles is shown in Fig. 2a. The diffractogram of cerasamples show peaks at  $2\theta$  values around at 28.2, 32.7 47.1, 55.9, and 69.1° corresponding to

(111), (200), (220), (311), and (400) crystal planes respectively, indicating a fluorite lattice for ceria (JCPDS 81-0792) [15]. All the peaks in the figure are characteristic of the standard cubic fluorite phase of CeO<sub>2</sub>. Studies have shown that the cubic fluorite structure of ceria is maintained even after the incorporation of lanthanum [5]. But CeLa shows a small shift to a lower angle and the FWHM of peaks becomes broader. Similar observation was reported by Hou et al [17]. These changes indicate the doping of La<sub>2</sub>O<sub>3</sub> into CeO<sub>2</sub>. Further, the peaks corresponding to La<sub>2</sub>O<sub>3</sub> (PDF-ICDD 73-2141) are not observed. Debye Scherrer equation Eq. (1) is used to calculate the average crystallite size and was found to be 12.9 nm.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

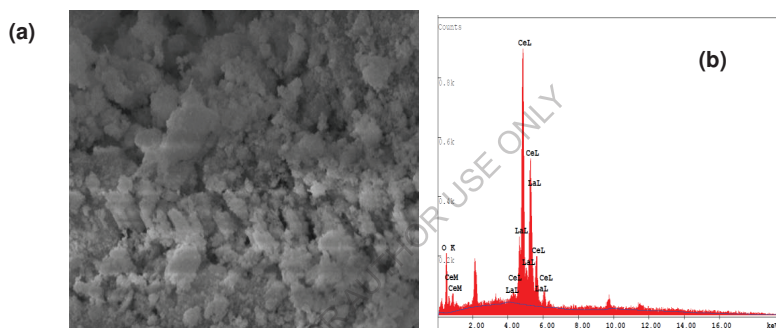
where  $D, \lambda, \beta, \theta$  are the average crystal size, wavelength, line broadening for the intense peak (111), and the Bragg angle respectively. The d spacing of (111) plane calculated using the Bragg's equation is 0.313258 nm and lattice parameter of CeLa was estimated to be 0.5384 nm. for (111) peak.

The FTIR spectrum of CeLa in Fig. 2b shows an intense band between 700-500 cm<sup>-1</sup> indicating the presence of Ce-O stretching vibration. The band at 854 cm<sup>-1</sup> could be assigned to the Ce-O-C stretching vibration [18, 19]. The broad peak between 3388 cm<sup>-1</sup> is due to the adsorbed water molecules [20].



**Figure 2.** (a) XRD profile (b) FTIR spectrum of CeLa

The SEM micrograph (Fig. 3a) shows the presence of nanocrystalline particles with aggregated with a non-uniform distribution, that reveals the formation of agglomerated spherical/granulated structures. The formation of such agglomerated granules could be due to the method of synthesis employed. Due to high-temperature treatment, the dispersion and size were found to be non-uniform. The particle size of the synthesized nanocomposite ranges from 80 to 100 nm. The weight percentage of Ce, La and O from EDX (Fig. 3b) analysis were found to be 75.1, 16.2 and 8.7 respectively.

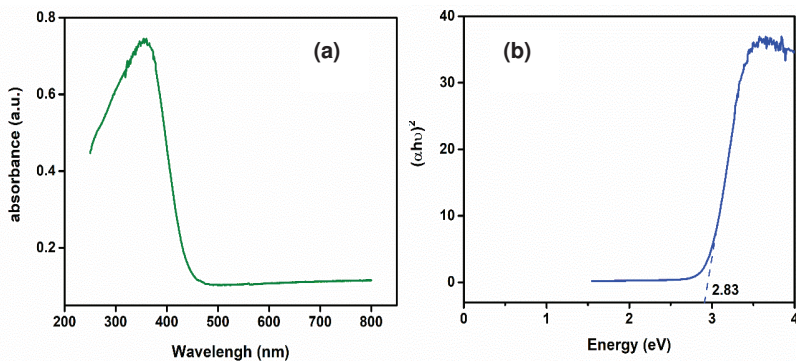


**Figure 3.** (a) SEM micrograph (b) EDAX spectrum of CeLa

UV-DRS spectrum (Fig. 4a) of CeLa explains the light response of the catalyst in the UV region. The band gaps of the semiconductors are calculated using Eq. (2), where  $\alpha$ ,  $h$ ,  $v$ ,  $E_g$  and  $A$  are the absorption coefficient, Planck constant, light frequency, band gap and a constant respectively [21].

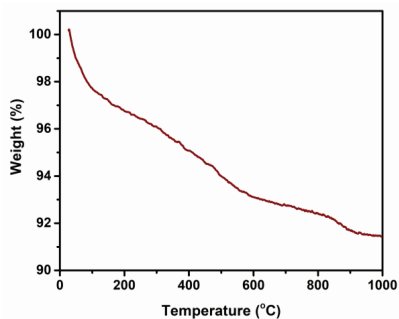
$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

The value of  $n$  is  $1/2$  for allowed direct transitions and 2 for the allowed indirect transitions. For cerium  $n=2$  and a plot of  $(\alpha h\nu)^2$  versus  $(h\nu)$  was drawn and the bandgap energy ( $E_g$ ) of 2.83 eV (Fig. 4b) was obtained by extending the straight-line range of the plots.



**Figure 4.** (a) UV-DRS spectrum (b) Tauc plot of CeLa

The thermal stability of CeLa was assessed using thermo gravimetric analysis. The analysis was carried out in the temperature range from 30-1000 °C at 10 °C/min heating rate. The TGA curve in Fig. 5 shows that there is a steady loss of mass from 30 to 200 °C due to the escape of moisture and adsorbed CO<sub>2</sub> present [22]. The small drop in mass from 200 to 500 °C may correspond to the loss of intercalated water molecules from the material. The mass becomes constant with temperature till 1000 °C and there is no appreciable weight loss above 600 °C which shows the stability of the system. The total weight loss upto 1000 °C is around 8 % of the total mass showing high stability of the prepared CeLa.



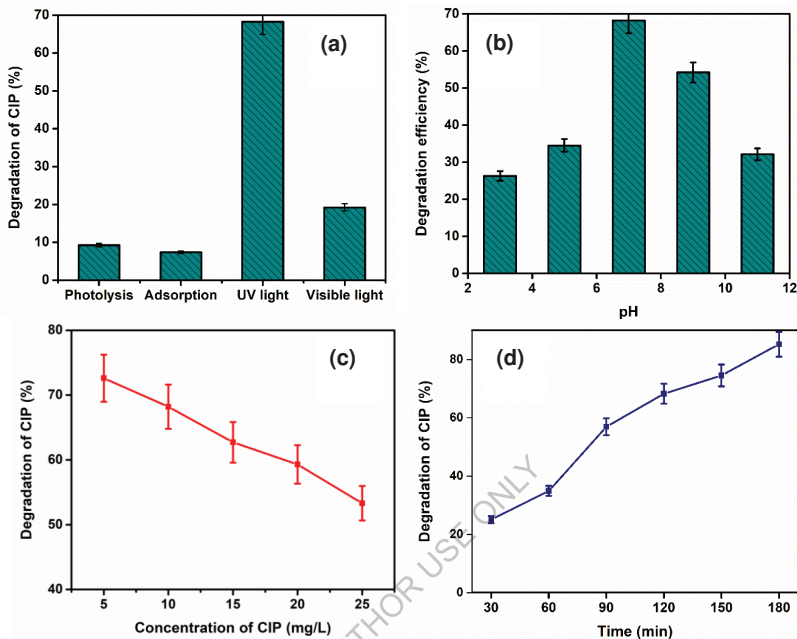
**Figure 5.** TGA curve of CeLa

### 3.2 Photocatalytic degradation of CIP

In order to understand the importance and the influence of photolysis and adsorption on the CIP degradation, experiments were conducted without CeLa catalyst under UV irradiation and an adsorption study with the catalyst under dark condition. The results were compared with the photocatalytic degradation of CIP. The low efficiency in the photolysis process is because of the low amount of hydroxyl radicals. Fig. 6a demonstrates that photolysis and adsorption gave insignificant degradations of CIP at 23 % and 9 % respectively. During photocatalysis (UV irradiation), the efficiency increases due to the increased production of hydroxyl radicals on the catalyst surface, which acts as a powerful oxidizing agent. CeLa shows 68.2 % degradation efficacy within 2h. Similar results have been reported for ZnFe<sub>2</sub>O<sub>4</sub>@CMC by Mohammad et al.[23]

To study the influence of pH on the CIP degradation, experiments were carried out under different pH conditions (CIP concentration = 10 mg/L, amount of CeLa= 0.3 g time=2 h). CIP can exist in three different forms, as zwitter ion, cationic and anionic species depending on the pH. At the acidic pH, both CeLa and CIP were positively charged leading to a repulsive effect on the adsorption of CIP on the catalyst surface. Similarly, in the alkaline pH, both surfaces attain negative charges causing less adsorption and decreased efficiency. At neutral pH, no repulsive forces exist between CeLa and CIP and maximum degradation is observed under these conditions (Fig. 6b). This increased efficiency can be attributed to the interactions between protons from CIP (-NH<sub>2</sub><sup>+</sup> and -COOH groups) and negatively charged catalytic surface. A similar pH study was also reported by Aghdasi and Shokri for the photocatalytic degradation of CIP using ZnO under UV light [24].

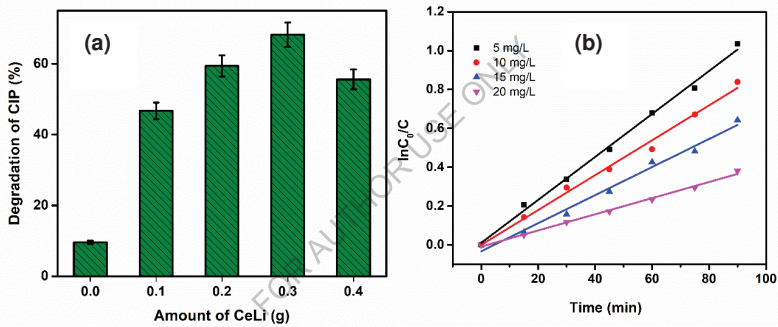




**Figure 6.** (a) Comparison of the photolysis, adsorption and photocatalytic processes (b) Effect of pH (c) Effect of concentration of CIP (d) Effect of time on the degradation of CIP

It is significant to study the effect of concentration of CIP on the degradation efficacy as it varies in the natural environment. Fig. 6c shows the effect of the initial concentration of CIP ranging from 5 to 25 mg/L. On increasing the initial concentration of CIP, the degradation efficiency decreases. The reaction was carried out under neutral pH using 0.3 g of catalyst for 2 h. At a higher concentration of CIP, fewer photons reach the surface leading to decreased electron-hole pairs. Accumulation of degraded intermediates on the CeLa surface also causes a negative effect due to less utilization of hydroxyl radicals on the surface of the catalyst. Fig. 6d depicts the effect of UV irradiation time on CIP degradation. As irradiation time increases, degradation efficacy also increases due to increased hydroxyl radicals. In this study, 65 % efficiency is shown after 2 h of time. After this time interval, there is no significant change in efficiency.

To determine the optimal dosage of CeLa catalyst for the CIP degradation, experiments were carried out with different amounts of photocatalyst to get maximum efficiency. The reaction has been carried out using 10 mg/L CIP at pH 7 for 2 h using CeLa catalyst in the range of 0.1 to 0.4 g per 100 mL. The results (Fig.7a) indicate that, when the dosage of CeLa increases, the CIP degradation efficiency also increases and reaches a maximum at 0.3 g. This is due to the increase in the active sites on the catalyst surface leading to increased hydroxyl and superoxide radicals. Further increase in the amount had no significant effect on the degradation efficiency. The addition of catalysts beyond the optimum value might lead to agglomeration and turbidity in the reaction mixture resulting in less photon absorption[25].

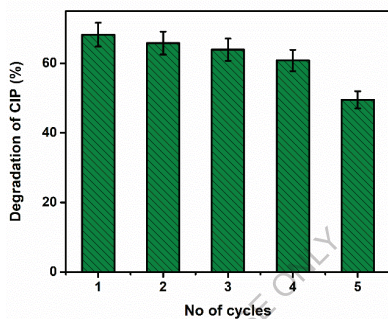


**Figure 7.** (a) Effect of the photocatalyst dosage (b) Pseudo first order kinetics for the degradation of CIP

Pseudo first-order equation was used to study the kinetics of the degradation of CIP using CeLa catalyst. The degradation rate constant  $k$  was calculated using Eq. (3). A plot of  $\ln \frac{[C_0]}{[C]}$  versus  $t$  gives a straight line (Fig. 7b) and  $k$  value is calculated as  $0.0089 \text{ min}^{-1}$  (10 mg/L) with  $R^2$  value of 0.99.

$$\ln \frac{[C_0]}{[C_t]} = kt \quad (3)$$

The reusability of the prepared CeLa was evaluated for five runs and the results are shown in Fig. 8. After each run, the photocatalyst was separated by filtration, washed and activated at 100°C, reused for the next cycle. The catalyst was stable during the first four cycles and shows a reduction in efficiency in the 5<sup>th</sup> cycle indicating deactivation of the catalyst due to pore blocking of the active sites.



**Figure 8.** Reusability study

#### 4. Conclusion

A lanthanum ion incorporated ceria nano-photocatalyst was synthesized using the environmentally benign phylogenetic synthetic method. The nanocomposite has shown itself to be a good photocatalytic system to degrade ciprofloxacin, an antibiotic drug present as a pollutant in water bodies all across the world. Incorporating lanthana into the ceria lattice has vastly improved its photo-catalysing abilities, seen from the improved performance in degrading ciprofloxacin. The catalyst can be reused for up to five cycles which establishes its robustness leaving scope for its practical use in scaled-up operations.

#### Acknowledgement

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## Chapter 4

### Metal Organic Frameworks: A Promising Material for NO<sub>2</sub> and NH<sub>3</sub> Gas Sensing

Sruthi Rajasekaran<sup>a</sup>, Sunaja Devi K R<sup>a\*</sup> and Mothi Krishna Mohan<sup>b</sup>

<sup>a</sup>*Department of Chemistry, CHRIST (Deemed to be University), Bangalore,  
Karnataka- 560029, India.*

<sup>b</sup>*Department of Science and Humanities, School of Engineering and Technology,  
CHRIST (Deemed to be University), Kengeri Campus, Bangalore, Karnataka- 560074, India.*

*\* E-mail: sunajadevi.kr@christuniversity.in, <https://orcid.org/0000-0001-7826-1620>*

#### Abstract

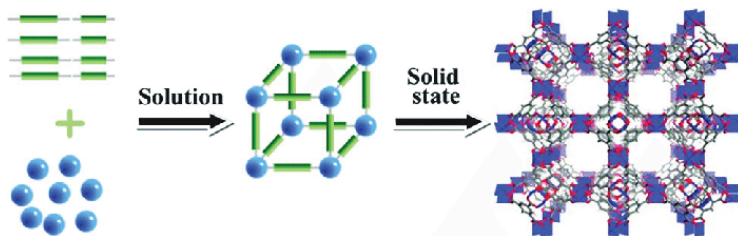
Sustainable development is becoming increasingly important in the field of environmental chemistry. There is an increasing need for the development of timely and precise control and monitoring of environmental pollutants. New sensing techniques are introduced, having several advantages such as high sensitivity, selectivity, and reliability. Metal Organic Frameworks (MOFs) are highly ordered crystalline coordination polymers that exhibit good structural composition and high porosity. The different strategies are employed for the preparation of MOFs to obtain highly ordered hybrid materials having the desired size and shape. In this review, we are highlighting the recent progress in MOF-based environmental sensors for gases, especially NO<sub>2</sub> and NH<sub>3</sub>.

**Keywords:** Metal Organic Frameworks;porous polymers;gas sensors;synthesis methods.

#### 4.1 Introduction

Metal organic framework (MOF) is a group of inorganic and organic moiety which are obtained by the combination of metal ions/clusters along with organic linkers or ligands to form a specific network geometry[1–3].MOF's are known to be porous coordination polymer and a kind of crystalline material. The preparation of MOF and its modified forms is an important milestone in the field of material chemistry. MOF based research works and its application in various field was started during the year 1997–1999[4–6]. The structure of MOF is in-between inorganic and organic materials. Some of the MOF's are flexible, yet they maintain a specific structure. Therefore, when it comes to the movement in framework, it depends on the change in

the external conditions such as temperature, pressure, chemical medium, etc. The response depends on the type of functional group used to functionalize MOF i.e. mainly depending on the guest and host interaction [7–10]. Fig. 1 shows the representation of the structure of MOF in which the metal ions and the linkers are involved [11].



**Figure 1.** Representation of the structure of MOF[11]

MOF has high crystallinity and has varieties of structures like 1D, 2D, and 3D having infinite assembly and ultrathin nature[12]. The intrinsic properties of MOFs include high and tunable porosity, excellent crystallinity, and good surface with large metal cavities. A transition metal ion having unpaired 'd' orbital will always accept the lone pair of electrons of the ligand, consisting of multidentate functional groups such as carboxyl group which helps in multi-coordination with metal ions. There is a subclass of MOF known as Zeolitic Imidazole Framework (ZIF) which exhibits promising features because of their surface morphology and exhibits enhanced the applications. With these features stated above, MOF had been utilized in the field of gas storage, gas sensing, energy conversion, and drug delivery[12–17].

The gas sensing application is explored more due to the porous nature of the MOF. The pores of the MOFs enhance the active metal site whereby introducing a coordinating constituent inside MOF, it helps in the construction of framework easily. Fine-tuning of the pore size also helps in giving a good structure to the framework. Metal oxides semiconductor-based MOF are used as gas sensors because of their small size, low cost, and reliability. They are always dependent on the adsorption nature, porosity, and surface area of MOF. MOF's are used in advanced chemical sensors that are used for the detection of toxic gases like ammonia at room temperature[4,18–20]. The exhalation of such toxic gases to the environment and human beings are dangerous and causes health problems. The concentration of these harmful gases in the



atmosphere can be reduced by using highly sensitive and selective sensors which is still a hurdle for the researchers. Therefore, MOF as a crystalline porous polymer has high capability in gas sensing because of its high interactive adsorption sites which promote the interaction with toxic gases to attain the sensing activity[18–21]. In this review, we are highlighting the recent progress on gas sensing especially NO<sub>2</sub>, and NH<sub>3</sub> using MOF based materials and their preparation strategies.

## **4.2 General Methods for the Preparation of MOF**

There are many ways for the synthesis of MOF which include solvothermal, microwave-assisted, mechanochemical, electrochemical synthesis, and slow evaporations [22]. Among all these available methods, majority of the researchers used solvothermal, microwave-assisted, mechanochemical synthesis which is explained as follows.

### **4.2.1 Solvothermal Synthesis**

The solvothermal technique is used for the preparation of MOFs in which soluble metal salts and organic high boiling solvents are employed. The product formed is recovered, dried, and undergo fast reaction kinetics owing to high crystallinity, phase purity, and size distribution through optimization of experimental condition. The major solvents used are diethyl formamide, acetonitrile, acetone, ethanol, and methanol, and in some cases, mixtures of solvents are also used to avoid solubility concern for different reactants. Even though it is the most preferred method, it has some drawbacks such as environmental risks with the use of different organic solvents, limited mass production per synthesis, tedious product washing process, and use of expensive apparatus like stainless steel autoclaves, teflon reactors, etc. [23].

Khaliesh Kamal and others synthesized Ni-MOF74 using 2,5 dihydroxyterephthalic acid (DOT) as the linker and mixture of DMF, ethanol, and water as a solvent using solvothermal method. In the first batch synthesis, ultrasonication is used to separate MOF products from a reactive medium, while the centrifugal separation was used in the second batch synthesis where methanol was used as a washing agent. The time for centrifugal separation was enhanced and rotation speed of 8000 rpm for 7 min. The MOF obtained through two batch processes showed good separation from the medium which leads to the excellent activation of pores[22]. The same technique of solvothermal synthesis was used by V. H. Nguyen et al. to study the photocatalytic activity of Bi(III) MOF. In this technique, DMF was used as the solvent to get a clear solution.

The final product Bi- BDC MOF shows a well-defined microstructure and homogeneity in the crystal[24].

#### **4.2.2 Microwave-Assisted Synthesis**

The microwave synthesis is a fast-moving technique widely employed for porous materials synthesis. Apart from the fast crystallization, potential advantages of this technique are selectivity, size distribution, morphology control, etc. Here, substrate and mixture are transferred to a teflon vessel and sealed to place it in a microwave[25]. Nowadays major research works depend on the microwave-assisted synthesis due to its standard description during the reaction where the medium depends on the efficiency and the ability of a substance to react with microwave and produce heat[26].

The microwave strategies have an alternate source which has advancement in creating rapid chemical process in small scale which can be used as a replacement for different strategies, like conventional heating (CH). Usually, the reactions of CH require a heater and an oil bath system. During the reaction, the reaction vessel acts as a mediator by exchanging with the thermal energy to the reaction solvent. Therefore, this technique provides a way to maintain a uniform reaction condition in the entire medium, where this shows the difference between an oil bath and microwave-assisted reactions[27,28]. The main benefits of this technique are rate enhancement, high product yield, product purity, high reproducibility, and expanded reaction conditions [29,30].

Thuan Van Tran et al. synthesized ZIF-8 MOF through a microwave-assisted method where the solvent used is DMF and ligand is trimethylamine that was mixed with Zn metal. This mixture is stirred vigorously and transferred into a teflon lined vessel and heated to 140°C for 15 min. The porous ZIF-8 crystals successfully created were used as an adsorbent for dye treatment[31]. Yanan Dong et al. synthesized a MOF MIL(101)Fe having enhanced adsorption efficiency using microwave-assisted synthesis method in which Fe solution was prepared using acetic acid and dimethylformamide under sonication followed by the addition of linkers. The linkers used are 1,4 benzene dicarboxylic acid and 2-aminoterephthalic acid and was added to the above-prepared solution, transferred to a teflon coated vessel, and heated to 110°C for 45 min in a microwave reactor. Finally, the precipitate obtained was centrifuged to 10000 rpm/min to get MOF MIL (101) Fe and used as an adsorbent for the removal of tetracycline in wastewater[32].

#### **4.2.3 Mechanochemical Synthesis**

Mechanochemistry, a chemical synthesis method, is enabled by mechanical force and widely known in metallurgy and mineral processing. The idea behind this type of synthesis is to promote chemical reaction where the starting material is ground with a minimal amount of solvent or without solvent. The application of mechanochemistry will enable a solvent minimization access and is the most promising and enhancing field for the production of MOF[33].

Barbara Szczesniak and coworkers synthesized MOF composites through the above-mentioned method in which Cu(BTC) was synthesized throughout the reaction without adding additional solvent. The mixture of  $\text{Cu}(\text{NO}_3)_2$  was dissolved in ZnO which were milled for 30 min with the rotation 500rpm. The solvent used here is ethanol and the products are washed and dried overnight, the precipitate obtained was immersed in ethanol/deionized water solution for 1 h, whereas the final MOF was obtained mechanochemically[34]. The solvent-free assembly of Zr-based MOF which was carried out by non-conventional synthetic approaches of mechanochemistry by K. Uzarenc and coworkers. In this method, a small amount of microporous MOF of Zr was obtained by assembling of organic linkers in which the capping agent was carboxylate and then exposed to organic vapors showing wide accessibility for the synthesis of MOF[35]. Mechanochemical method was used to synthesize Co Zn-ZIF MOF in which the mixture of ZnO and 2-methylimidazole were placed in a ceramic pot along with zinc acetate dihydrate and then milled at a rotation rate of 150rpm for 1 h. The product formed is rinsed with methanol, dried at 40°C, and used for adsorption studies[36].

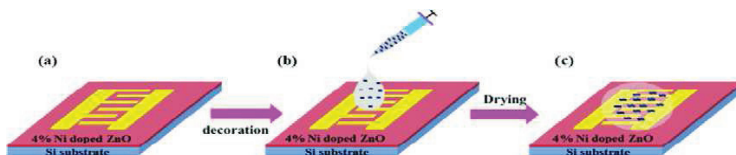
### **4.3 Metal Organic Framework for Sensor Applications**

MOF has wide applications like gas sensors, gas storage, Drug delivery, and catalysis. Gas sensing performance varies with respect to the types of MOFs used because of their crystalline nature, porosity, and surface area.

#### **4.3.1 Gas Fabrication and Gas Sensing Test**

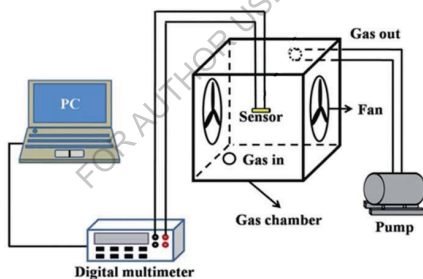
Fabrication of MOF for gas sensing is an important process. MOF is generally prepared using any of the above-mentioned methods. This synthesized MOF was grounded by the addition of terpeneol and glutinous solution that was evenly sprayed on the electrode substrate chosen. The preferred electrode substrate is alumina and the process is repeated three to four times to obtain sensing electrode material. Here, for sensing fabrication, the binder used is terpeneol

which enhances the stability of the material[37]. Fig. 2 illustrates the fabrication of MOF on a substrate for sensing[38].



**Figure 2.** Fabrication technique of a gas sensor [38]

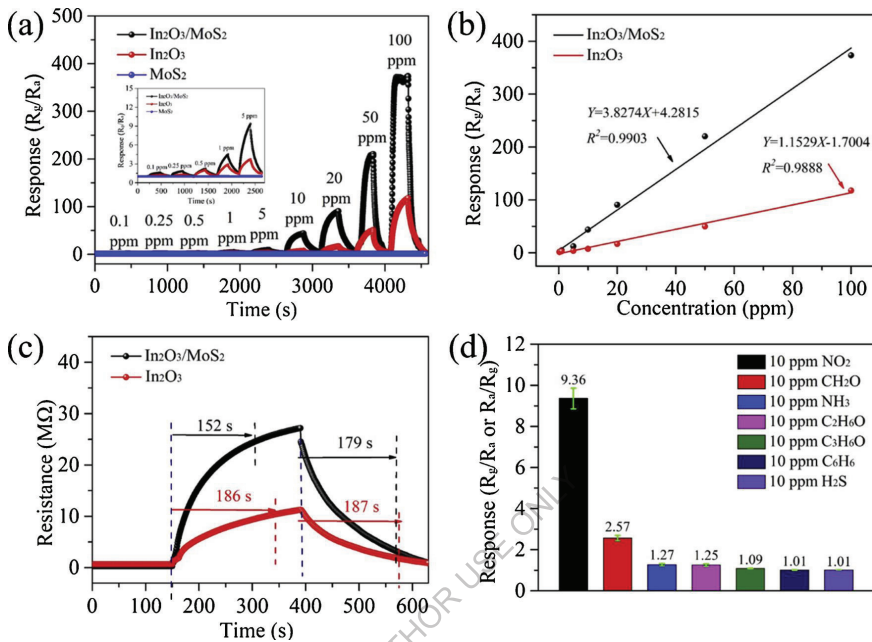
For Gas sensing test, a small amount of the sample is immersed in a mixture of terpineol and ethylcellulose solution which forms a viscous paste, where they are pasted on a ceramic substrate tube by using one main electrode and a reference electrode. Heating of wire with some alloys (like nickel-chromium) inserted to control the working temperature of the sensor. Then the sensors are welded on a socket and the time is monitored for the sensor to reach 90% adsorption[39,40].Fig. 3 gives the schematic representation of a gas sensing testing instrument.



**Figure 3.** Illustrates the Gas sensing testing instrument[39]

#### 4.3.2 NO<sub>2</sub> Gas Sensing

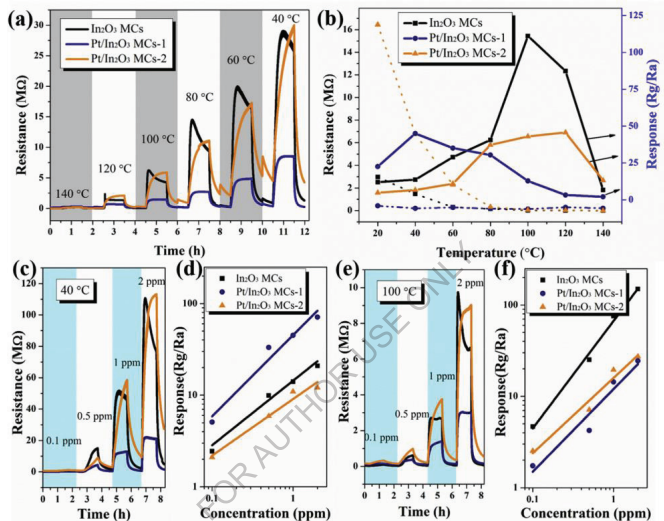
Nitrogen dioxide (NO<sub>2</sub>) is one of the colorless, flammable, and hazardous gas widely used in automotive and industrial applications. Due to the emission of a large amount of NO<sub>2</sub> to the atmosphere, it is necessary to fabricate highly sensitive sensors to detect even a low concentration of NO<sub>2</sub> gas. From the literature, one could understand that MOF based materials are a promising field for NO<sub>2</sub> detection. During the calcination process, the organic ligand present in MOF will easily decompose into small molecules without disturbing the morphology of the sample and generates cavities that help in gas sensing[41–43].



**Figure 4.** Responses and (b) function fitting curves of  $\text{In}_2\text{O}_3/\text{MoS}_2$  composite and individual  $\text{In}_2\text{O}_3$  sensor toward various concentrations of  $\text{NO}_2$  at  $25^\circ\text{C}$  (c) Response-recovery curves of  $\text{In}_2\text{O}_3/\text{MoS}_2$  composite and individual  $\text{In}_2\text{O}_3$  sensor toward 20 ppm  $\text{NO}_2$  (d) The selectivity of the  $\text{In}_2\text{O}_3/\text{MoS}_2$  composite sensor toward different interfering gases of 10 ppm, and the error bars are obtained from five different sensors [41].

Indium oxide-based MOF MIL-68 synthesized by hydrothermal method was used for  $\text{NO}_2$  sensing performance in the range of 250 ppb to 100 ppm [41]. After adsorption, TGA experiments were carried out to examine the weight loss to understand the adsorption capacity of the synthesized material. The  $\text{In}_2\text{O}_3/\text{MoS}_2$  composites act as sensors and show response towards  $\text{NO}_2$  at 0.1 – 100 ppm at room temperature [41]. The measurements were carried out for different concentrations of  $\text{In}_2\text{O}_3/\text{MoS}_2$  composite and exhibited a response value of 371.9 towards 100 ppm of  $\text{NO}_2$  (Fig. 4). This composite showed a dynamic response at high concentration. The graph of the fitting relationship shows that the experimental data of the detection limit as 8.8 ppb having the signal to the noise ratio of 3. Moreover, the selectivity of  $\text{In}_2\text{O}_3/\text{MoS}_2$  film sensors

was also compared with different interfering gases like ammonia, ethanol, methanol, etc., with the same concentration which proved that selectivity is high in the case of  $\text{NO}_2$ . When it comes to the reproducibility part of the film sensor, it was exposed to 5, 10, and 100 ppm and it was measured for every 5 days in 30 days to study the reproducibility and exhibited a constant result demonstrating its long-term stability.



**Figure 5.** Dynamic response curves of the gas sensors under various temperatures for 1 ppm of  $\text{NO}_2$ . (b) Resistances in air (dotted curve) and responses of the sensors to 1 ppm of  $\text{NO}_2$  at different operating temperatures. Dynamic response curves of the sensors for different  $\text{NO}_2$  concentrations at 40 °C and (e) 100 °C. Linear fitting curves of the sensor responses at (d) 40 and (f) 100 °C[44].

Yunshi Liu et al. synthesized an  $\text{In}_2\text{O}_3/\text{MoS}_2$  porous micro columnar structure in which MOF MIL – 68 was obtained by reduction method followed by ultrasonication and the detection of  $\text{NO}_2$  was compared near to the room temperature [44]. By comparing the Pt/  $\text{In}_2\text{O}_3$ , the sensing performance is more for  $\text{In}_2\text{O}_3$  MCs -1 when compared with  $\text{In}_2\text{O}_3$  MCs -2 which shows relatively low temperature after exposure to the air inside the sensor chamber. Fig. 5 explains the dynamic response of sensors at a different concentration ranging from 0.1-1 ppm at 40 °C and

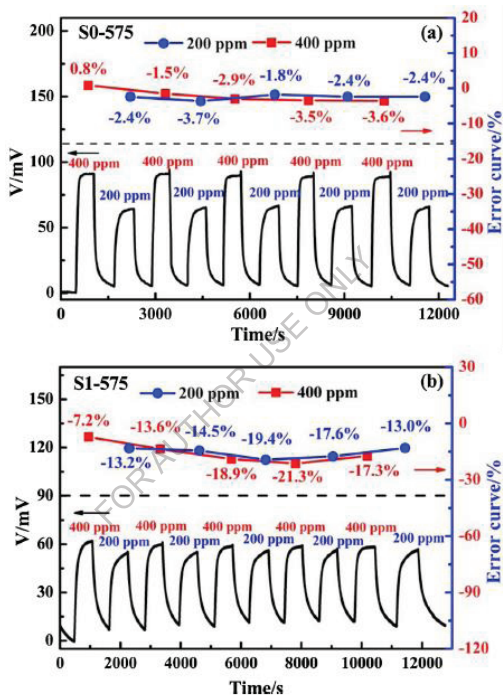
100 °C. Here, the Pt/ In<sub>2</sub>O<sub>3</sub> MC -1 showed sensing at around 5.2 -100 ppb level at 40 °C whereas, the others were in a linear relationship around the range of 0.1-2 ppm. In<sub>2</sub>O<sub>3</sub> MCs obtained from MIL-68 showed a feasible fabrication technique for sensing materials with a low concentration of NO<sub>2</sub> showing a response towards sensors and recovery performance.

Synthesis of MOF ZIF-8 coated with In<sub>2</sub>O<sub>3</sub> nanofibers was carried out by electrospinning and subsequent calcination by Rui Wang and coworkers [45]. This material is used for the detection of NO<sub>2</sub>. After the adsorption study, the weight loss was calculated using TGA analysis. In<sub>2</sub>O<sub>3</sub>/ ZIF-8 NFs showed a remarkable response to 1 ppm NO<sub>2</sub> compared to individual In<sub>2</sub>O<sub>3</sub> sensors. In<sub>2</sub>O<sub>3</sub> cubes embedded in graphene sheets using a one-step microwave-assisted hydrothermal technique was used to detect the NO<sub>2</sub> gas [46]. The dynamic resistance varies for fabricated In<sub>2</sub>O<sub>3</sub>/rGO. The resistance decreased when it is exposed to NO<sub>2</sub>. The response and recovery characteristics of the fabricated In<sub>2</sub>O<sub>3</sub> cubes/rGO based sensor was 5ppm and 50% relative humidity (RH) at room temperature. The long-term stability of the sensor was also evaluated by exposing the sensor to 5 ppm NO<sub>2</sub> under 50% RH at room temperature for 2 weeks where the stability variation was found at only 3 %. To understand the selectivity towards NO<sub>2</sub> sensing, In<sub>2</sub>O<sub>3</sub> cubes/rGO composites were exposed to various interfering gases like ammonia, ethanol, acetone, hydrogen, and methane, where the sensor exhibits a large response towards NO<sub>2</sub> gas. In<sub>2</sub>O<sub>3</sub> cubes/rGO, a unique hybrid material, shows a good significant response to NO<sub>2</sub> gas with a concentration lower than 1 ppm without interfering with any other additives at room temperature.

Hao Tian and others synthesized SmFeO<sub>3</sub> porous hollow microsphere through precipitation process, to detect the sensing nature of NO<sub>2</sub>[47]. The TGA traces show weight loss. The NO<sub>2</sub> sensing performance of SmFeO<sub>3</sub> was characterized and exposed to 1ppm NO<sub>2</sub> and pure N<sub>2</sub> at different temperatures. The sensor resistance variation shows the activation of bulk adsorption phenomenon at elevated temperatures. The dynamic variation of sensor resistance shows different NO<sub>2</sub> concentrations ranging from 50ppb to 1ppm. Therefore, SmFeO<sub>3</sub> hollow porous microsphere shows excellent sensitivity, selectivity, and cost-effective route to NO<sub>2</sub> detection for gas sensor applications.

Works were carried on with Co<sub>3</sub>V<sub>2</sub>O<sub>8</sub> derived from metal organic framework through solvothermal reaction and show excellent sensing towards NO<sub>2</sub> [48]. The sensing behavior was calculated at different temperatures like 550, 575, 600, and 625 °C, and the sensors were labeled

as SO-550, SO-575, SO-600, SO-625 respectively, and showed good response recovery for various concentration of NO<sub>2</sub> with the sensitivity ranging from 50-500 ppm. Fig. 6 represents the recovery transit curve for NO<sub>2</sub> detection. It showed long term stability even with the interfering gases like CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, NO, and CO. This particular sensor fabricated from MOF showed better performance at 575° C (SO-575) for NO<sub>2</sub> sensing.



**Figure 6.** (a) The continuous response-recovery transients to 200 and 400 ppm NO<sub>2</sub> at 575 °C for S0-575 (b) and the continuous response-recovery transients to 200 and 400 ppm NO<sub>2</sub> at 575 °C for S1-575 [48]

Metal Organic Framework Tb(BTC) materials were used in the detection of NO<sub>2</sub> gas sensors which is carried out by the spin coating process [49]. For NO<sub>2</sub> sensing the calibration curves show a low value for the limit of heating and the recovery process was possible by gentle



heating where the particles decay progressively as the amount of NO<sub>2</sub> is increased in the concentrations ranges from 5–500 ppm. Quenching of NO<sub>2</sub> also takes places and its concentration ranges from 0–50 ppm which shows that signal is becoming saturated and reaching a maximum value of 64 % quenching for 500 ppm NO<sub>2</sub>.

Mg incorporated metalorganic frameworks works were carried out through solvothermal reaction to detect the sensing performance of NO<sub>2</sub>[50]. Dynamic resistance plots of gas sensors fabricated from Mg-MOFs-I and II (prepared using two different linkers) were exposed to 1, 10, and 50 ppm NO<sub>2</sub> and exhibit selective sensing even in the presence of interfering gases. The sensors showed good reversibility even after stopping NO<sub>2</sub> gas, in which the resistance was recovered to their original values. TGA showed a decrease in the weight and thermally stable upto 300 °C. Pd-O-CO<sub>3</sub>O<sub>4</sub> templated metal organic framework functionalized by SWCNTs, demonstrated a unique sensing platform for a variety of sensing layers for real-time detections [51]. Here, Pd-O-CO<sub>3</sub>O<sub>4</sub> was synthesized by precipitation and subsequent reduction process to improve the sensing of NO<sub>2</sub>. The sensors exhibited NO<sub>2</sub> detection property at 100 °C with a sensitivity of 44.11% at 20 ppm with a low detection limit of 1 ppm. The resistance changes were measured, and the recovery kinetics were obtained to be 10–20 ppm at high concentration ranges with an appreciable response at low concentration ranges from 1-5 ppm.

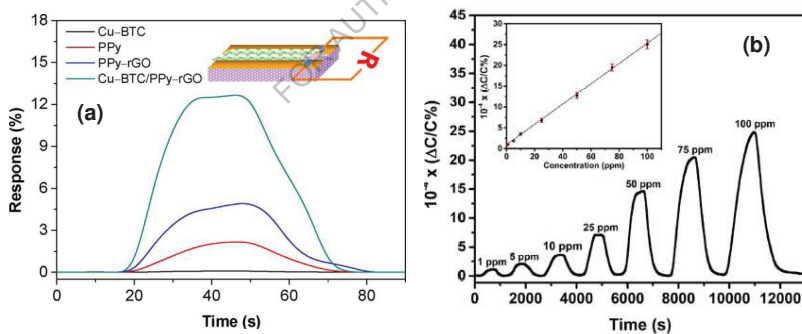
#### 4.3.3 NH<sub>3</sub> Gas Sensing

Ammonia (NH<sub>3</sub>) is a colorless gas with a highly toxic nature which can be an irritant to eyes, skin, and respiratory tract. It is also inflammable at a volume concentration of approximately 15-28 % in air. Exposure of NH<sub>3</sub> at a low concentration of 50-100 ppm can cause health problems. Therefore, effective and accurate detection of low concentration of NH<sub>3</sub> is essential to the environment. There is a great demand for ammonia detection which leads to rapid progress in the field of ammonia gas sensors. Therefore, in recent years, MOF has attracted more attention in gas sensing because of its advantages like high porosity, surface area, and permeability of host-guest interaction [52].

Ying yin et al synthesized Cu-BTC on nanocomposites by chemical oxidative polymerization and examined it for the performance of NH<sub>3</sub> sensors [52]. The gas sensing performance of PPy-rGO/Cu –BTC sensor was found to show no change in the resistance owing to poor conductivity. This material showed a higher response compared to PPy-rGO with PPy towards NH<sub>3</sub> gas which proved higher sensitivity and response is for CU-BTC/PPy –rGO rather

than PPy-rGO sensors. The reproducibility of Cu-BTC/PPy-rGO based  $\text{NH}_3$  sensor showed a response that was estimated to be 50 ppm (Fig. 7a). When it was repeated for 5 cycles, the sensors showed a good reproducibility where the sensing condition is perfect and consistent. Therefore,  $\text{NH}_3$  gas sensor based on Cu-BTC/PPy-rGO nanocomposite fabrication was very easy and the sensing performance was reliable and used in a wide variety of fields.

A. Hussien et al. synthesized NDC-Y-fuc MOF by solvothermal method and used it for the sensitive detection of  $\text{NH}_3$  [53]. The pre-functionalized integrated device electronics (IDE) chip was self-assembled and placed inside the vial and sealed. The gas sensing tests were performed fully automatically where nitrogen gas was used as the carrier gas to dilute the concentration ranging from 1 to 100 ppm. The growth of NDC-Y-fuc MOF crystal on the IDE substrate enhances the ability to monitor sensor film permittivity upon gas absorption. The sensor detected  $\text{NH}_3$  at a range of 1 to 100 ppm with a linear response where the detection limit was 92 ppb (Fig. 7b). The stability of NDC-Y-fuc MOF showed a good reproducibility at 10 and 25 ppm keeping it for more than 2 weeks under the same conditions. Therefore, stability, durability, and selectivity of this MOF were excellent with great sensing towards  $\text{NH}_3$  even in the presence of interfering gases like  $\text{NO}_2$ ,  $\text{CH}_4$ , and  $\text{C}_7\text{H}_8$ .



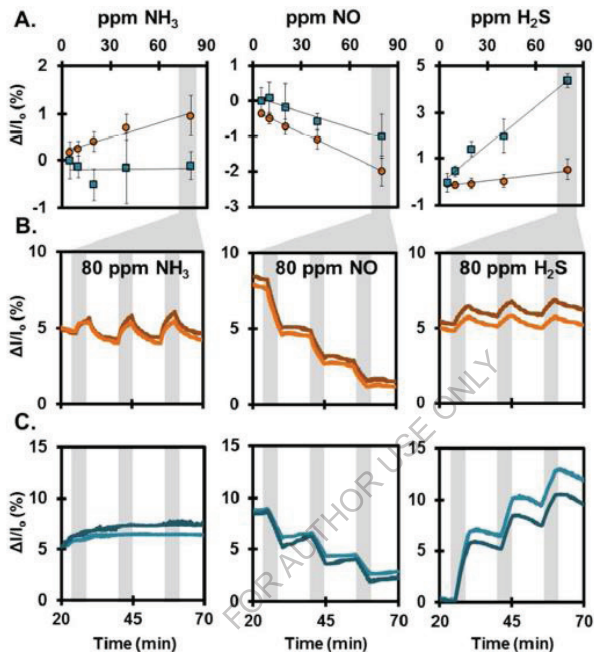
**Figure 7.**(a) Response of the prepared thin films to 50 ppm  $\text{NH}_3$  at room temperature [52].  
 (b) Detection of  $\text{NH}_3$  in different ranges of ppm concentrations: from (1–100 ppm). Inset:  
 Linear response for the NDC-Y-fuc-MOF in the corresponding range [53].

KivancSel and coworkers used different MOFs called TMA-M-MOF for NH<sub>3</sub> gas sensing. The metal ions (M) used for the synthesis include Ba(II), Cd(II), Pb(II), and Zn(II) [54]. The thermal characteristics of TMA-M-MOFs were studied through TGA where the weight loss was compared with N<sub>2</sub> atmosphere. Among the various TMA-M-MOFs, Zn showed the highest conductivity with an increase of nearly more than 50 times from its initial conductivity. The investigation showed high gravimetric yield for TMA-M-MOFs when exposed to NH<sub>3</sub> vapor and saturation occurred after 1 h at room temperature, indicating that it can be used in a biological environment. Mixed valence Cobalt(II/III) MOF denoted as FJU56(a) has been used for NH<sub>3</sub> sensing [55]. The MOF FJU56(a) showed excellent thermal and chemical stabilities with exceptional NH<sub>3</sub> sensing selectivity of 1.38 ppm having reversibility and durability. The mixed-valence framework shows a good response towards NH<sub>3</sub> sensing with high selectivity and is a sustainable material for environmental pollutants.

Cu-BTC MOF/graphene-based hybrid material was used for ammonia sensors in which the chips used are exposed to continuous cycles for different concentrations of NH<sub>3</sub> followed by purging with dry air [56]. This hybrid material exhibited enhanced electrical transport properties needed for a sensing material. Crystalline porous structures are reversible sensors and the ability for the amorphous phase that is formed by the collapse of MOF does not have the efficiency to absorb gases and that causes a change in the electrical signals. Thus, Cu-BTC MOF/graphene base hybrid materials are capable of detecting NH<sub>3</sub> as a sensor along with adsorption of gas at dry condition and give good performance towards NH<sub>3</sub> sensing.

A simple and rapid approach for integrating MOFs into chemiresistive devices on a polymeric substrate was explained[57]. The product was named as Cu<sub>3</sub>HHTP<sub>2</sub> and Ni<sub>3</sub>HHTP<sub>2</sub> and used for the detection of NH<sub>3</sub>. The utility of MOF in chemiresistive sensors involves an innovation that enables rapid fabrication of sensors for detecting and differentiating gaseous analytes at different ppm concentrations. Gases like NH<sub>3</sub>, H<sub>2</sub>S, and NO which are known to be highly toxic are exposed to a limit of 50, 10, and 25 ppm respectively where the fatal concentration is 5000, 500–1000, and 200–700 ppm respectively. The concentration dependence and limit of detection was decreased according to the concentration of gaseous analyte with the recovery of 10 min/exposure of 5 min cycle. Co-efficient variation of Cu<sub>3</sub>HHTP<sub>2</sub> for NH<sub>3</sub> was 23 % whereas for Ni<sub>3</sub>HHTP<sub>2</sub> was not found. Therefore, this chemiresistive sensor based on

conductive MOFs showed a good result on detecting and differentiating  $\text{NH}_3$  along with NO and  $\text{H}_2\text{S}$  at different concentrations. Fig. 8 illustrates concentration dependent curve and sensing trace curve for  $\text{Cu}_3\text{HHTP}_2$  and  $\text{Ni}_3\text{HHTP}_2$ .



**Figure 8.** (a) Concentration dependent sensing response (left to right,  $\text{NH}_3$ , NO, and  $\text{H}_2\text{S}$ ) for  $\text{Cu}_3\text{HHTP}_2$  and  $\text{Ni}_3\text{HHTP}_2$  orange and blue respectively. Error bars represent standard deviation from average exposures (3 x 80 ppm, 9 devices) (b) Representative sensing traces (3 x 80 ppm) for  $\text{Cu}_3\text{HHTP}_2$  and (c) representative traces (3 x 80 ppm) for  $\text{Ni}_3\text{HHTP}_2$ [57].

#### 4. Conclusion and Perspectives

The scope of implementing MOFs as a gas sensing material has been intensely expanded over the past few years. Moreover, tuning the pores of MOF is a powerful method for the interrogation of current material chemistry research for the various gas sensing application. In the present review, MOFs as a sensing material for gas detection has been demonstrated. MOFs shows a unique structure having diverse properties like large surface area, tunable porosity, reversible adsorption, and tunable chemical functionalization. As discussed, MOF-based

materials have shown excellent sensor performance for NH<sub>3</sub> and NO<sub>2</sub> gases. However, their sensing performance in terms of selectivity, sensitivity, and stability needs to be enhanced for a better practical application. New strategies for the synthesis of functionalized MOFs having critical pore structure for various applications need to be developed. In future, the stability of MOFs needs to be enhanced especially when they are used for sensing applications that work under different acid/base conditions. The selectivity and reliability are the two important requirements of a sensor which needs to be enhanced. Generally, most of the sensor demonstrations in the literature were performed using laboratory conditions. Therefore, for sustainable development, the sensor performance of MOFs in a polluted environmental condition needs to be assessed in the coming years

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## Chapter 5

### Membrane Technology – Key of green method

Dr.P.Nikhil Chandra<sup>a,b \*</sup>

<sup>a</sup> P.G. and Research Department of Chemistry, Sree Narayana College, Kollam,  
Kerala, 691001 India

<sup>b</sup>Advanced Centre of Environmental Studies and Sustainable Development (ACESSD),  
Mahatma Gandhi University,  
Kottayam, Kerala, 686560 India

\*e-mail: pnikhilchandra@gmail.com

#### Abstract

Global increase in demand for materials, energy and products drives materials science researchers to propose new solutions everyday able to promote development while supporting sustainable development. Membrane technology can play significant role to this advancement. Membrane methods are identified as the most interesting aspects of materials engineering in strategic industrial sectors such as water treatment, desalination, energy production and depletion and reuse of renewable materials. The integration of membrane technology with innovative methods can be used to exploit the potential advantages derived from their synergic uses is important. Study into the use of membrane based processes applied in the industry is an interesting area for modern science and technology. The purpose of this chapter is to describe and discuss various aspects of membrane technology in the industry or research lab which focus on energy conversion, environmental protection and process intensification in this broad field.

#### 5.1 Introduction

Broadly speaking, the membrane science is a field that deals with membrane material, design, development and its performance. Hence it can be simply be categorized into material selection, material characterization and evaluation, membrane preparation, membrane characterization and evaluation, membrane transport phenomena, membrane module design, and process performance (Meares et al (1976), Turbak et al (1981), Starzak et al (1984)). Membrane technology describes the incorporation of scientific and engineering aspects for the transport or rejection of components, species, or substances through or by the membranes. Membrane technology uses mechanical processes for separating gas or liquid streams from mixtures (Baker et al (2004), Nunes and Peinemann (2001)). Due to its multidisciplinary nature,

membrane technology is used in different industries, including water treatment for domestic and industrial water supply, chemical, pharmaceutical, biotechnological, beverages, food, metallurgy, and other separation processes. Different applications of membrane processes are schematically represented in Fig.5.1.

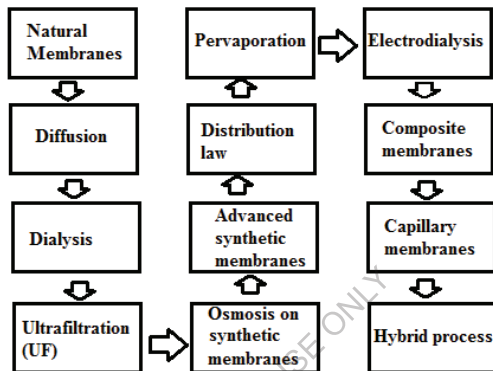
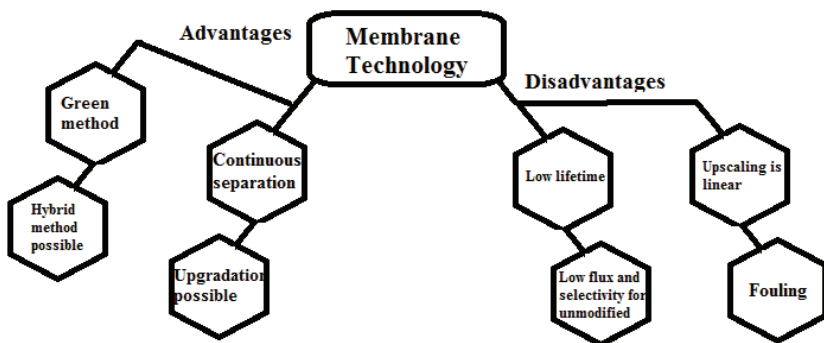


Figure 5.1. Pathways in membrane development

Membrane technology involves continuous separation under mild conditions with relatively low energy consumption and without the need of any additives. We can upgrade the technology by combining with other separation processes, forming hybrid processes. Factors like concentration polarization and membrane fouling, low membrane lifetime, and low selectivity and flux are some serious threat to the quality of this process. Fig.5.2. depicts the common benefits and drawbacks of membrane technology. But, these parts are common in all separation processes. Membrane operations now gained interest in areas like membrane reactors and membrane contactors. Thus all these typical unit operations of process engineering could be renamed as membrane unit operations like membrane distillation, membrane crystallizer, membrane reactors, membrane condensers and membrane gas separation. The potentialities of this technology are evident from significant positive results achieved in large scale. The problems related to pre treatment of streams, membrane life time, aging, fouling, can be overcome by combining advanced methods.



**Figure 5.2.** Overall view of membrane technology

Now a days, process intensification has emerged as a new design philosophy in most cases in which membranes methods got adapted to the redesigning of industrial uses. This new philosophy has redesigned membrane unit operations in practice with quantification. Thus the introduction of process intensification metrics were adopted in many cases for comparing membrane performance with those of traditional operations. Advancement in membrane technology has experienced exquisite development for desalination and wastewater treatment. So it has become an attractive alternative to many conventionally used techniques. Significant progress in this field of design of membranes drastically improved several separation performances. Selection and optimization of membrane technology intensified many properties for the identified applications which are crucial because they dictate the efficiency of removal as well as the cost incurred during the process. Membranes and its methods have become increasingly important in new industry which connects with our life. Since 1960, with the introduction of synthetic membranes a significant breakthrough was seen for its industrial applications. The earliest recorded study of membrane phenomena can be traced back to the middle of the eighteenth century with prototypes of membranes. Rapid research and development in membrane technology helped and increased its areas of action like water and dairy purification, water desalination, waste water reclamation, food and beverage production,

energy conversion and storage, gas and vapor separation, air pollution control and hazardous industrial waste treatment, blood dialysis, proteins and microorganisms separation, etc. Modification in membrane improved many of its capabilities to restructure production processes, protect the environment and public health, and provide new technologies for sustainable growth. The development of composite membrane with better chemical, thermal and mechanical properties, transport characteristics could decrease its capital and operation costs.

Membrane technology now acquired a big place in industry as they have the advantages of highly selective separation, continuous, economical and automatic operation at modest temperature, and easy integration into existing systems, as well as a sustainable method. Membrane processes are of different types as per its driving force. Pressure driven methods like reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), or gas separation (GS); or partial-pressure-driven processes, such as pervaporation (PV) comes under this category of membrane processes. Other types involve concentration gradient driven processes such as dialysis, temperature driven processes, such as membrane distillation (MD) and electrical potential driven processes, such as electrodialysis (ED). New hybrid processes are now evolved such as membrane contactors, membrane reactors and membrane bioreactors (MBRs), in which the function of the membrane is integrated with conventional processes to provide highly efficient performance. Membrane bioreactors combine membrane technology and biotechnology, where the membrane acts as a partition that separates the liquid and the gaseous medium which combines a chemical conversion process with a membrane separation process to add reactants or remove products of the reaction. It is also possible to combine different membrane processes to overcome the limitations of individual systems, and to maximize the productivity of the target separation processes. Dead end and cross flow are the two important modes of membrane filtrations. In dead end mode, the entire feed flow transports towards the membrane perpendicularly while in cross-flow operation, the feed stream moves parallel to the membrane surface and only a portion of the feed stream passes through the membranes under the driving pressure. In the former case, the retained particles and other components would accumulate and deposit on the membrane surface. In the later case, motion of the feed flow along tangential way to the membrane surface can result in higher permeation fluxes as the stream continuously removes retained material. Methods like back washing, ultrasonic vibration or periodic flow can also be employed to remove the deposited material from the membrane surface

and hence increase in permeation rate. All these processes can improve membrane life span to a great extent. The more complex equipment used by the cross flow mode than the dead end mode increase its operating cost much higher than the dead end mode. The energy needed to circulate the feed flow makes it less energy efficient also.

The major concerns involved in membrane technology are the loss of its separation performance due to membrane fouling and additional costs for cleaning and replacement. Deposition of permeation material within the structure of membranes sometimes cannot be removed in simple back washings. Membrane fouling caused by pore blocking, pore narrowing or adsorption, irreversible cake layer formation, etc. decrease membrane permeability and flux decline and alters solute retention. One of the biggest problems in membrane separation is fouling which is related to factors like feed solution properties, the nature of the membrane and operating conditions. Mitigation of fouling is achieved and reported several times by modifying the membrane surface and optimizing operating conditions. Sometimes the feed is pretreated before membrane filtration to improve the fouling tendency.

## **5.2 Application of membrane technologies**

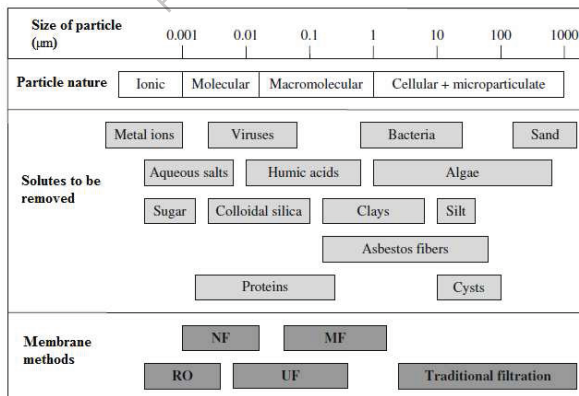
### **5.2.1 Water treatment**

Water scarcity is one of the major issues affecting every continent around the world. Millions of people with more than one third of the global population were still lacked access to improved sources of drinking water. There are various types of membrane separation processes for water treatment which involves four major processes – microfiltration (MF), nanofiltration (NF), ultrafiltration (UF) and most commercially used reverse osmosis (RO). All membrane processes require precisely applied pretreatment in order to prevent frequent and/or irreversible membrane fouling and for longer uses. Boiling or evaporating water was used to separate water from salt. In the late of 1960s desalination by Reverse Osmosis (RO) entered into the market when the membrane manufacturing process became efficient enough for supply. Records showed that more than 15,000 industrial scale desalination plants had been installed worldwide by the year 2002, and reverse osmosis made up to 45% of the total capacity. Further studies showed that there is an increase of levels approaching 60% in 2006 which would rise to 75% in 2020. The world total desalination capacity presently is approximately estimated as 30–50 million m<sup>3</sup>/day. Combination of one stage RO process with composite membranes for seawater desalination plants provides good salt rejection greater than 99.3%. For brackish water



desalination, polymeric membranes with sodium chloride rejection > 95% are typically enough. Spiral wound membrane modules were preferably used in industrial level seawater desalination plants due to ease of operation, permeation rate, packing density, fouling control as well as initial, operating and replacement costs.

Reverse osmosis process is able to eliminate the almost all dissolved solids, bacteria, viruses and other germs contained in the water. Its operational pressure ranges from 10 to 80 bars depending on its application in which water will flow from the more concentrated solution to the more dilute solution through the membrane. The process involves no phase change and it is a relatively low energy process makes its more versatile. A high pressure is applied to the concentrated side will cause this process to reverse and the solvent flow away from the concentrated solution, leaving a higher concentration of solute. Most of the RO membranes were made of polymers like cellulosic acetate and polyamide which comes under asymmetric or skinned membranes and thin film composite membranes. RO membranes used in industrial applications are of pore diameter ranging from approximately 5 to 15 Å (0.5–1.5 nm). This small pore size helped the RO methods to concentrate dilute solutions for recovery of salts and chemicals with low power requirements. But, the major issue with RO is its higher potential of fouling. Major applications of RO involves in the field of power generation, cleaning of contaminated surface water and groundwater, in potable water from sea or brackish water, in food processing and electronic industries, water used in chemical, pulp, food and paper industry.



**Figure 5.3** Membrane based filtration processes

Microfiltration processes were proved to remove micron sized particles from liquids. The membranes used in these filtrations are having pore sizes ranging from 0.1 to 10.0  $\mu\text{m}$  through which microorganisms cannot pass. The membrane materials are generally natural or synthetic polymers such as cellulose acetate (CA), polyvinylidene difluoride, polyamides, polysulphone, polycarbonate, polypropylene and polytetrafluoroethylene (PTFE) with new generation materials like ceramic membranes. The most widely used application of MF is the treatment of the municipal water without any disinfectants such as ozone and chlorine. It is a commonly used technique for the clarification, separation, and purification of proteins. An important role in the pretreatment of food processing wastewaters for the reduction of the polluting load and/or for the recovery of valuable compounds was also reported. The major advantages of MF method involve low operating pressure, low energy consumption, ease in usage, relatively cheap, no energy consuming phase transfer needed etc. Ultrafiltration technology is being used worldwide for treating waters. This method has been used in several municipal drinking water applications for so many years worldwide. It can be used to separate a solution that has a mixture of some desirable components and some that are not desirable. It acts as a selective barrier and is capable of retaining species in the range of 300–500,000 Da of molecular weight. It uses membranes with pore sizes ranging from 10 to 1,000  $\text{\AA}$  (0.001–0.1  $\mu\text{m}$ ). UF is used in many industries to separate molecules like sugars, biomolecules, polymers and colloidal particles. The driving force for transport across the membrane is purely pressure difference. UF usually processes operate at 5–10 bars, although in some cases increases up to 25–30 bars and the separation is achieved by concentrating the large molecules present in the feed on one side of the membrane. Separation of macromolecules such as protein is done in UF method from low molecular weight solvents. Polymers used for UF membrane preparation generally includes polymeric materials such as polysulphone, polypropylene, nylon 6, PTFE, polyvinyl chloride and acrylic copolymer, sometimes uses inorganic materials such as ceramics, carbon based membranes and zirconia. These membrane materials show characteristic porosity, morphology, surface properties, mechanical strength and chemical resistance. Some other applications of UF process for water and wastewater treatment include making of ultrapure water, lowering of high COD levels, selective removal of dissolved toxic metal ions, and are widely used in dairy industries and wine or fruit juice clarification.

Nanofiltration is ultimate form of filtration that uses membranes to separate different fluids or smaller ions or particles with more time to spare. It is considered as alternative RO method due to its similarity and efficiency, but uses larger membrane pore structure as operate at much lower pressures, normally 7–14 bars, and passes some of the inorganic salts. NF is usually used in applications where high organic removal and moderate inorganic removals are desired. NF shows excellent applications in concentrating sugars, divalent salts, bacteria, proteins, particles, dyes and other constituents that have a molecular weight greater than 1,000. Polymers used in NF membrane manufacturing includes cellulose acetate and aromatic polyamide with characteristics such as salt rejections from 95% for divalent salts to 40% for monovalent salts and an approximate MWCO of 300 for organics. One of the major advantages of NF over RO is that NF can typically operate at higher recoveries and thus conserve total water. NF is not so effective on small molecular weight organics, such as ethanol/methanol. The use of NF method to produce good drinking water is very effective as it have good molecular rejection characteristics for divalent cations, for example, calcium and magnesium. Thus they can effectively remove hardness in place of conventional chemical softening. It can also reject higher molecular weight organics that contribute to taste and odour which improves the efficiency of downstream disinfection processes.

### 5.2.2 Other membrane methods in water treatment

Membrane technology mainly uses the above described methods for water and wastewater treatment. Besides these methods, there are other membrane technologies for water and wastewater treatment.

a) **Dialysis.** Dialysis is a membrane process where separation is based on their concentration gradients between a semi permeable membrane. The method is capable of passing small solute molecules, such as salts and small organic species, while retaining colloids and solutes of higher molecular weight. The principle behind the permeation is by diffusion rather than by the hydrodynamic flow that would occur in a porous medium. The important applications of dialysis include hemodialysis, purification in different labs, separating in refining industry.

b) **Electrodialysis** is a process in which ions are transported through ion permeable membranes from one solution to another under the influence of a potential gradient. The difference in potential gradient creates potential field and the electrical charges on the ions which allow them to be driven through the membranes fabricated from ion exchange polymers. The ability to

selective ion transport and reject ions of the opposite charge is highly useful in concentrating, removal or separation of electrolytes can be achieved. Reports established that ED is efficient in desalination of seawater especially at lower concentrations. Applications of ED include electroplating and etch bath rinse water, removal of organic acids from beverages, wastewater treatment including radioactive ones, regeneration of ion exchange resins used in ultra pure water production.

c) **Donnan dialysis** uses an ion selective membrane with similar working of ion exchange resins. In the case of anion exchange membranes, anions will diffuse through the membrane while cations will be retained until equilibrium is reached while in the case of cation selective membranes, cations will diffuse through the membrane while anions will be retained. Potential difference plays the force behind separation which can be controlled by adjusting solution concentrations. Major applications of ion exchange include pH control, recovery of acids and bases from salts, water softening etc.

d) **Membrane bioreactor** can be expressed as a hybrid method of conventional biological degradation and membrane separation into a single process. Here microorganisms are responsible for biodegradation and suspended solids are separated from biologically treated water by a membrane filtration unit. Bioreactor holds the entire biomass providing both perfect control of the sludge retention time for the microorganism and physical disinfection of the effluent.

### 5.2.3 Waste water treatment

Wastewater treatment and its reuse are a feasible solution and a sustainable alternative method to conserve water, which is important in the current scenario to face the increasing municipal, industrial, and agricultural demands. Water reuse is not typically considered to have problems with water scarcity but in which the continuous growth in population and to uplift infrastructure and industrial development have increased stress on water supplies. The process of water reuse has also numerous obstacles, the main one being quality control to reduce the risk of human exposure, practices that vary considerably from region to region. New water recycling projects have the potentiality to reduce wastewater treatment and disposal costs which helps to decrease the discharge of pollutants to the environment and to provide high-quality water. Membrane and conventional activated sludge plants can be utilized for the treatment of wastewaters which involves four stages, called primary, secondary, tertiary and, sometimes, quaternary treatment.

The membranes can be used for total retention of all types of biomass and guarantees production of high quality treated water. The developments in membrane technologies created the possibility of integrating different membrane operations with all the important benefits with very good results. Development of integrated membrane systems by combining MF or UF with RO or NF can be applied to achieve better quality water. MF and/or UF can be assigned as pretreatment steps for better feed water for the RO/NF membranes. This integration creates water with a lower turbidity and sludge content index and, therefore, with less potential fouling and more microbiology control can be achieved. Pretreatment is the critical step for a successful RO plants as fouling is mainly caused by suspended solids, colloidal material or ions dissolved in raw water. It is also important to ensure that the quality of water fed to the RO module is high enough to avoid variability in the quality of water it produces. Integrated Membrane Systems (IMS) are more acceptable due to its feasibility, modularity, relative insensitivity in cases of raw water changes, process reliability, plant availability and lower operating costs.

Porous hydrophilic polymer membranes can be now applied instead as membrane based dehumidification systems. The membrane operates as a contactor between the humid gas phase and a liquid coolant phase. Thus, this type has recently been proposed for the recovery of evaporated waste water from industrial gases. New generation membrane condensers can be installed for various waste water treatments. It holds the principle as follows. The waste gaseous stream from an industrial plant at a certain temperature is fed to the membrane condenser kept at a lower temperature for cooling the gas up to a super saturation state. The hydrophobic nature of the membrane prevents the penetration of the liquid into the pores, allowing the dehydrated gases pass through the membrane and retaining the liquid water at the retentate side. The possibility of controlling by tuning the operating conditions as well as the condensation of contaminants in the liquid water recovered in the retentate side of the membrane condenser could prove its ability to work in different modes.

#### **5.2.4 Membranes for Energy**

The modernization of conventional power plants and refineries is important in present global condition. Intercontinental and governmental agreements to reduce their emission of CO<sub>2</sub> in a transition period when petroleum and coal are still the predominant fuel sources is now became a big challenge. In this scenario, membranes and its technologies have a huge opportunity to become a key player. Fuel cells are futuristic source with zero emission in which energy

converters fed with hydrogen or renewable fuels like methanol and ethanol to power vehicles, portable devices or to supply electricity to buildings. Different proton conducting polymer electrolyte materials have been investigated for high temperature operation to produce efficient fuel cells. Membrane reactors play an important role in pre-combustion capture and biomass conversion for hydrogen production. The stream coming out from a production plant or a coal gasification plant contains approximately 50% hydrogen and between 40-45% CO. Hydrogen must be recovered and CO is usually reduced in an upgrading stage, producing more hydrogen at the same time. The improvement in efficiency with lower environmental impact on one side and the reduction of the reaction/ separation/ purification stages is much needed in designing plants. An innovative approach for concretizing these technological aspects is the use of membrane reactors, combining the reaction and H<sub>2</sub> separation by means of a selective membrane. Development of membrane based methods, mostly Pd catalyst based one, allows the recovery of a hydrogen rich stream which does not require further separation. Additionally to the enhancement of conversion or recovery of hydrogen stream the use of membrane reactor allows the attainment of a stream already concentrated and compressed in CO<sub>2</sub> (> 80%) which is easily recoverable. This method can also be employed and adapted for biomass exploitation, another source of hydrogen.

The hydrogen production from biomass is a carbon neutral process because the CO<sub>2</sub> released during hydrogen production is consumed by a further biomass generation. The use of membrane technology in industry has a lot of examples like H<sub>2</sub> from refinery industrial gases, natural gas dehumidification, separation and recovery of CO<sub>2</sub> from biogas and natural gas. Membrane separation is widely accepted due to its simplicity. When a gas mixture is fed to one side of the membrane, one or more components of the gas mixture preferentially permeate through the membrane. Thus, retaining the rest of the gaseous stream in the retentate makes it a simple method of gas separation. The selection of the suitable separation process and membrane material should be driven by specific considerations, strictly related to the output to be obtained.

The use of membranes as CO<sub>2</sub> capturing sink is another flourishing area of interest. Carbon dioxide is produced in huge streams from areas like power and hydrogen production, heating systems and natural gas and biogas purification. But the use of membrane technology for CO<sub>2</sub> separation has a lot of hurdles to overcome and it should also strictly relate to the conditions of the stream to be treated.

### 5.2.5 Membranes for chemical industries

Ocean being the largest source of dissolved salts (~3.3%) is a reserve not only of water but also of chemical resources. It contains very essential elements from hydrogen to uranium, even though the seven elements like Na, Mg, Ca, K, Cl, S, and Br account for around 93.5% of all the dissolved salts. As of now, a small fraction of chemicals is currently extracted mainly the sodium salt used in kitchen and it's by products like potassium chloride, magnesium salts and bromide salts. United States Geological Survey showed the presence of huge amounts of minerals in the sea that are larger than the estimated reserves on land. Combined application of evaporative method with operations such as Membrane Crystallization can be utilized for the recovery of fresh water and salts from seawater. Membrane crystallization is a modern membrane technology in which crystallization process promote crystal nucleation and growth in a well controlled pathway starting from under saturated solutions. It uses evaporative mass transfer of volatile solvents through hydrophobic membranes in order to concentrate feed solutions above their saturation limit. This creates a supersaturated environment where crystals may nucleate and grow.

The presence of the polymeric membrane in the crystallizing solution induces heterogeneous nucleation at super saturation levels while the membrane matrix acts as a selective gate for solvent evaporation, modulating the final degree and the rate for the generation of the super saturation. Nucleation at super saturation would not be adequate for spontaneous nucleation in the bulk of the solution. The final properties of the crystals produced both in terms of structure and morphology is influenced by controlling the transmembrane flow rate. Membrane crystallization can be customized for simultaneously extraction of water and minerals from the brine and also increasing their overall recovery factor and recovering the dissolved salts in the form of high quality crystals. The chloralkali process or double alkaline process is an industrial membrane process for the electrolysis of sodium chloride solutions which is used to produce chlorine and sodium hydroxide which are commodity chemicals required by industry.

Mining applications of membranes includes a wide range of applications like reuse of mine water, treatment of secondary effluents, treating waste water, recycling mine drainage. Membrane methods are employed for the recovery of high value metals such as gold and uranium. Other valuable metals like copper, zinc, cobalt, molybdenum and tungsten are also separated from bleed and waste streams in mining plants. The recovery of valuable catalytic

materials from catalytic industries and metal recovery from electroplating industries also employs membrane technology.

### **5.2.6 Nuclear Waste Treatment**

A broad spectrum of low and intermediate level liquid radioactive wastes was produced by nuclear industry worldwide. Treatment methods like chemical treatment, adsorption, filtration, ion exchange, and evaporation have been used throughout the industry to treat these wastes. The inability to remove all contaminants with high operating costs with large quantities of secondary solid waste produced created the importance of new innovative techniques. Advancement in membrane technology has been gradually introduced into nuclear power plants for treatment of low radioactive waste. Membrane based methods like reverse osmosis, nanofiltration, ultrafiltration, precipitation ultrafiltration, complexation ultrafiltration, microfiltration, osmotic concentrator, electrodialysis, diffusion dialysis and Donnan dialysis, and liquid membranes are now employed but only few methods have been commercialized until now. A new process named membrane distillation has been introduced in which separation employs porous lyophobic membrane, non-wettable by the liquid. The driving force in this process is a gradient of partial pressures of the components of the solution in gaseous phase.

### **5.2.7 Air pollution applications**

Air pollution is a serious threat to humans and other living organisms which is often created by the emission of pollution generated by industry, power plants, car transport, and agricultural and municipal waste. It involves the emission of hazardous acid gases like  $\text{SO}_2$  and  $\text{NO}_x$  and volatile organic and hydrocarbon compounds. These compounds which would destroy the ozone layer and contribute greatly to greenhouse effect and finally the climate change. Different membrane methods are used to eliminate these substances. The process of gas separation through membranes is done on the mechanism of dissolution and diffusion. Gases usually show low affinity to polymers and therefore its solubility also. Solubility of a given gas in polymer increases along with the increase in affinity to polymer; for example, the solubility of carbon dioxide is higher in hydrophilic polymers than in hydrophobic ones. Selective membrane absorption can be applied for the removal of volatile organic compounds which integrates the advantages of absorption and membrane gas separation.

A membrane based vapor separation system is now applied in practice to treat the breather pipe vent gases of storage tanks enables emission reduction during car refueling without creating any



additional emissions. The removal of SO<sub>2</sub> from exhaust gases is another possibility of membrane technology. Sulfur dioxide, which was being recovered by membrane absorption in the form of sodium sulfite, may be again used in the production process. Support liquid membranes have been developed for the removal of acidic components such as CO<sub>2</sub> and H<sub>2</sub>S from natural gas and other process gases. Usually, in this method a thin layer of the absorption solvent placed in the pores of the membrane by capillary force. Thin layer over membrane surface shows negligible mass transfer resistance and with the high contact surface area between the phases causing a higher mass transfer to occur.

### **5.2.8 Food and beverage applications**

Many of the bottled water industry have adopted membrane technology for large scale production. Bottled water manufacturers want to produce in large scale in an economical fashion and as such they treat the local water to remove almost all of the constituents. Thus they add back a package of ingredients to give a recognizable taste and feel to that particular brand of bottled water. They utilize membranes to exclude bacteria and other microorganisms and to produce clean water. Soft drink manufacturers and beer producing distilleries also make use of membrane technology for fast and prompt method of membranes to produce quality water. Membrane facilities in beer production treat the water to acceptable ionic content including hardness and alkalinity for use and continuous beer stabilization is obtained. This would improve operating efficiency of the brewery and continuous clarification and final filtration of the beer. Similarly, the wine clarification can be achieved by membranes by effective removal of suspended solids, yeast and bacteria. This automation of the filtration process reduces losses, improves economics and minimizes labor when producing wine. Concentration of natural juices as well as its color can be controlled by using membrane methods. Juices can be purified and effectively membrane filtered for fine particles and gives it a haze free property that allows for longer shelf life of various juices. The dairy industry is effectively using membrane technologies for many years. The various processes in dairy like filtration, concentration, selective removal, demineralization etc were efficiently done with the help of membrane automation.

### **5.2.9 Specific industrial applications**

The field of biochemistry/biotechnology and its related industries are well decorated with the advancement of membrane technologies. By this method, it is now possible to extract amino acids and lipids and reused in blood and other cell cultures. Advancements in enzyme production

which is highly important in many industrial processes and which improve the speed or efficiency of many biochemical reactions have been facilitated by the use of microfiltration. Separation of sugars such as dextrose and maltose from fibrous and undesirable proteins can easily be now done with membranes. Extraction of gelatin, egg whites, soy protein and other natural products in medical as well as pharma industries was found improved very much by using microfiltration and ultrafiltration. Extraction of valuable volatiles and organic solvents like methanol removal from organic mixtures, aroma extraction can be done effectively with membranes. Membrane fractionation and recovery can be very well suited for natural essential oils and flavors industries. Paint and adhesive industries, automotive and appliance industry uses membrane based techniques for a wide range of applications like recovery, cleaning, purification etc. Fine chemicals and pharmaceutical industries also use membranes for recovery and are used within the processes.

#### **5.2.10 Future membrane technologies & applications**

Membrane processes continue to have new horizons and industry for a wide range of applications worldwide. The hyper salinity of produced water from conventional oil sources represents high osmotic pressure. This can offer potential for green energy production if the osmotic energy is converted into mechanical energy. PRO (pressure retarded osmosis) is newer method that can convert osmotic energy into electrical energy using a hydro turbine and generator almost like conventional type. The project needs much innovative process design with research and hardware development, including a new generation of forward osmosis membranes. The multimillion oil and gas industry urgently needs the removal of hazardous H<sub>2</sub>S from sour water which must be removed from produced water prior to any further treatment. Membranes could be an alternative technology over the currently used expensive method for sour water treatment. Reports showed that hollow fiber hydrophobic membrane contactors (G543 - 3M Liqui Cel, USA) used in gas separations is found able to remove H<sub>2</sub>S from sour water and trap it in a receiving solution. A novel UF membrane for oil water separation is under development by researchers at Qatar and Akron Universities with the potential for enhancing separation efficiency and selectivity of the block copolymer membranes pores by chemical modification will be evaluated and compared with commercial membranes. New aquaporin-graphene based forward osmosis composite membranes are under preparation in which presence of aquaporin (protein channels) would permit the transport of up to a billion water molecules per second. They

are investigated to showed salt rejection and water permeability two or three times greater than most of the commercialized membranes. Affordable ceramic membranes are that high sintering temperature and high energy input in most circumstances are necessary for ceramic based membranes. The range of more specialized approaches which have a case specific impact, an active development in laboratories is ongoing and the first scaled up implementation is expected within the next decade. Great challenges remains in the case of thick dense perovskite ceramic membrane fabrication need to be carefully controlled. This advancement can be extended to composite ceramic membranes such as dual phase membrane and molten salt membrane and to other temperature resist bioceramics and bioglasses based membranes. Research in micro and nanofabrication enable the precise tailoring of polymer surface topography which been explored for separation membranes, so that established barrier properties can be combined with different shapes. Additive manufacturing or 3D printing is a different membrane fabrication method so that membranes of different shapes, types, and designs could be obtained. This potentially helps to design more precisely, fabricate and control than using the available methods today. By further establishing and consolidating *building blocks* and *tools* for membrane fabrication, *revolutionary* visions for in situ, *in place* and *on demand* membrane systems will be realized step by step in the next decades.

### **5.3 Conclusion**

Today, the success and wide spread use of water purification technology has come to symbolize the growth of membrane based technologies. The success and improvements in membrane performance is visible with new better membranes and materials, increased solute rejection and flux, improved membrane life and process designs with the lowest energy consumption helped to improve in many types of processes and fields with an increases in plant capacity. Cost effective and environmentally sensitive concentrate management is now recognized as a significant reason behind the extensive implementation of membrane technologies. The development of hybrid as well as integrated systems have been proposed for the extraction of valuable resources with minimization of the environmental impact and the recovery of energy. However, despite of these advancements, there are still some drawbacks which prevent the wider commercialization of polymeric membranes in many applications. It should be noted that the development in membranes technologies with physicochemical properties for specific functionality is crucial for its implementation in industry.

Various types of membranes with its modification with innovative properties have a promising contribution to make in various applications. In this context, different green methods are available for membrane synthesis with a vast variety of green chemicals which are commercially available, and more chemicals are being developed or discovered in green and sustainable ways. Hence, the ultimate goal of green synthesis with green approach is fully achieved.

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## Chapter 6

### Highly efficient, One-pot green synthesis of novel pyrazolo [4',3':5,6]pyrano[2,3-*d*]pyrimidines *via* multicomponent reaction in ethyl lactate as a biodegradable solvent

Santhosh Govindaraju<sup>1</sup> and Sumaiya Tabassum<sup>2\*</sup>

<sup>1</sup>*Department of Sciences and Humanities, School of Engineering and Technology, CHRIST (Deemed to be University), Kumbalagodu, Mysore Road, Bengaluru 560074, India.* <sup>2</sup>*Department of Chemistry, Surana College, South End Road, Basavanagudi, Bengaluru 560004, India.*

\*Corresponding author: Email: [sumaiya87org@gmail.com](mailto:sumaiya87org@gmail.com)

#### Abstract

A green, rapid and an efficient one-pot protocol has been developed for the synthesis of some novel pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine derivatives from the cyclo condensation reaction of the reaction of benzaldehyde, phenylhydrazine, ethyl acetoacetate, and barbituric acid in the presence of ethyl acetate as a biodegradable solvent. The methodology is environmentally benign, catalyst-free, excellent yields, broader substrate scope, high conversion rate, operational simplicity, excellent functional group tolerance, shorter reaction time, and use of a green solvent. Most significant of all, the synthesis of pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine occurs at room temperature and without chromatographic separation.

#### 6.1 Introduction

Heterocyclic rings are found in a wide variety of naturally occurring substances and they form the structural motif of many biologically active scaffolds. They are considered as privileged structures [1] and form a very important tool having extensive applications such as building blocks, industrial compounds [2-4], sanitizers [5], corrosion inhibitors [6,7], and copolymers [8,9]. Moreover, fused-pyrimidine analogs show diverse biological activities [10-14] and are present in the genetic components such as DNA and RNA [15-16] substances.

The rapid and uncomplicated synthesis of heterocycles is therefore one of the main goals of medicinal chemists all over the world [17]. Moreover, a library of new heterocyclic compounds has been successfully synthesized by MCRs which can be used for structural activity

studies. MCRs can act as an interface between organic synthesis and chemical biology [18] thereby saving money and time.

Multicomponent reaction (MCR) [19] is one of the most powerful tools in organic synthesis as complex molecules can be generated in a one-step process. MCRs are a boon to chemists all over the world as the desired product can be synthesized in a one-pot process wherein three or more reactants combine to form the target molecule in excellent yields [20]. MCRs involve the formation of multiple bonds in a single step operation [21] without changing the reaction parameters such as isolation of intermediates, extraction, purification, or addition of further reactants. Therefore, MCRs cover most of the principles of green chemistry as it shows high environmental sustainability, atom efficiency [22], step efficiency, reduced use of solvents, and energy. The scaffold diversity in organic molecules can be further enhanced by diversity-oriented synthesis (DOS) [23] and divergent structures can be synthesized in shorter reaction duration. The variations in MCRs in terms of catalysts, solvents, and starting components make it an ideal model for the synthesis of heterocycles. The pharmacologically active substances generated by MCRs help us to intensify the exploration of large chemical space of unknown structural frameworks thereby enhancing the efficiency of the process.

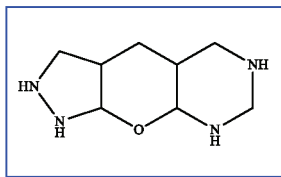
The greatest challenge faced by chemists is in the design and implementation of green protocols in organic synthesis. Since the processes are vast it is difficult to verify a process as completely green and scientists now use the term greener than other completely green products and processes. There is no systematic and reliable method to ensure that the chemistry implemented is green, since the number of chemical synthesis pathways is vast, and in general it is only possible to verify if a proposed manufacturing process is “greener” than other substituents. The search for green solvents is imperative to counter the environmental concerns, a range of greener or more sustainable solvents such as water [24], glycerol [25], PEG [26], sCO<sub>2</sub>, ionic liquids [27] and Deep eutectic solvents [28] have been proposed. The concerns in environmental protection along with sustainable development in terms of green chemistry principles encouraged chemists to shift from harmful solvents to green solvents in 1980s. Despite these facts and increasing interests, very little attention is being given to bio-solvents to replace the volatile organic solvents used. In this regard, the lactate ester family solvents, such as ethyl lactate play a pivotal role as a greener alternative to traditional organic solvents.



Ethyl lactate also called lactic acid ethyl ester is effective in many organic transformations [29] and is considered as an environmentally benign solvent [30]. It is industrially produced by a reversible esterification reaction between ethanol and lactic acid. It is clear to slightly yellow liquid, and it is found naturally in trace quantities in a wide variety of foods, such as wine and chicken. It is also formed as a biodegradable by-product in the biomass fermentation process of micro-organisms. Ethyl lactate has attracted much attention in recent years, as its effectiveness is similar to that of hydrocarbon solvents. Ethyl lactate has numerous advantages as it is non-corrosive, non-carcinogenic, non-nonozone-depleting, and is biodegradable and recyclable. The high applicability of ethyl lactate is due to its high solvency and also owing to its high boiling point, low vapor pressure, and low surface tension. Ethyl lactate shows excellent cleaning capacity [31] compared to chlorinated solvents and it effectively cleanses the greases, oils, adhesive and solid fuels present on the metal surface. Moreover, ethyl lactate follows at least eight principles of Green chemistry proposed by Anastas and Warner [32].

## 6.2 Importance of pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines

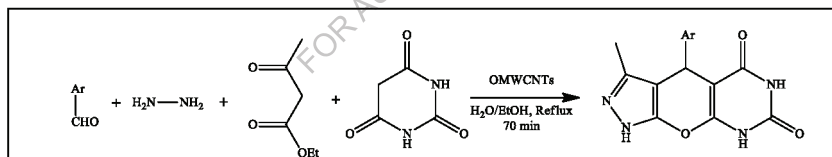
Pyrazole, Pyran, and Pyrimidine skeletons are each privileged heterocyclic pharmacophoric motif possessing diverse therapeutic potential [33]. Pyranopyrazole is an enchanting template of pharmaceutical interest displaying an array of activities such as anticancer [34], hypotensive [35], antidepressant [36], and hypoglycemic activities. Moreover, the Pyranopyrimidinenucleus is a key structure in various natural products [37] with well-flourished applications as antibronchitic [38], antitumor [39], hepatoprotective, antimicrobial, and antitubercular agents. As a result, the synthesis of fused heterocycles utilizing multicomponent strategies has been extensively studied. Given their interesting biological significance, these frameworks appeal synthetic, medicinal and biochemists as the integration of these bioactive cores into one architecture-pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine (Fig. 6.1) could result in exploring very interesting activities of paramount eminence to mankind.



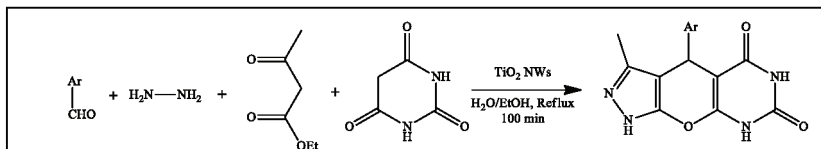
**Fig. 6.1:** Schematic representation of pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine

### 6.3 Literature survey on the synthesis of pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines

Few approaches have been documented in the literature for the synthesis of a wide variety of pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines which employ the use of OMWCNTs[40] (Scheme 6.1), TiO<sub>2</sub> nanowires[41](Scheme 6.2), DABCO [42]and Oleic acid [43]. These reported protocols suffer from one of the other drawbacks such as the use of toxic bases, prolonged reaction times, and preparation of the catalyst, unsatisfactory yield, and lack of generality.



**Scheme 6.1:** Synthesis of pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines by S. Khodabakhshiet al.[40].



**Scheme 6.2:** Synthesis of pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines by S. Dastkhoonet al.[41].

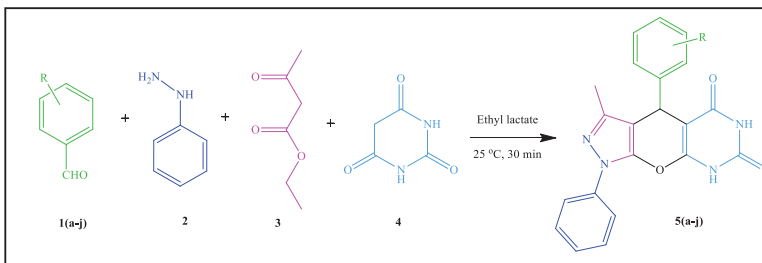
### 6.4 Objectives of the study

1. To synthesize novel pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines by a green protocol in excellent yields.
2. To characterize the synthesized compounds by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS spectral analyses.

## 6.5 Present work

Although structural complexity and step economy are achieved in minimum steps and minimal side products, the use of catalysts, flammable organic solvents, and tedious purification processes often underscores the green facets. Consequently, an ideal synthetic etiquette would be to use a catalyst-free condition with or without a solvent. Achieving sustainability *via* the use of green solvents especially biodegradable solvents that are harmless, safe, which can be recycled and reused have become one of the popular alternatives from both environmental and economic points of view.

Although a large number of synthetic protocols have been reported in recent years, their scope is still sub-optimal and are accompanied by one or the other drawbacks such as longer reaction time, use of flammable solvents, harsh conditions, unsatisfactory yields, requires preparation of the catalyst and employs expensive catalyst. This reveals the scarcity of an efficient plan for the easy access of this decisive scaffold. This propelled us to unveil for the first time, a clean, competent, safe, profitable and high yielding eco-compatible approach for the synthesis of dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines *via* a catalyst-free one-pot four-component cyclo condensation reaction of varied substituted aromatic aldehydes, phenylhydrazine, ethyl acetoacetate, and barbituric acid in ethyl lactate at 25 °C for 30 min (Scheme 6.3).



**Scheme 6.3:** Synthesis of dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidones.

## 6.6 Results and discussion

As part of our continuous pursuit of developing new domino reactions for the synthesis of heterocyclic compounds in concordant with eco-friendly protocols, we destined to synthesize dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidones under significantly benign conditions.

To optimize the reaction conditions, a pilot reaction was performed between benzaldehyde, phenylhydrazine, ethyl acetoacetate, and barbituric acid as model substrates. The model reaction was investigated in different solvents under catalyst-free conditions at various temperatures and the results are enlisted in **Table 6.1**.

To ascertain the effect of solvents, the model reaction was initially performed in the absence of solvent and it was seen that the only trace amount of product was obtained (**Table 6.1**, Entry 1). Detrimental effect was obtained when the reaction was performed in *n*-hexane (Entry 2). The reaction afforded poor yield when it was carried out in toluene (Entry 3). In presence of polar aprotic solvents (EtOAc, CHCl<sub>3</sub>, CH<sub>3</sub>CN, DCM, DMF, and DMSO) at reflux and at 100 °C the reaction renders, low yield (Entries 4–9). The reaction proceeded sluggishly in polar protic solvents like AcOH, H<sub>2</sub>O, EtOH, EtOH:H<sub>2</sub>O (1:1) fetching moderate yields (Entries 10–13).

The reaction progressed steadily when polyols (Glycerol, Ethylene glycol) were employed (Entry 14,15). Although polyols proved to be capable of promoting the reaction, in their case, a gummy solid was obtained which makes the separation of the product difficult. To our delight, the reaction gives the best yield (95 %) when ethyl lactate was used as a solvent (Entry 16).

As shown in **Table 6.1**, the best results were obtained at 25 °C in the presence of ethyl lactate (5 mL). The resulted high yields in the presence of ethyl lactate may be attributed to the high mass transfer of the solvent.

**Table 6.1:** Optimization of solvent and conditions for the synthesis of **5a**<sup>a</sup>

Entry	Solvent <sup>b</sup>	Temperature (°C)	Time (h)	Yield (%) <sup>c</sup>
1	No solvent	100	10	Trace

2	<i>n</i> -hexane	Reflux	10	ND
3	Toluene	100	10	10
4	EtOAc	Reflux	10	15
5	CHCl <sub>3</sub>	Reflux	10	10
6	CH <sub>3</sub> CN	Reflux	10	15
7	DCM	Reflux	10	15
8	DMF	100	10	25
9	DMSO	100	10	25
10	AcOH	100	10	30
11	H <sub>2</sub> O	Reflux	10	45
12	EtOH	Reflux	10	50
13	EtOH:H <sub>2</sub> O (1:1)	78 °C	10	55
14	Glycerol	100 °C	10	60
15	Ethylene glycol	Reflux	10	60
16	Ethyl lactate	25 °C	0.5	95

<sup>a</sup>Reaction conditions: benzaldehyde (1 mmol), phenylhydrazine (1 mmol), ethyl acetoacetate (1 mmol), barbituric acid (1 mmol) and solvent (5 mL)

<sup>b</sup>5 mL.

<sup>c</sup>Yield of isolated product

To purview the scope and generality of the designed green protocol, we employed benzaldehyde, phenylhydrazine, ethyl acetoacetate, barbituric acid, and ethyl lactate to our optimized conditions and the results are presented in **Table 6.2**. To our delight, in all the cases the substrates congregated propitiously into the corresponding pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines in excellent yields. It was also observed that the reactions with aromatic aldehydes bearing both electron-donating/withdrawing groups proceeded well to give the corresponding products in exceptional yields.

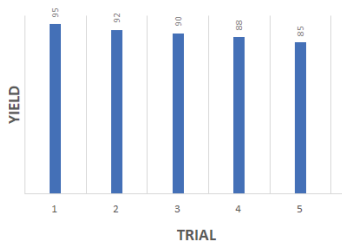
**Table 6.2:** Synthesis of novel pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines

Entry	R	Product	Yield (%) <sup>a</sup>
1	H	<b>5a</b>	95
2	4-NO <sub>2</sub>	<b>5b</b>	93
3	3-NO <sub>2</sub>	<b>5c</b>	91
4	3,4-(OCH <sub>3</sub> ) <sub>2</sub>	<b>5d</b>	94
5	3,4,5-(OCH <sub>3</sub> ) <sub>3</sub>	<b>5e</b>	94
6	4-CH <sub>3</sub>	<b>5f</b>	90
7	4-OH	<b>5g</b>	91
8	2-OH, 4-OCH <sub>3</sub>	<b>5h</b>	93
9	2-OH, 3,5-Cl	<b>5i</b>	92
10	4-Cl	<b>5j</b>	94

<sup>a</sup>Isolated yields

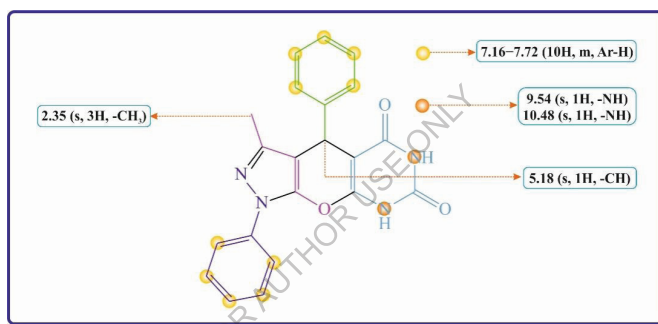
### 6.7 Reusability of catalyst

For this propose, the reaction of a mixture of aryl aldehyde (**1**, 1 mmol), phenylhydrazine (**2**, 1 mmol), ethyl acetoacetate (**3**, 1 mmol), barbituric acid (**4**, 1 mmol), and ethyl lactate (5 mL) was mixed and then stirred at 25 °C. After completion of the reaction, as monitored 5 mL of water was added to the reaction mixture to precipitate the product and to separate. After isolation of the product by filtration, water was removed by direct distillation at 100 °C and the ethyl lactate obtained was washed with diethyl ether (2 X 5mL). The regenerated ethyl acetate was successfully used for the next run under the same reaction conditions. The reusability results are summarized in Figure 1.2. It can be seen that the solvent system can be reused in four cycles with no appreciable change in yield.



**Fig. 6.2: Reusability of ethyl lactate**

## 6.8 Structural assignment



**Fig. 6.3: <sup>1</sup>H NMR chemical shift values of 5a**

The IR spectrum of the compound **5a** displayed absorption bands at  $\nu$ 3240, 3051, 2986, 1658, 1129  $\text{cm}^{-1}$  confirming the presence of N-H, aromatic C-H, alkyl C-H, aromatic C=C, and C-O-C bonds respectively.

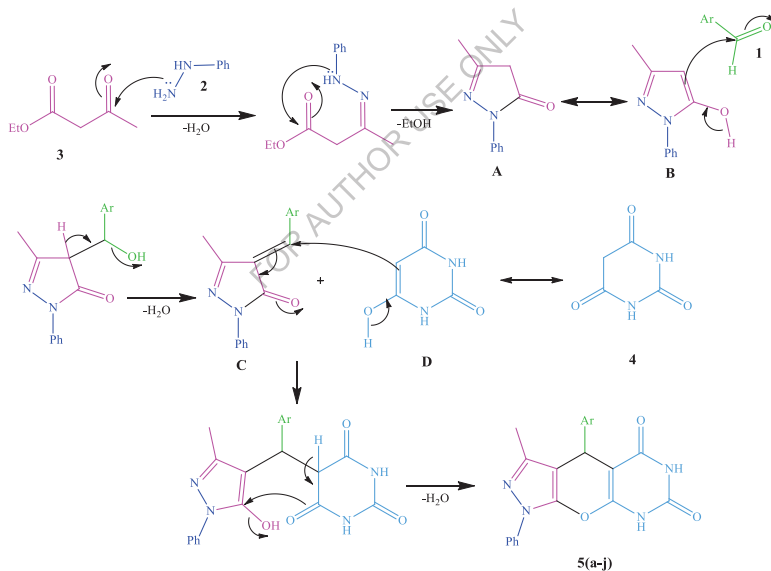
Its <sup>1</sup>H NMR spectrum indicated the presence of three singlets at  $\delta$ 2.35, 9.54, and 10.48 ppm for the -CH<sub>3</sub> and two -NH groups. A sharp singlet appeared at  $\delta$ 5.18 ppm corresponds to the -CH group of the pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine ring. Moreover, multiplets in the range  $\delta$ 7.16–7.72 ppm appeared for ten aromatic protons of the two phenyl rings.

The <sup>13</sup>C NMR of **5a** compound showed a characteristic signal at  $\delta$ 11.5, indicating the presence of the -CH<sub>3</sub> group. The signals at  $\delta$ 154.8 and 168.7 ppm confirm the presence of two C=O groups.

The HRMS of the above-mentioned compound showed a molecular ion peak  $[M+H]$  at 373.1304 corresponding to its molecular mass.

## 6.9 Mechanism

A plausible mechanism for the formation of the substituted pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines in ethyl lactate is envisaged and outlined. It is reasonable to assume that; the first step may involve an intermolecular cyclization between ethyl acetoacetate (**3**) and phenylhydrazine (**2**) to give phenyl pyrazolone **A**. The enol form of the pyrazolone **B** may react with the aldehyde (**1**) by a Knoevenagel condensation to give an adduct **C**. The enolic form of the barbituric acid **D** may react with the Knoevenagel adduct **C** by a Michael addition which on dehydration and on intramolecular addition may give the final product (**5**) as shown in the **Scheme 6.4**.



**Scheme 6.4:** A plausible mechanism for the formation of pyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidines



## 6.10 Experimental section

### 6.10.1 Material and methods

Reagents and solvents of commercial-grade were used without further purification except for liquid aldehydes which were distilled before use. The progress of the reactions was assessed by TLC [analytical silica gel plates (Merck60 F<sub>254</sub>)]. Melting points were determined on a RAAGA, Indian make apparatus. The FT-IR (ATR) analyses were carried out on Cary 630 FT-IR spectrophotometer equipped with a diffuse reflectance sampling interface (Agilent Technologies, USA). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Advanced Bruker instruments operating at 400 MHz and 100 MHz respectively in DMSO-*d*<sub>6</sub>. Chemical shifts are reported in δ ppm. HRMS data were obtained on a Varian IonSpec QFT-MS spectrometer using electrospray ionization technique.

### 6.10.2 Typical procedure for the synthesis of dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidones

In a dry 50 mL round bottom flask, a mixture of aryl aldehyde (**1**, 1 mmol), phenyl hydrazine (**2**, 1 mmol), ethyl acetoacetate (**3**, 1 mmol), barbituric acid (**4**, 1 mmol), and ethyl lactate (5 mL) were mixed and then stirred at 25 °C. After completion of the reaction (TLC), water (5 mL) was added. Ethyl lactate dissolves in water and the insoluble crude products were isolated by simple filtration. The crude products were then dissolved in ethanol and were allowed to stand at room temperature. The crystalline solids were collected and dried.

The filtrate containing ethyl lactate was extracted with diethyl ether (2×5 mL) to remove any organic compounds dissolved in the aqueous phase. The aqueous layer was separated and the water was evaporated under reduced pressure to give pure ethyl lactate which was used for the next run under similar reaction conditions.

## 6.11 Conclusions

We have developed an efficient and a clean method for the preparation of fourteen novel dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidones *via* a one-pot four-component cyclo condensation reaction in ethyl lactate at 25 °C. The recyclable solvent improves both the environmental impact and the economic profile of the present method when compared to the conventional protocols. The presented method has numerous advantages such as the use of ethyl

lactate as a “green” reaction medium, high yield, shorter reaction durations, milder reaction condition, and catalyst-free and simple workup procedure.

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## Appendix

### Spectral data

#### **3-methyl-1,4-diphenyl-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine-5,7(1*H*,4*H*)-dione (5a):**

Yellowish powder; m.p209–210 °C;

IR (v cm<sup>-1</sup>):3240, 3051, 2986, 1658, 1610, 1592, 1129;

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ2.35 (s, 3H, -CH<sub>3</sub>), 5.18 (s, 1H, -CH), 7.16–7.72 (m, 10H, Ar-H), 9.54 (s, 1H, -NH), 10.48 (s, 1H, -NH) ppm;

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 11.5, 31.5, 80.7, 119.0, 121.1, 123.0, 124.2, 127.7, 129.2, 129.7, 137.8, 145.7, 146.8, 149.9, 153.9, 154.8, 168.7 ppm;

HRMS (ESI): *m/z* [M + H]<sup>+</sup>calcd for C<sub>21</sub>H<sub>17</sub>N<sub>4</sub>O<sub>3</sub> 373.1301, found 373.1304.

#### **3-methyl-4-(4-nitrophenyl)-1-phenyl-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine-5,7(1*H*,4*H*)-dione (5b):**

Brownish powder; m.p246–247 °C;

IR (v cm<sup>-1</sup>): 3230, 3153, 3027, 2938, 1670, 1528, 1589, 1330;

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ2.31 (s, 3H, -CH<sub>3</sub>), 5.59 (s, 1H, -CH), 7.34–8.13 (m, 9H, Ar-H), 10.59 (s, 1H, -NH), 12.50 (s, 1H, -NH) ppm;

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 13.4, 32.1, 86.7, 119.4, 120.5, 122.2, 123.1, 125.6, 128.9, 136.0, 145.0, 146.2, 148.5, 149.9, 152.6, 154.3, 166.4 ppm;

HRMS (ESI): *m/z* [M + H]<sup>+</sup>calcd for C<sub>21</sub>H<sub>16</sub>N<sub>5</sub>O<sub>5</sub> 418.1151, found 418.1150.

#### **3-methyl-4-(3-nitrophenyl)-1-phenyl-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine-5,7(1*H*,4*H*)-dione (5c):**

Dark yellow powder; m.p 220–221 °C;

IR (v cm<sup>-1</sup>): 3128, 3115, 3040, 2926, 1657, 1579, 1570, 1327;

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 2.29 (s, 3H, -CH<sub>3</sub>), 5.42 (s, 1H, -CH), 7.14–8.13 (m, 9H, Ar-H), 10.40 (s, 1H, -NH), 13.10 (s, 1H, -NH) ppm;

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 13.4, 32.1, 87.3, 119.3, 120.5, 121.5, 123.1, 125.6, 129.0, 134.6, 137.3, 146.2, 147.9, 148.1, 150.2, 152.6, 154.2, 166.5 ppm;

HRMS (ESI): *m/z* [M + H]<sup>+</sup>calcd for C<sub>21</sub>H<sub>16</sub>N<sub>5</sub>O<sub>5</sub> 418.1151, found 418.1149.



**4-(3,4-dimethoxyphenyl)-3-methyl-1-phenyl-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine-5,7(1*H*,4*H*)-dione (5d):**

Yellowish powder; m.p216–217 °C;

IR ( $\nu$   $\text{cm}^{-1}$ ): 3211, 2930, 1680, 1615, 1538, 1516, 1427, 1138;

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  2.29 (s, 3H,  $-\text{CH}_3$ ), 3.58 (s, 3H,  $-\text{OCH}_3$ ), 3.79 (s, 3H,  $-\text{OCH}_3$ ), 5.03 (s, 1H,  $-\text{CH}$ ), 6.99–7.71 (m, 8H, Ar-H), 9.99 (s, 1H,  $-\text{NH}$ ), 12.05 (s, 1H,  $-\text{NH}$ ) ppm;

$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  12.7, 35.0, 55.9, 110.3, 111.4, 119.2, 122.8, 123.4, 126.5, 129.5, 130.2, 136.5, 144.7, 145.8, 149.5, 150.7, 153.6, 154.6, 167.2 ppm;

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{20}\text{N}_4\text{O}_5$  433.1512, found 433.1510.

**3-methyl-1-phenyl-4-(3,4,5-trimethoxyphenyl)-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine-5,7(1*H*,4*H*)-dione (5e):**

Yellowish powder; m.p211–212 °C;

IR ( $\nu$   $\text{cm}^{-1}$ ): 3244, 2942, 1680, 1620, 1590, 1501, 1411, 1146;

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  2.08 (s, 3H,  $-\text{CH}_3$ ), 3.52 (s, 3H,  $-\text{OCH}_3$ ), 3.69 (s, 6H,  $-\text{OCH}_3$ ), 5.18 (s, 1H,  $-\text{CH}$ ), 7.24–7.46 (m, 7H, Ar-H), 11.37 (s, 1H,  $-\text{NH}$ ), 13.92 (s, 1H,  $-\text{NH}$ ) ppm;

$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  13.9, 32.7, 55.8, 59.6, 87.0, 103.3, 119.5, 122.0, 125.1, 128.5, 132.2, 134.4, 137.3, 146.9, 150.7, 154.3, 156.4, 157.6, 168.4 ppm;

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{23}\text{N}_4\text{O}_6$  463.1618, found 463.1615.

**3-methyl-1-phenyl-4-(*p*-tolyl)-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine-5,7(1*H*,4*H*)-dione (5f):**

Dark yellowish powder; m.p230–231 °C;

IR ( $\nu$   $\text{cm}^{-1}$ ): 3147, 3028, 2927, 1655, 1580, 1519, 1350;

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  2.18 (s, 3H,  $-\text{CH}_3$ ), 2.31 (s, 3H,  $-\text{CH}_3$ ), 5.19 (s, 1H,  $-\text{CH}$ ), 6.90–7.71 (m, 9H, Ar-H), 11.63 (s, 1H,  $-\text{NH}$ ), 13.90 (s, 1H,  $-\text{NH}$ ) ppm;

$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  14.0, 24.3, 31.6, 85.6, 87.0, 119.5, 121.9, 125.3, 128.5, 129.7, 130.8, 134.3, 137.6, 138.2, 146.3, 151.8, 152.6, 157.6, 166.3 ppm;

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{19}\text{N}_4\text{O}_3$  387.1457, found 387.1460.

**4-(4-hydroxyphenyl)-3-methyl-1-phenyl-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine-5,7(1*H*,4*H*)-dione (5g):**

Dark yellowish powder; m.p 247–248 °C;

IR ( $\nu$   $\text{cm}^{-1}$ ): 3141, 3046, 2908, 1658, 1521, 1542, 1368;

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.20 (s, 3H,  $-\text{CH}_3$ ), 5.18 (s, 1H,  $-\text{CH}$ ), 6.68–7.72 (m, 9H, Ar-H), 10.48 (s, 1H,  $-\text{OH}$ ), 11.34 (s, 1H,  $-\text{NH}$ ), 13.67 (s, 1H,  $-\text{NH}$ ) ppm;

$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  33.1, 13.2, 88.4, 113.8, 119.8, 122.4, 123.5, 125.1, 126.5, 28.5, 129.0, 137.3, 145.1, 150.5, 155.6, 156.3, 167.7 ppm;

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{17}\text{N}_4\text{O}_4$  389.1250, found 389.1253.

**4-(2-hydroxy-4-methoxyphenyl)-3-methyl-1-phenyl-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine-5,7(1*H*,4*H*)-dione (5h):**

Yellow powder; m.p 219–220 °C;

IR ( $\nu$   $\text{cm}^{-1}$ ): 3165, 3032, 2901, 1664, 1510, 1500, 1361;

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.25 (s, 3H,  $-\text{CH}_3$ ), 3.78 (s, 3H,  $-\text{OCH}_3$ ), 5.25 (s, 1H,  $-\text{CH}$ ), 6.43–7.76 (m, 8H, Ar-H), 9.76 (s, 1H,  $-\text{OH}$ ), 10.86 (s, 1H,  $-\text{NH}$ ), 11.92 (s, 1H,  $-\text{NH}$ ) ppm;

$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  12.4, 23.0, 84.6, 60.1, 103.1, 105.7, 106.3, 118.3, 119.5, 126.8, 128.1, 129.4, 130.8, 139.1, 147.5, 150.0, 156.7, 157.2, 158.1, 167.8 ppm;

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{19}\text{N}_4\text{O}_5$  419.1355, found 419.1352.

**4-(3,5-dichloro-2-hydroxyphenyl)-3-methyl-1-phenyl-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine-5,7(1*H*,4*H*)-dione (5i):**

Yellowish powder; m.p 219–220 °C;

IR ( $\nu$   $\text{cm}^{-1}$ ): 3138, 3068, 2932, 1643, 1509, 1512, 1323;

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.19 (s, 3H,  $-\text{CH}_3$ ), 5.32 (s, 1H,  $-\text{CH}$ ), 6.66–7.77 (m, 7H, Ar-H), 10.91 (s, 1H,  $-\text{NH}$ ), 11.87 (s, 1H,  $-\text{NH}$ ) ppm;

$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  14.8, 23.5, 32.3, 86.5, 117.1, 119.5, 120.7, 125.2, 127.7, 128.3, 128.8, 130.3, 140.5, 145.2, 149.5, 150.2, 156.3, 167.5 ppm;

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{15}\text{Cl}_2\text{N}_4\text{O}_4$  457.0470, found 457.0473.

**4-(4-chlorophenyl)-3-methyl-1-phenyl-6,8-dihydropyrazolo[4',3':5,6]pyrano[2,3-*d*]pyrimidine-5,7(1*H*,4*H*)-dione (5j):**

Yellowish powder; m.p 224–225 °C;

IR ( $\nu$   $\text{cm}^{-1}$ ): 3149, 3576, 2925, 1697, 1569, 1515, 1313;

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.25 (s, 3H,  $-\text{CH}_3$ ), 5.28 (s, 1H,  $-\text{CH}$ ), 7.05–7.37 (m, 9H, Ar-H), 12.27 (s, 1H,  $-\text{NH}$ ), 13.52 (s, 1H,  $-\text{NH}$ ) ppm;

$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  14.1, 17.7, 33.6, 81.7, 118.5, 120.1, 124.8, 127.5, 128.9, 130.3, 130.8, 133.6, 136.8, 140.3, 146.3, 149.7, 153.8, 167.2 ppm;

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{16}\text{ClN}_4\text{O}_3$  407.0911, found 407.0914.

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Santhosh Govindaraju <sup>a</sup>, Sumaiya Tabassum <sup>b</sup>

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- 86. Marriage as misalliance in Jaishree Misra's Ancient Promises**  
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## **01. The 21st Century Pedagogical Practices of English Language Teachers**

**Dr. Malini Ganapathy**, School of Languages, Literacies and Translation,  
Universiti Sains Malaysia, 11800, Penang, Malaysia

In the context of English Language education in the 21st century, teachers today must be prepared to change according to innovative teaching pedagogies, and effectively teach by utilising technology. The study aims to gauge the level of knowledge of in-service teachers regarding 21st century pedagogical skills, and the types of skills in-service teachers use when teaching. The quantitative study employed a questionnaire to gather data from 70 experienced English teachers from schools in Klang Valley, Malaysia. Results show that in-service teachers are generally well-informed of the knowledge and practices of 21st Century Pedagogy Skills. Teachers are aware that technologies have a hand in engaging students' learning, but they are not practicing the integration of technology sufficiently for optimum benefit in the classroom. Thus, teachers have to be more proactive in practicing the relevant 21st century pedagogical skills. This study suggests further research on the reasons as to why teachers are not in the habit of practicing the relevant 21st Century Pedagogical skills despite having sufficient knowledge.

**Keywords:** 21<sup>st</sup> Century Pedagogy; technology; English Language Education; Teachers

## **02. The Implementation of Professional Development in Indonesian Classroom Teaching Practice**

**Dr. Muhammad Jafar**, Universitas Muhammadiyah Bone, South Sulawesi,  
Indonesia

This paper reveals the teachers' implementation on the professional development of EFL teachers in Indonesian EFL classroom. It has three kinds of procedure of collecting data, namely (1) observation and field note, (2) Interview, and (3) document analysis to collect data on the teachers' Implementation towards the professional development of EFL teachers within three research subjects of the Indonesian Junior High School context. Research result reveal that there were the real differences in the way of the

Junior High Schoolteachers' implementation on the professional development in Indonesian EFL classroom and these differences influence the practices of using the professional development in the EFL classroom context. The combine of the teachers' attitude toward the professional development and their classroom teaching practices acquire to the three categories of the Junior High Schoolteachers such as: (1) Highly Implemented Professional Development (HIPD); (2) Moderate Implemented Professional Development (MIPD); and (3) Low Implemented Professional Development (LIPD). What is evident is that the more positive response of the teachers toward the Professional Development, the better the implemented they have in Indonesian EFL classroom. This research has attempted to expand on scientific understanding of EFL teachers' professional development in Indonesian Junior High school.

**Keywords:** Professional Development, Competence, Junior High School

### **03. Ensuring Holistic, integrated and Inclusive Learning in 21st Century: Building Meaningful Implementation Mechanism of NEP-2020**

**Dr. J N Baliya**, Head, Department of Educational Studies Central University of Jammu

Education is the key weapon which we can use to change the world has been rightly remarked by Nelson Mandela as it helps in providing various tools which will improve the quality of life in modern society both sociologically as well as economically. New Policy on Education-2020 is a first educational policy of 21st century which actually aimed to ensure inclusive and equitable quality education in order to promote lifelong learning opportunities for all learners at school level and at higher education level. With the changing world, it can become enormously important that children not only learn the things, but more importantly they will learn how to learn, think critically and rationally so that education will more become useful and fulfilling to the learners in the real-life situations. Thus, NEP appears to be providing direction for holistic, integrated, comprehensive and all-inclusive high-quality education without neglecting 21st century skills, value system and man making life skills activity. It is acclaimed as that this NEP-20 is for the 21st century and to bring much needed reform that Indian

education system has been waiting for the last 34 years. But we all know that the recommendations of any policies and commissions will have its relevance if it can be implemented properly with good plan of action. This paper actually focused on the various implementation strategies to be adopted a by NEP 2020 at different levels of education in order to make the policy more relevant. Some of the implementation strategies of NEP include launching of PARAKH portal, Standard Setting Accreditation, States and UTs also constitute their own task force to steer implementation of the NEP provisions in their respective jurisdiction, reforming in teacher education as well as in school curriculum framework etc.

#### **04. Introducing Soft Skills in Vocational Education: A Step to Increase Employability in Traditional Manual Working Areas?**

**Daniela Lacramioara (Clara) Moraru**, Educator, Strategist, International Consultant, Luxembourg, Europe

The transformation of the workplace has been accelerated by the continuous digitalization, by societal changes and recently by the COVID-19 pandemic. These changes imply completely new challenges for the field of tertiary vocational education and training. Since the share of employment in low-wage occupations may decline by 2030 for the first time, the problem that compels this research is a perceived gap between the skills required by the employers who now hire traditional manual workers and the actual skills these workers have, and a crucial need for a pedagogical transformation in the teaching and learning practices used by the vocational training institutes from Luxembourg, which suggested this research, to adequately train workers to meet those needs.

The Osnabrück Declaration on vocational education and training (2020) highlights the urgent need to transform traditional pedagogical practices in order to prepare students with the breadth of skills needed for the future: “We are currently witnessing an increase in labor market needs for a different mix of skills and qualifications as well as structural changes in the VET landscape.” To close the identified skills gap between education and the workforce, and thereby helping the state stay competitive in the global market and economy, Luxembourg’s vocational training institutes take a novel approach to prepare the traditional manual labour profiles for the

workplace. In this context, in addition to technical skills, which are no longer enough for workers to compete in this highly competitive global work environment, they start teaching within their curricula social skills (communication, conflict management, team work and negotiation), personal skills (leadership, self-evaluation, adaptability and flexibility) and methodological skills (learning to learn, analytical skills, creativity and innovation, problem solving), generally called soft skills and sometimes employability skills. They endeavour to bring these skills to the level needed for finding and maintaining employment, as well as to managing a successful career in the chosen field on the long term. Given the difficulties to improve soft skills in general, all the more if geared specifically to increase career opportunities, such a change deserves a closer scientific look.

The research sets out to accompany the effort undertaken by the training institution over 18 months. It will critically assess the opportunities and risks associated with the new training approach. It will also determine if and to which extent there is an interdependence between the impact, the new training measures have on the social skills of the candidates and their readiness for the labour market.

Finally, it will give all actors involved in this process (training and work place) a voice with respect to their positions and their own diverse histories.

## **05. COVID-19: Adapting to a New Norm in Malaysian Education,**

**Dr. A S A Ferdous Alam**, Assistant Professor, School of International Studies, Universiti Utara Malaysia (UUM), Sintok, Kedah, Malaysia

The recent Corona Virus Disease 2019 (Covid-19) outbreak has had a global impact on society, especially in the areas of social sciences and behavioural aspects. Despite the virus's alarming rate of spread, new vaccinations and therapies are still being tested in clinical trials. As a result, social distancing will be the most appropriate method for dealing with this situation. Throughout this debate on the adaptation of Covid-19 on virtual education in the context of the Malaysian education system, the various issues and problems and the pending solutions due to the pandemic were emphasized. In this research paper on the adaptation of Covid-19 in Malaysia, the results on teaching and learning from home, using technical innovation, group work, and preparedness in education, government

alternatives, internet connectivity, and the student evaluation process were highlighted.

**Keywords:** Covid-19, Malaysian Education, Teaching, Learning

## **o6. The Method of Learning Sacred Text in Islamic Boarding School (Case Study at Madura Island Indonesia)**

**Dr. Umar Bukhory, M. Ag**, Senior Lecturer, State Islamic Institute of Madura, Indonesia

Most materials of Islamic Studies inside Islamic Boarding School (Pesantren), especially in Madura Island are learned by the students as the Sacred Text because of its closed relationship with their religiosity (Islamic) experiences. This study would like to understand how was the students learn these materials inside several Islamic Boarding Schools in Madura Island Indonesia and how those methods applied in their daily learning activity. Using participatory observation and dept interview, this research shows that there are about three methods used by the student to learn the materials of Islamic Studies inside Pesantren: a) Learning through Teachers, b) The Strategy of I'lan, and c) Autodidact (Self-Learning). There are two techniques to apply the three methods above, containing: a) The I'lan with understanding the materials or not understanding it yet, and b) the Studies with understanding the materials. Both techniques have different characteristics. The first technique is based on teacher guidance, depends entirely on the text, and made memorizing the prime goal of learning. But the second technique is also based on teacher guidance which the prime goal is to understand the materials.

## **o7. Right to Education in the Midst of Pandemic**

**Cris T. Zita**, Head of the English Department

**Dr. Juan A. Pastor MNHS**, Department of Education

The vision of the UN is to transform lives through education, recognizing the important role of education as a main driver of development and in achieving the other proposed SDGs. UN is committed with a sense of



urgency to a single, renewed education agenda that is holistic, ambitious and aspirational, leaving no one behind. This new vision is fully captured by the proposed SDG 4 'Ensure inclusive and equitable quality education and promote lifelong learning opportunities for all' and its corresponding targets. It is transformative and universal, attends to the 'unfinished business' of the EFA agenda and the education-related MDGs, and addresses global and national education challenges. (2030 UN Incheon Declaration)

The whole world was shocked by this global pandemic brought by the COVID-19. This greatly affected the sector of education and brings chaos on how and why education should continue. In line with this, Flexible Learning Options were provided by some education specialists in order to pursue learning despite pandemic. Flexible Learning Options is defined as the alternative ways provided for learners who are identified as Students-At-Risk-of-Failing and Students-At-Risk-of-Dropping and for those who are not able to engage with mainstream schooling like over-aged and working individuals, and those who have financial challenges and family concerns. The following are the Forms of Flexible Learning Options: E-Learning, Blended Learning, Computer-assisted Learning, Computer-managed Instruction, Distance Learning, Independent Learning, Mobile Learning, Multimedia Learning, Online Learning, Open Learning, Resource-based Learning, and Virtual Learning. These forms of flexible learning coupled with technology will open opportunities to make learning a continuous process despite pandemic. Furthermore, there are Four Types of Distance Learning that will have a positive impact on the learners and teachers such as MODULAR DISTANCE LEARNING, ONLINE DISTANCE LEARNING, TV-BASED INSTRUCTION/RADIO-BASED INSTRUCTION and BLENDED DISTANCE LEARNING. Lastly, eLearning Platforms / Mediums that can be used for online classes are also available to help make all digital and technology based learning possible and these are Edmodo, Quipper, Microsoft Office 365 / Microsoft Teams, Google Classroom and Google Meet, Flipgrid, Zoom and Facebook Messenger Rooms. With all these possibilities and opportunities, education should not stop but rather level up using and partnering with technology to be a highly digitize citizens.

## **o8. Development of Indonesian Local Language Learning Materials in a Multilingual Teaching Model**

**Saidna Zulfiqar Bin Tahir**, Director of Research and Community Service  
Institution of Universitas Iqra Buru, Maluku, Indonesia

The death of local languages in Maluku without a proper burial is a tragic incident for this nation who proud of the richness of regional languages as an identity and national asset. 31 out of 726 local languages in Indonesia have become extinct, and 240 others are threatened with extinction should have made the government aware of protecting, conserving and empowering them in learning in schools and colleges, not only a paper of laws and regulations that have uncertain implementation. So this research tries to empower local languages by developing materials (syllabus, lesson plans, and textbook) local language learning in a multilingual model for digital natives in Buru regency. This study employed a research and development (R&D) approach using the ADDIE model design where the researcher analyzed the situation and needs of students in local language learning and designed and developed local language learning materials in a multilingual learning model. Thus, it is more easily absorbed by learners and make more efficient with teachers who have multilingual skills, and implement products that have been developed on a small, medium and large scale in 6 elementary schools in the city of Namlea, then applied the results of product implementation to be widely disseminated. The study results found the appropriate material model for local language learning in Maluku and effective learning materials for introducing and preserving local languages as regional identities and assets.

**Keywords:** Local Languages, Material, Multilingual, Learning Model

## **o9. Assessing Prospects of Sustainable Development for Education in Bangladesh: Global Education Perspectives**

**Md. Amir Hossain**, Assistant Professor, Department of English, IBAIS  
University, Bangladesh

This study would like to influence the dynamic aspects of globalization policy and practice on Bangladesh education system to foster teacher and

student performance, learning and teaching strategies, curriculum, syllabus design, and lesson plan. The study offers a novel meta-model for education, a core element of society, and the foundation of democratic choice. The failure and prosperity of a country primarily rely upon education policy and practice. In this sense, education must be age-oriented to fulfill the demand of the younger community. The younger community can benefit from world education if they are endowed with practical knowledge, conversant skill, and the capability and rights needed to pursue their basic human needs. For this purpose, the study would like to examine the conceptual shifts from third-world educational pedagogy to the sustainable development of Bangladesh to global education policy and practice. It seeks the vital role of international education in bringing about an epoch-making change in Bangladesh education system. Data would be collected from libraries, where books, journals, monographs, theses, reports, letters, articles, newspapers, magazines, and above all, internet sources would be readily available or accessible. Finally, the study aims to focus on the dynamic change of sustainable development for education by comparing the global education system.

**Keywords:** Sustainable Development, Bangladesh Education System, Global Education Policy

## **10. Plagiarism as a kind of Academic Misconduct: Reasons and Guidelines to avoid it**

**Dr. Azadeh Nemati**, Assistant Professor, Department of English Language Teaching, Jahrom Branch, Islamic Azad University, Jahrom, Iran

Academic misconduct has become widespread in the university as a result; the way of responding to this issue is of great importance. Plagiarism is a kind of academic misconduct that can take many forms and may be intentional or unintentional. In this presentation the researcher will talk about academic misconduct as opposed to academic integrity. Also different types of plagiarism will be introduced as a kind of academic misconduct. Furthermore common reasons of plagiarism will be discussed and some ways of avoiding plagiarism will be introduced.

## 11. Teaching and Learning for 21<sup>st</sup> century world

**R Vivekanantharasa**, Lecturer, Department of Secondary and Tertiary Education, Faculty of Education, The Open University of Sri Lanka, Sri Lanka

**“Technology will not replace great teachers but technology in the hands of great teachers can be transformational”** is a famous quote from the eminent teaching, learning, and leadership consultant and speaker: George Couros. According to this, the concept of digital transformation in education is broadened in every nook and corner of the world. Twenty first century world is in information age. The necessity of seeking information is broadened among people. In accordance with that, people manipulate technology in seeking information in various ways. There is no contradiction in accepting that the education for 21<sup>st</sup> century is fully technology integrated. Accordingly, teaching and learning process for this 21<sup>st</sup> century information world has been changed in various ways due to the current COVID-19 pandemic situation across the world. All education systems are moving forward to digital transformation, especially including teaching, and learning process. In which ways teaching and learning process have been transformed and as educators how do we have to adopt them in our methods when we engaged in pedagogy. We have move forwarded from the traditional approach to the digital transformation of teaching and learning. As a result, the digital transformation in teaching and learning happens in different ways, such as blended method of teaching and learning, hybrid method, and Google classroom. How this each digital transformation technique and the expansion of it are accentuated in 21<sup>st</sup> century. Not only school education system, but all other education systems are also under this digital transformation.

**Keywords:** Digital Transformation, Blended Teaching, Hybrid Teaching, Google Classroom

## **12. English as Language a Link Language for Teaching Purpose in India: A Study in Brief**

**Dr Manpreet Kaur**, Astd. Prof in English, GCW Parade, Jammu

Language is an expression of human personality. It is a tool for communication. Edmund Spenser was the pioneer who revealed the poetic beauty of English language through his exceptional pieces of literature like 'Faerie Queene' and 'Shepherd's Calendar'. In India, English language teaching in our educational institutions has taken a special significance. In India, English is the link language, serving to connect the people of various regions and diverse backgrounds. It is the Lingua Franca of the people from the South, North, East and West of India. It is the official language among the central and state governments. In a country like India with enormous diversity of population, the number of languages being spoken here is equally mind boggling. Different languages are spoken in different regions. Under such circumstances, communication would have been impossible; the legacy of the English rulers has succeeded in uniting us after attaining independence.

**Keywords:** Language, Communication, English, Diverse, Connect.

## **13. Educational Games as a Learning Method**

**Dr. Jugnu Khatter Bhatia**, Principal, Satyug Darshan Institute of Education and Research, Faridabad, Haryana, India

Game-based learning is a teaching-learning method that allows learners to explore different parts of games as a form of learning. Games can be designed by educators and other education specialists in a way that balances academic subjects such as history with the strategies, rules and social aspects of playing a game. Due to technological growth, game-based learning may generate negative connotations because of its close association with video games, which inevitably raises questions about its consequences. However, these games are typically designed at different ability levels according to levels of learners and with the aim of helping the learners to retain the information that they learn and apply it to other similar nature problem-solving situations. Many of these educational games are relevant to

real life situations and will help learners to make informed decisions when doing so matters. Game-based learning can also be done as a collaboration between learners and educators. This type of educational game creation enhances the playing experience and can lead to a depth and scope of game that are not available through other types of learning experiences.

**Keywords:** Educational games, Interactive learning, Active participation, Teaching strategy, Game-based learning

#### **14. Literature Online: Effective Teaching at a Distance in College Level with Technology**

**Dr. A Karthika Unnithan**, Guest Lecturer in English, Department of English, Sree Vivekananda College, Kunnankulam, Thrissur, Kerala, India

The teaching of literature poses significant challenges when transferred from face-to-face to a distance learning setting. Focusing on a wide variety of contexts, considerations to this paper bring to the fore some of the main difficulties of teaching literature at a distance. These are blended around 3 major angles, which are mirrored in the three sections of the paper. They are 1) curricula or genre-specific pedagogies in virtual literature classrooms 2) Specific digital applications and online resources in literary studies and 3) positive estimate of the potential of the still new platforms for virtual teaching in literature during the Covid pandemic time. One of the main limitations of the following study is that it is mainly focussing on the contextual setting of Indian scenario. As schools and colleges across India, embrace online learning during Covid pandemic period, critics prefer to portray Internet as the killer of direct and conscientious learning. This concurs with the American literary critic J. Hillis Miller's maxim in his article "Literary Study Among the Ruins" in the journal *Diacritics* that "If you are watching a movie or television or playing a computer game or surfing the Internet, you cannot at the same time be reading Shakespeare. People spend, all the statistical evidence suggests, more and more time doing the former." (Johns Hopkins University Press, Volume 31, Number 3, Fall 2001, pp. 57-66) Thus, when learning environments are not in the traditional classroom context they must compete with digitally generated distractions. Any study that claims to aid in the study of literature online should answer these concerns. Overall, this study would indicate that teachers of literature have

reason to be enthusiastic about the potential for their (often text-based) subject in online learning.

**Keywords:** Interactive Teaching, Online Learning, Virtual Literature Classroom, Pedagogy, Digital Literature Resources

### **15. Virtual Training- A Way Forward for In-service Teachers**

**Dr. M M Roy**, Assistant Professors, DIET Ghumanhera, SCERT Delhi

**Dr. Meena Sehrawat**, Assistant Professors, DIET Ghumanhera, SCERT  
Delhi

The outbreak of pandemic Covid-19 has affected every sphere of life; education is no exception to it. With this a sudden shift has taken place and that is the adoption of online teaching learning. Teachers are adopting and adapting various means that they have never tried before. Being in the profession of teaching and to deal with children it becomes mandatory for every teacher to refresh and apprise themselves with latest developments. To meet the growing needs of online education in the state it becomes imperative to provide sound in-service education for teachers to update their skills, knowledge for handling online teaching. SCERT, Delhi has taken a new initiative towards In-service programmes and capacity building through- Virtual training. It is a valuable way for teachers to obtain new and continuing training especially during Covid times where they have to use various platforms to reach and teach their students. This training involved a variety of multimedia elements including info graphics, audio, video, and web links which could not be accessed in the normal classroom training programmes. The analysis showed that the teachers were satisfied with the topics covered in the training. They were likely to use the teaching methodology, strategies, videos and other resources given in the modules during their teaching learning process. They were very much satisfied with the academic and technical support provided by the team as and when required. Majority of the teachers recommended such trainings to their fellow teachers.

**Keywords:** Capacity building, In-service Education, Virtual training and Way Forward

## **16. Understand the Role of Re-designing Strategic Human Resource Management (SHRM) Practices for Fostering Entrepreneurial Sustainability**

**Dr. Pooja**, Assistant Professor, Government SPMR College of Commerce

**Dr. Renu Bala**, Assistant Professor, Government College for Women,  
Parade

**Rakesh Sharma**, Research scholar, Lovely Professional University, Jalandhar

Workplace practices and Strategic Human Resource Management (SHRM) has become a key in re-examining and revising how jobs and its processes fit together to gain efficiency and employee productivity. The objective of this paper is to understand the policy framework for strategic management and development of human resource management (HRM) that have surfaced in the SME located in the Battal Ballian Industrial Estate of District Udhampur, J&K State. Besides, the study also explores the various labour management problems namely: labour turnover, seasonal non-availability, shortage of skilled and unskilled labour, strikes and high rate of absenteeism, competitors take away and low productivity. Further, the role of education, age and experience in solving labour-related problems has been investigated. Based on the extant literature and the nature of problems and relationship investigated in this study, the study proposed that the following SHRM practices such as flexible hours, part-time and temporary work, incorporation of piece rate wage system, enhanced bonus, introduction of Employee Provident Fund Scheme, continuous training & counselling and contracting to freelance contractors, e.g. specialists etc., are useful to enhanced smooth and consistent business operations and yielded better efficiency and productivity. Further, the study argued that Flexible Work Arrangements (FWAs) and Qualitative Flexibility (QF) will enable each individual to be well trained, have diverse skills and strong motivation towards their work.

**Keywords:** Productivity; Flexible Work Arrangements (FWAs); Qualitative Flexibility (QF), Strategic Human Resource Management (SHRM) Practices; Industrial Relations; Performance; Efficiency.



## **17. English for Employability: Need of English Language Training for Engineering Graduates in India**

**Dr. Pritam I. Thakur**, Assistant Professor in English, Vidya Pratishthan,  
Indapur, Pune

The article analyzes the practicality of English language offered in the designing universities in India. Many designing alumni in India are discovered to be unemployable because of their deserted interpersonal abilities and absence of confidence. There have been a great deal of examination papers that have repeated the significance of improving designing alumni's employability abilities; nonetheless, the issue of helpless relational abilities becomes persistent in India. This study has basically led to comprehend the truth in English homerooms of designing universities to unwind the secret behind the lackluster showing of many designing alumni in India. It has been distinguished that numerous third year understudies are as yet inadequate with regards to certainty to confront their grounds arrangements that are to happen in their last year of study. In addition, it has been tracked down that the techniques of employees should be upgraded as huge number of understudies needs more intelligent meetings to improve their language abilities. The study results have shown proof of shack between the English teachers' philosophy and designing understudies' certainty levels and furthermore highlight the significance of reasonable preparing programs needed for designing understudies.

**Keywords:** CLT, ESP, employability, communication skills, teaching methodologies, etc.

## **18. Female Participation in India's Higher Education**

**Dr. Rajni Pathania**, Assistant Professor, The Maharaja Sayajirao University  
of Baroda, Gujarat

The present study seeks to investigate and analyze women's participation in higher education in India. This study is based on secondary data gathered from various issues of AISHE and other published reports of the Government. The results of this study reveal that the enrolment of women students in higher education has increased; it means the Indian

Economy has been able to deal with inequalities in higher education. Further results also indicate that more females are seeking enrolment in traditional courses like Master in arts, commerce, nursing, library science, Physiotherapy, architecture, fashion management, and hospital administration. On the other hand enrolment of females in professional courses like law, computer and business administration still have lower enrolment rate than males. Since the positive policy adopted by the central government like scholarship schemes and fee concessions for women, the participation of women in higher education is constantly increasing.

**Keywords:** Participation, Inequalities, Enrolment, Scholarship, Fee concession

### **19. Impact of Employee Retention Strategies on Employee Productivity**

**Dr. Renu Bala**, *Assistant Professor, Government College for Women, Parade, UT of Jammu and Kashmir, India*

**Mr. Rajesh Bhardwaj**, *Assistant Professor, Government Gandhi Memorial Science College, UT of Jammu and Kashmir, India*

**Purpose:** Employee retention strategies play an important role in an organization to enhance employee productivity. The purpose of this study is to identify the various employee retention strategies that can increase employee retention rate and also understand the role of employee retention strategies on employee productivity.

**Approach:** A model is proposed that illustrates the various employees retention strategies like employee empowerment, employee training, job security, employee motivation and employee-employers relationship that affects employee retention rate in an organization and also demonstrates the relationship between employee retention strategies and employees performances.

**Findings:** The study argued that employee retention strategies such as employee empowerment, employee training, job security, employee motivation and employee-employers relationship are essential for an organization to enhance employee retention rate and increase employee performance.

**Implications:** The theoretical framework of this study would encourage the company to constitute their employees as an important resource as they are difficult to retain and costly to acquire. The study would also help to examine the impact of employee retention in an organization.

**Limitations:** The study being conceptual in nature requires empirical research to measure and assess the impact of all suggested employee retention strategies on employee retention and employee productivity.

**Keywords:** *Employee retention, employee participation, employee motivation, job security, employee training, employee-employers relationship, work environment, employee productivity.*

## **20. Need for Digitalization in Higher Education in India**

**Dr. S Tephillah Vasantham**, Assistant Professor, Department of Business Administration, The American College, Madurai

Modernized advancement in India has been progressing all through the several years, changing the way in which under studies learn thoughts in school. The customary chalk and talk procedure has prepared for more canny preparing systems as schools are logically accepting progressed answers for keep themselves next to each other with the mechanical changes. As the current period of under studies is proficient with PCs, I-pads, and phones, these imaginative techniques for showing guarantee more collaboration from under studies. Nevertheless, usage of modernized progressions in establishments of high level training is at this point in its beginning phases and attempts are being made to change these advances to acclimate to the necessities of University under studies. Along these lines, content improvement is yet to create in schools and universities across India. India's dynamic economy with a blooming average workers and more than 200 million Internet customers has made the country the third greatest online market after China and the United States. With such a broad impact, there is potential for an extension in the use of cutting edge developments in the tutoring field. Regardless, shortfall of establishment, defenceless force access and low Internet entrance in the semi-metropolitan and common zones have held down headway of automated organizations in schools.

**Keywords:** Digital Education, Computerized Learning, Internet Learning, Customized Learning Approach And Redid Learning Approach.

## **21. Women's Rights in Education**

**Dr. Sunil S. Bidwaik**, Assistant Professor, Sharadrao Pawar Arts & Commerce College, Gadchandur, Chandrapur

Sustainable Development Goal 4 (SDG 4) is the educational goal. The Agenda is “*a plan of action for people, planet and prosperity*”. It aims to “*ensure inclusive and equitable quality education and promote lifelong learning opportunities for all*”, especially girls and women, by 2030. Several organizations are working to meet this goal through various strategies, from advocating to revise school curriculums and policies, to promoting equal access to technology in schools. UNICEF is prioritizing girls Secondary education initiatives that tackle discriminatory gender norms, and address menstrual hygiene management in schools. Education Cannot Wait, the world's first fund dedicated to education in crisis and conflict, is promoting safe learning environments, improving teachers' skills, and supporting gender responsive education programs.

Every woman, man, youth and child has the human right to education, training and information, and to other fundamental human rights dependent upon realization of the human right to education. Equality of access to all levels of education is crucial to empowering women and girls to participate in economic, social and political life of their societies. Education unlocks a woman's potential, and is accompanied by improvements in health, nutrition, and well-being of women and their families. Despite widespread agreement that all people have the fundamental human right to education, 100 million children, at least 60% of them girls, do not have access to primary education. 960 million adults in the world are illiterate, and more than two-thirds of them are women. Women and girls continue to face discrimination at all levels of education, a fact which poses tremendous obstacles to their advancement. Women, in a patriarchal society, have had a social disadvantage which has prevented them from accessing opportunities available to men more freely. Throughout history, women folk have had to go through certain social deficits and bear the weight of various expectations

which were quite different from the men folk. These norms more often than not led them to be at a position of disadvantage and led to a struggle. One such position was regarding their education in Indian society.

**Keywords:** Gender equality, Awareness, Human rights, Human capabilities, Sustainable Development.

## **22. University Students' Perceptions of Mobile Learning during COVID-19 Pandemic: A Case Study at Aligarh Muslim University**

**Dr. Uzma Siddiqui**, Assistant Professor, Department of Education, Aligarh Muslim University, Aligarh, Uttar Pradesh, India

The purpose of the present study was to measure the university students' perceptions of using mobile for learning during COVID-19 pandemic. The study was descriptive in nature. The sample was taken from six departments of Faculty of Social Sciences, Aligarh Muslim University and consisted of 300 students. Standardized questionnaire was administered for measuring their perceptions. The collected data were analyzed using descriptive and inferential statistics. The statistical results clearly indicated that most of the students have negative perceptions of mobile learning, although most of them agreed that mobile learning is helpful to cover the study gap to a certain extent during this COVID-19 pandemic time. Based on these findings, some pedagogical suggestions are being made that will help the educational institutions and teachers to enhance the teaching-learning process using mobile learning.

**Keywords:** Mobile Learning, University Students, Perceptions, COVID-19

## **23. Educational Games as a Learning Method with reference to English as a Second Language**

**Dr. Vishal A. Patel**, Empaneled Language Trainer, Finishing School, KCG, Gujarat, India

Today is the time of technology and innovations. Every now and then new machineries are invented to lessen the human efforts. Similar is the process in learning language. People are interested in simpler and more entertaining way of learning, which has prompted new methods and

approaches to be developed by the researchers. In this paper, the researcher intends to study the importance of educational games as a learning method with reference to English as a second language. It also focuses on the implementation of the same with different age groups and their response to it.

**Keywords:** English as a Second Language, Education, Learning Method, Games, Age-Groups

## **24. Flipped Classroom Teaching**

**Dr.Sonia Khajuria**, Associate Professor, Govt.College for Women, Parade Ground, Jammu (UT of Jammu and Kashmir), India

Flipped Classroom is a form of blended teaching-learning pedagogy. In Flipped Classroom teaching, the teacher focusses on the active learning of the students. Contrary to the traditional classroom teaching, Flipped Classroom gives more freedom to teachers to use their creativity in developing various outside- class and inside-class activities for students that promote learning and development of higher skills. In traditional classroom, students listen to teachers, follow other guided instructions and take notes whereas in Flipped Classroom students learn at home and in the classroom they solve problems or have discussions. Flipped Classroom teaching allows all students to learn at their own pace. Teachers create flexible spaces where students choose when and where they learn. Class time is used for active learning and learners are better nourished. Post-Covid pandemic, traditional classrooms will pave way for Flipped Classrooms.

**Keywords:** Flipped Classroom, Blended Learning, Outside-Class Activities, Inside-Class Active Learning, Problem Solving

## **25. Building a Learning Organization: Towards Developing more Holistic Teacher Education Institutions**

**Amlesh Kumar**, Research Scholar, RIE (NCERT), Bhubaneswar, Utkal University, Bhubaneswar

**Prof. B. N. Panda**, Dean (Research), RIE (NCERT), Bhubaneswar

The change is the only permanent thing in this world. Recent advancement in the field of teaching-learning practices forces every teacher education institutions to always keep changing and innovating. Teacher education institutions that are not capable to innovate and alter them will find themselves in trouble by facing increasingly tough competition from other institutions. The pressure caused by the constant need of innovation will force teacher education institutions to become a learning organisation. As we know learning organization is a philosophical thought given to an organization which facilitates the learning of all its members so that the organization can continuously transform itself. By building a Learning Organisation recent teaching-learning advancements can be adopted by the teacher education institutes. Through this the desired learning outcome and opportunity of institutional members to keep on learning will also enhanced. By applying the Learning Organisation structure in teacher education institutions the satisfaction of the every stakeholders will be increased. In the process of building up a learning organisation the administration, management, teachers and students have key role to play. Apart from that the transformative educational leadership is needed that is fully committed to building a learning organization towards developing more holistic teacher education institutions.

**Keywords:** Learning Organization, Holistic, Learning, Building, Teacher Education Institutions.

## 26. Education Quality

**Anita Kumari**, Principal (D.El.Ed.), Delhi College of Vocational Studies and Research, Baprola, Najafgarh, Delhi, India

In ancient period India was known as “World Guru”. Its reason was our quality of education and Indians were able to face the life’s problems successfully and lived happily. According to our ancient Vedas there are four purusharth of life – Religion (Dharma), Wealth (Artha), desire (Kaam) and Salvation (Mokshya). These gave us mantras for successful life. So that our aim of ancient education was to achieve salvation. For achieving this aim, Teacher taught the lesson from the real life situation and gave extra activities for practice the lesson. Thus students were learnt to face the problems of daily life. But at present we have lost our position of “World Guru” due to decreasing of education quality. At this time all round development of the personality is our aim of education, which is also, based on our four purusharth and curriculum as well as co-curricular activities our part of our education. However we are not able to achieve our aim of education and make balanced personality of the child. In this paper we will discuss about all these things.

**Keywords:** Education, Personality, All round development, Four purusharth, Quality education

## 27. Education as an Instrument of Modernization among Female Teachers

**Anu Salaria**, PhD Scholar, Department of Education, University of Jammu, Jammu & Kashmir, India

The study on which this paper is based was conducted to find out the impact of level of Education on Modernization among female teachers. A random sample of 200 female teachers teaching in government elementary, secondary and higher secondary schools was selected for data collection. The study involves level of education, locality and social caste as independent variables. Modernization scale developed by Singh, Tripathji and Lal (2012) was used to study the modernization among female teachers. The data was analyzed using mean, standard deviation



and t-test. Findings of the study revealed that female teachers have shown highest modernization on the dimension of 'Position of women' followed by 'Education', 'Marriage' and they have been found least modernized on socio-religious dimension. Significant differences have been found between graduate and post-graduate female teachers in general, between rural graduate and rural post-graduate female teachers, between urban graduate and urban post-graduate teachers and between graduate and post-graduate teachers of general category on different dimensions of modernization. Implications of these results are discussed for teachers, curriculum framers, educational administrators and policy framers in the paper.

**Keywords:** Impact, Level of Education, Modernization and Female Teachers

## **28. Role of Games and Activities as Educational Tools in Language Learning Classrooms**

**Asha Khurana**, Lecturer English, Directorate of Education, Delhi, India

Games and activities play a major role in language learning. They break the dull and cumbersome process of language learning into a fun filled and joyful learning experience. The researcher here carried out an action research with class 11 and 12 students who were 160 in number and spread into four groups. The researcher teaches English core of CBSE curriculum to class 11th and 12th grade. She interpreted her classroom lessons with various games and activities. These classroom practises generated a lot of enthusiasm and love for learning English language among the learners. This improved their speech, their answers and ultimately their CBSE class 12th grades. There are a plethora of games and activities that can be taken into language learning classrooms to teach the lessons. The only need is to align the same with the learning objectives set for the task in hand.

**Keywords:** Games and Activities, Joyful Learning, Learning Objectives

## 29. A Comparative Study of Therapeutic Therapists' and Special Educators' Teaching Aids

**Bhavana S**, Assistant Professor and HOD, Department of Psychology,  
Surana College

**Subramanya V**, Assistant Professor, Department of BBA, Surana College

In every classroom, teaching aids are an essential component. Helps learners develop reading comprehension skills, demonstrate or reinforce an idea, and relieve anxiety by introducing knowledge in a fresh and exciting way. In every way, teaching aids are inexpensive, easy to create, and can be improvised. The teaching aids are selected based on the learners' mental abilities for its effectiveness. In therapeutic approach, rewarding healthy habits and teaching new skills are used in counselling, both Parents and other caregivers are taught how to provide moment-by-moment guidance to special children. Play skills, learning techniques, and self-care are also the subject of OT services for people with learning disability. Thus in our present study we have obtained the responses from special educators and therapeutic practitioners in understanding the behavioural components of the children with special needs and learning disability. A comparative study is made to analyze and interpret the affectivity of their learning capacities by increasing knowledge needs through different teaching techniques, which enhances their curriculum and extra curriculum updates.

**Keywords:** Teaching aids, Guidance, Reinforcements, Rewards, Behaviors, OT (Occupational Therapy).

## 30. Making Online English Language Teaching Effective

**Disha Esther Ramtek**, Guest Lecturer, Kalaniketan Polytechnic College,  
Jabalpur (M.P.), Assembly of God Church, 850, Napier Town, Jabalpur,  
Madhya Pradesh, India

It has been a year since the Indian education system has seen a major shift due to the ongoing pandemic. Teachers are trying to learn and adjust themselves with the technology. Old ways and methods of teaching now

require changes or a new touch. Even after having many years of teaching experience teachers are facing difficulty in adjusting to the present e-learning trends.

This paper aims to understand how much the English language teachers aware of the e-learning tools available are and to suggest some e-learning tools to make online English language teaching effective. To collect data for this research a survey was conducted using an online questionnaire. Responses of English language teachers from all over India were received. Through selected responses of fifty teachers, it is concluded that the teachers are trying hard to make their online classes effective but they are not well informed of the e-learning tools.

Many teachers complain that due to online mode of education, students have taken back seat and it has become extremely difficult to engage them. Hence it has become extremely important to find new ways to make online classes interesting and constructive. New problems need new solutions and smart students need smart teachers.

**Keywords:** E-Learning, E-Learning Tools, English Language Teaching, Online Classes, Effective Teaching.

### **31. Redesigning ELT: An Ecolinguistic Approach**

**Durbadal Datta**, Research Scholar, Seacom Skills University, Kendradangal, Near Santiniketan, Birbhum, West Bengal, India

In India the National Education Policy 2020 lays emphasis on organic living in proximity with nature, environmental education, sustainable development, and national textbooks with local content and flavour. On the other hand, a recent series of catastrophic events – wildfires, floods, locust plagues, and the COVID-19 pandemic – have shaken the world's environmental conscience so terribly that a paradigm shift in education is essential to combat the present situation and to promote learning to live in harmony with nature. In case of English Language Teaching (ELT), the whole curriculum is to be redesigned to meet the individual, national as well as global need. This paper deals with the need for a paradigm shift and developing an outline for the new paradigm from the perspectives of

ecolinguistics. An ecolinguistic approach to ELT can build up the learner's perception of both language and the linguistic environment.

**Keywords:** National Education Policy, Curriculum, local content, Ecolinguistics, Ecological Awareness.

### **32. Environmental Ethics: A Critical Analysis**

**Faiyaz Ahammad**, Research Scholar, Department of Education, Aligarh Muslim University, Aligarh, India

Environmental ethics is the study of normative issues and principles relating to human interactions with the natural environment. It comprises an increasingly significant field of applied ethics, crucial for the guidance of individuals, corporations and governments in shaping the principles affecting their lifestyles, their actions and their policies across the entire range of environmental issues. Debates include theories of normative ethics and of meta-ethics, and the adequacy of individualist, holist and ecofeminist stances. It is characteristically concerned with the good of future generations and of nonhuman species as well as that of contemporary human beings. Its scope includes the interpretation and application of the precautionary principle and of policies of sustainable development, grounds and policies for biodiversity preservation, and the nature and basis of obligations to assist adaptation to global warming, and to mitigate the anthropogenic greenhouse gas emissions widely recognised to constitute one of its principal sources.

**Keywords:** Anthropocentrism, Biodiversity, Climate Change Mitigation, Ecofeminism, Environmental Ethics, Future Generations, Intrinsic Value, Non-Human Creatures, Precautionary Principle, Sustainable Development

### **33. Youtube: A Revolution in Modern Education --- Learning with Entertainment**

**Isha Rani Das**, Assistant Professor, Department Of English, Vivekananda Mission Mahavidyalaya, Chaitanyapur, Purba Medinipur, West Bengal, India

From the ancient 'gurukul' to the present world home-learning, the education has advanced and undergone a great change. The pupils

have been burdened with information coupled with understanding and reasoning in the present situation when they have to attend the drab and dreary online class where there is very limited scope for the lively mutual discussion as in the physical classroom. Though YouTube has been going on since February 2005, it has recently been a lucrative app for the teachers and learners for its cheap, qualitative and liberal democratic nature. It has been a revolution in the arena of modern education. When all the world is struggling with the fatal covid 19 and education system has been home-based online learning, the students who miss their daily classes on virtual mode or are unable to stay in the class for various unavoidable issues, have found the bunch of educational video clips on YouTube a real boon as it not only gives the experienced and knowledgeable persons' output but also makes the concept of a topic clear through the colourful motion pictures--- a powerful entertaining TLM for students. The inquisitiveness of knowledge is being fed by the experts and professionals in an attractive audio-visual way on YouTube - a three penny nutritious digital platform.

**Keywords:** YouTube, Revolution, Lucrative App, TLM, Digital Platform

### **34. *Paravidya* and *Aparavidya* – The All Comprehensiveness in Upanishad Teaching Learning: An Overview**

**Jijeesh T K**, Asst.Professor, Dept. Of English, EMEA Arts and Science College, Kondotty

Upanishad knowledge is considered traditionally the Supreme testimony of Indian knowledge system. Among the most important literature in the history of Indian religion and culture, the Upanishads played an important role in the development of Spiritual ideas in India. Knowledge or Vidhya is considered as the most important means for liberation.

*Vidhya* means knowledge in Indian Philosophy. Knowledge is classified by Upanishad into two - *Paravidhya* and *Aparavidhya*. Upanishad Wisdom Says that the comprehensiveness of the knowledge is achieved only by the combination of *Paravidhya* and *Aparavidhya*.

*Aparavidhya* is the knowledge of the world. It is the knowledge about the phenomenal world as its content. It is essential for every human being for the life. But, *Paravidhya* is higher Wisdom than the former one.

That is , the supreme knowledge . The knowledge of the Atma. Paravidya cuts the bonds of ignorance and leads to realization of God. That is moksha, the Supreme aim as far as Upanishad philosophy is considered.

**Keywords:** *Vidhya* / knowledge, The Upanishad Philosophy, Paravidhya , Aparavidhya, The comprehensive knowledge.

### **35. Yogic practices and Emotional Intelligence as the True Medicine to Maintain the Intellectual Powers of the Secondary School Pre-Service Teachers**

**Km Seema**, Research Scholar, Department of Education, HPU Shimla

In the present pandemic situation, human being is facing many problems related to their economic status, ethical values, day today's life, physical problem and professional issues because this pandemic has crushed the whole world and it is affecting the lifestyle, goals, relationships, attitude of the people as well as professionals like doctors, engineers, teachers etc.. It is decreasing the emotional and spiritual values among people. So in this crucial stage yoga has come as a true medicine to maintain the intellectual powers of the professionals. Yoga is practising by the whole world because yoga is considered as "controlling of the mind." It is the reunion of the body, mind and spirit. Yogic practice includes specific techniques such as "Asanas", "Pranayama" and "Dhyana". These are true medicines to attain the highest level of consciousness and to balance the emotional intelligence. Emotional intelligence consist empathy, self-control, successful relationships and self-motivation. But due to rapid change in the world, these values are decreasing. Emotional intelligence is an ability to monitor once on and other's feelings and emotions. Studies reveal that emotional intelligence is the key to success. It is necessary for teachers to balance their emotions so that they could maintain their intellectual powers. It is possible through the yogic practices that are helpful to maintain the emotions.

**Keywords:** Yogic practices, emotional intelligence, intellectual powers, pre-service teachers.

### **36. Efforts of Prevention of Substance use Among School Students in India**

**Lalit Mohan Joshi**, Ph.D. Research Scholar, IASE, Jamia Millia Islamia, New Delhi, India

The problem of substance use such as smoking, drinking or consumption of other intoxicant substances by school students in India is a growing concern. The substance use is also a cultural phenomenon as the different cultures may have different opinion about substance use as well as different approaches of prevention of the substance use. In India, there have been several efforts in the direction of prevention of substance use among the school students. Institutes like National council of educational technology and research, National institute of social defence etc. have published the resource documents for teachers and other stakeholders. National policy for drug demand reduction 2014, National educational policy 2020 etc. have also emphasised upon the need to keep the school students away from substance use. This paper articulates the efforts in India towards prevention of substance use and presents a critical review of the same in terms of underlying assumptions, approaches and feasibility of successful implementation.

**Keywords:** Substance use, Prevention, Policy perspective, Institutional efforts, Review

### **37. Degree of impact of collaborative virtual education with special reference to the rural area, Ramanagara**

**Mahamad Khaleel M**, Research scholar, All-Ameen Research Foundation, Bangalore

There is a unevenness between Urban and Rural in the field of education. while all urbanites are blessed with elite institution in their vicinity, Rural students are not offer from the benefits of higher centres of learning. To strike a balance between these two extremes and their needs, therefore it is of Paramount important to explore the possibility to materialize the dream of makings available all the Innovations and advancement achieved in the field of education equally to all section of the

students. This is the result of a questionnaire circulated by me among the rural area of students, teacher and public.

### **38. Teaching Learning and Education Smart Phones & Mobile Applications**

**Manimegalai S**, Asst. Prof of English, Ananda College, Affiliated to Alagappa University, Devakottai, Sivaganga, Tamil Nadu, India

From last year onwards COVID-19 has created an enormous challenge to learning education on a global scale. Since that we are all learn through Smart Phones and Some various Mobile Applications. Here i want to give some innovation strategies to enhance m- teaching, learning method to develop the knowledge of the modern student which through the Smart Phones during the critical time of COVID-19. The rapid worldwide adoption of mobile technologies like smart phones and tablets has become increasingly pervasive in the educational landscape and has impacted the way that learners access, share and interact with information. Mobile devices have allowed learners to access course content, complete assignments through Google class room application, receive instruction and connect with their peers regardless of geographic location. This type of digital learning it should be possible by the interest of the student. This portability has dramatically shifted how both instructors and students view and engage in the learning process. As the concept of m-learning has evolved learners to connect with the information in new ways to enable for deeper learning.

**Keywords:** m-Learning, Smart watch, Digital learning, Smart device, Google classroom. ,

### **39. Art Based Interventions in Academics: The Robust Connect Between Language, Literature, Education and Music**

**Meena Shanker**, Assistant Professor, Govt. Polytechnic College, Kannur, Kerala, India

The connect between language, literature, education and music has expanded ever since the beginning of time and has intersected its purpose across varied realms by integrating language, literary, educative, academic



and musical abilities in learners. This has resulted in the refinement of the psyche and enhanced the synthesis of music and knowledge skills by focus on cognition and learning abilities. In this context, music education, applied music, music analysis, music psychology and musical concerns address the challenges of the academia and expound the role and significance it plays in elevating a student to muster language abilities and up thrust the all-round development of a pedagogue. As a sublime mode of communication, the nuances of this art form and the musical interactions and ensemble broaden the dimensions of music pedagogy to generate and integrate music as not just part of aesthetics, but as part of academics. This will aid students with learning disabilities, and autistic children to celebrate learning as art based and enjoy music to integrate all art based education with erudition, passion and purpose to echo a paean of integrated, joyful and prolific learning.

#### **40. Social Media Usage: A Mediator for Collaborative Learning and Psychological Wellbeing of Higher Education Students during Lockdown**

**Miss. Sasmita Behera**, Research Scholar, Central University of Odisha,  
Koraput

During the time of lockdown, social distancing and limited contact with others, the proliferation of Social Media as compared to many years ago has now become a major subject of discourse in different sectors of the society and also changing trends in education, politics, technology, sociology, and psychology. Social Media platforms are meant to connect people and helped the world remain connected, largely increasing usage during the pandemic. Since, many people are asked to remain home; they have turned to Social Media to maintain their relationships and to access entertainment to pass the time. Social Media is widely used by the students and teachers also for their learning purpose during the pandemic. However, the Covid-19 Pandemic has affected the usage of Social Media by the world's general population from ground to top level. Social Media has become an effective tool to support their educational communication and collaborations with their friends and also faculty members. Social Media Usage improves peer interaction and course engagement of students and also students' interaction with faculty members. However, many related

studies stated that interactivity with peers, teachers, online knowledge sharing behavior and course engagement of students have positive significant effect on collaborative learning during this Pandemic. Relating to psychological wellbeing, Social Media Usage has become an asset for giving assistance, makes the students steady and more interactive psychologically whereas on the other side, due to the excessive use of it, it results in worse psychological wellbeing like- depression, anxiety, psychological imbalance, frustration, etc.

**Keywords:** Social Media Usage, Collaborative Learning, Psychological Wellbeing, etc.

#### **41. The Role of Multilingualism in Education**

**Mr. Anand Rakhmaji Waghmare**, Research Student in English Literature,  
Dr. A. P. J. Abdul Kalam University Indore

India is supposed to be a sociolinguistic monster, and this monster is immense and unique concerning the customs. The nerve arrangement of this monster is multilingualism. Indian multilingualism is tremendous in size, with more than 1600 primary languages reducible to about 200 dialects for a populace of about 1.27 billion individuals, with the number of inhabitants in a considerable lot of the phonetic minorities being bigger than numerous European nations. Language is human personnel, it coevolves with us, and monolingualism, which even in typical conditions is an uncommon marvel, is past creative mind in a setting, for example, India where English has coincided with native dialects over a significant stretch. Truth be told, the greatness of multilingualism in India has made researchers wonder about how correspondence occurs and how friendly union is kept up. The present paper analyses the role of multilingualism in the Education sector.

**Keywords:** multicultural, multiethnic, multilingual, monolingualism, etc.

## **42. Impact of Physical Activity and Exercise on Physical Fitness: A Study on the root cause and solutions for Overweight and Obesity in young Men and Women**

**Mr. K P Kannan**, Ph.D Research Scholar, Department of Physical Education, OPJS University, Churu, Rajasthan

There are increasing numbers of young men and women who without wanting to be involved in any particular sport or game, are nevertheless concerned to maintain or improve their levels of physical fitness through some form of personal exercise programmes. Jogging and running are popular at the moment, although many other kinds of activities such as cycling, swimming and aerobics help more in this regard. People today are very much aware of the importance of maintaining physical health. Various means have been suggested as keys to improve one's well-being but the fact of psychological stability is still too often downplayed either because its importance is not fully recognized or there is no known way of strengthening the stability. Today's fast moving world takes its own toll on the human body in the form of various kinds of stress that may lead to overweight and obesity. Playing various sports for recreation or professionally imparts key benefits to overcome stress that leads to maintaining physical fitness. A fit person is able to carry out the typical activities of living such as work and still have enough energy and vigor to respond to emergency situations and to enjoy leisure time activities. Regular physical activity can do much to prevent disease and illness. It can help you look your best. Besides looking better people who do regular physical activity feel better and do better academic work and are less depressed than people who are less active. Regular physical activity results in physical fitness which is the key to the meet emergencies and demanding day-to-day situation. Being physically active builds fitness which in turn provides you with many health and wellness benefits.

**Keywords:** Physical Fitness, Exercise, Overweight, Obesity, Health

#### **43. A Comparative Study of Teacher Techno-Pedagogical Competency based upon Gender, Stream and Experience of Senior Secondary Teachers in Uttarakhand**

**Mrs. Sobha**, Research Scholar, *Department of Education, H.N.B. Garhwal Central University Srinagar, uttrakhand*

The research article focuses on the teacher techno-pedagogical competency of senior secondary teachers of Uttarakhand with respect to gender, stream and experience. The sample of the study consisted of 411 senior secondary teachers of Uttarakhand. To collect the requisite data for the present study, the investigator used standardized tool of teacher techno-pedagogical competency scale (2013) developed by Dr. S. Rajsekhar & K. Satyaraj. The data analysis was done with the help of mean, SD, 't' value and one way ANOVA test. The results revealed that there were no major difference of gender, stream and experience of senior secondary teacher in relation to their techno-pedagogical competency.

**Keyword:** Teacher Techno -Pedagogical Competency, Senior Secondary Teacher.

#### **44. The Importance of Teaching in Our Life**

**V Vaniha Jeyakumari** B.Sc, M.A, M.C.A, M.Phil, B.Ed., B.A., M.A.,  
Assistant Professor, KG College of Arts and Science, Coimbatore

This paper focuses on the importances of Teaching. Teaching provides knowledge. Every teacher teaches something to the students of schools, colleges, universities etc. The students enrich their knowledge from their teachers. Consider an English teacher teaching Macbeth. After her teaching, the students will come to get knowledge about how to capture kingdom, know who are witches and what they do, how a woman thirst for the post and later suffers, what skill is required for ruling etc. It is sure that what a teacher teaches to his / her students, that knowledge will be imparted to them. With the knowledge they gained in their schools and colleges they are able to survive in the world. They earn and support the family. They give their service to their society. They prosper slowly. They make their life happy and others happy. Even books teach us something. Bible says don't lie. Like

this Bhavat gita says something. Quran says something. All scriptures teach wisdom. History books teach something. With the help of teachers and books 'teaching we are able to live our life.

**Keywords:** Knowledge, Life, Books, Teachers, Teaching, Wisdom.

#### **45. Online Classroom: Challenges in Educational Activities**

**Ms. Anuradha Bisht**, Lecturer, Delhi College of Vocational Studies and Research, Baprola, Najafgarh, Delhi, India

Corona pandemic has forced everyone to be within the four boundaries of their homes. Everyone is working from their homes through online mode. Essential activities like sale, purchase, service, even education also being offered online. Schools and educational institutions are using virtual mode to teach their students. Virtual classrooms have being prepared by using various apps like Google meet, zoom, teams etc. Schools are also sending videos and notes in their respective groups for the smooth functioning of their online classrooms. It seems very relaxing and easy to get online education but about skills or practical work? Education doesn't mean to impart theoretical knowledge in their students, but education seems to be a powerful tool that enhance personality of a child and bring out hidden talent of a student. Here online classrooms bring lots of challenges for institutions to map educational activities in an online space like noise from outside, household distraction, relaxing or comfortable mode, non-availability of resources for practical work, side effects on eyes and body , technical issues etc.

**Keywords:** Corona, Pandemic, Virtual, Educational, Skills

#### **46. Happiness Curriculum: A New Vision towards Education**

**Ms. Poonam Pandita**, M.Ed Scholar, Department of Educational Studies,  
Central University of Jammu, Samba, Jammu, J&K, India

**Mr. Sachin Kumar**, M.Ed Scholar, Department of Educational Studies,  
Central University of Jammu, Samba, J&K, India

**Ms. Chetna Suri**, M.Ed Scholar, Department Of Educational Studies,  
Central University Of Jammu, Samba, J&K, India

The present education system is emphasizing upon skill based education and trying to prepare the individual to deal with the global world. For achieving this goal, our education system introduces a rigorous curriculum for the students in which they have to study four or five subject's everyday and thus they have to learn about the multiple concepts. This busy schedule has caused a lot of burden on the children and they feel stressful and anxious all the time. This thing also restricts the child to think critically and with open mindedness and also due to this they don't find time to discover their inner potential. So for addressing it Delhi Government has taken the initiative to introduce Happiness curriculum in their schools where children can learn in stress free environment with no fear of formal assessment. If we look at our NEP:2020, It is also giving the idea of happiness curriculum because this policy is also emphasizing on activity based learning and also have recommended some bag less days for children 6 to 8 standard. So, this paper explores the need and importance of Happiness curriculum in our education system.

**Keywords:** Happiness Curriculum, Open Mindedness, Inner Potential, Happier Environment, Stressful

#### **47. Strengthening Physics Teachers' Pedagogical Content Knowledge through Explorations with Agent-based Modelling**

**Ms. Shruti Chopra**, Research Scholar, Deptt. Of Teacher Training & Non Formal Education (IASE), Faculty of Education, Jamia Millia Islamia, New Delhi, India

*The study investigated the development of 30 senior-secondary school physics teachers' knowledge of content (kinetic theory of gases) and students' conceptions using agent-based modelling (Netlogo). The data collection procedures of the study involved interviews with each participant and a video-recording of each workshop session. The data collected through pre-intervention interviews illustrated that teachers lacked an in-depth conceptual understanding of the microscopic behaviour of particles and struggled with providing adequate opportunities to students to visualise microscopic phenomena. Through an engagement with hands-on explorations, teachers explored how the interactions between individual agents resulted in complex dynamic phenomena. It was observed that the intervention resulted in a substantial growth in not only teachers' subject-matter knowledge but also the knowledge of learners' difficulties and ways of addressing them through agent-modelling approach.*

**Keywords:** Physics, Pedagogical Content Knowledge, Agent-Based Modelling, Netlogo, Kinetic Theory of Gases

#### **48. A Study on Behavioural Attributes of Special Educators and Facilitators in TLE**

**Navyashree R M**, Assistant Professor, Department of English, Surana College

**Tejaswini Y**, Assistant Professor, Department of Psychology, Surana College

A variety of motivations, characteristics, abilities, and expertise make up behavioural attributes. These are shown by how a person acts in a given situation and can be a significant factor in predicting job results. It is important for a special education teacher to recognize the potentials of students because each will have a unique capability, and they will be

responsible for ensuring the goals met. A teacher's understanding of the diversity of their classroom is important because it will help them better understand students' previous experience and learning styles. Thus, in our present study we have compared the behavioural attributes of both special educators and facilitators to understand the differential perception in the process of teaching, learning and evaluation through survey method. From the study conducted we have also known the students' needs which will determine on building an effective learning methodology and boost the level of understanding

**Keywords:** Behavioural attributes, Capabilities, Instructors, Specialist, Learning methodologies

#### **49. A Study of Work Motivation of Secondary School Teachers In Relation To Teacher Efficacy and Organizational Climate**

**Neha Bharti**, PhD Scholar, Department of Education, University of Jammu, Jammu

The present study aims to investigate the significance of difference in work motivation, teacher efficacy and organizational climate with respect to gender, type of schools and area of service. It also examined how teacher efficacy and organizational climate are related with work motivation and joint contribution of teacher efficacy and organizational climate in predicting work motivation of secondary school teachers. 200 secondary school teachers were selected randomly from four districts of Jammu province of union territory of Jammu & Kashmir. Teacher efficacy Scale by Dr. Vishal Sood and Ms. Sapna Sen (2017), Organizational Climate Scale for teachers by Dr. (Mrs.) Venita Singh (2015) and self-constructed Work Motivation Scale were used to collect the data. The results of the study reported that there is no significant difference in teacher efficacy and perception of organizational climate of the secondary school by the teachers with respect to gender, type of schools and area of service. Significant difference in work motivation of secondary school teachers was observed with respect to type of schools. But gender and area of service had no influence on work motivation. Teacher efficacy and organizational climate has significant and positive relationship with work motivation. It is also found that teacher efficacy and organizational climate significantly



contribute in predicting work motivation of secondary school teachers. Therefore, to improve teachers' motivation to work, there is a need to boost teachers' sense of self-efficacy and provide healthy work environment.

**Keywords:** Teacher Efficacy, Organizational Climate, Work Motivation

## **50. Comparative Study of Mental Health among Adolescence**

**Nimta Devi**, Ph.D Research Scholar, P.G Department of Education,  
University of Jammu

*An individual's main goal is to find a way to adapt to changes in the environment. He would only be able to accomplish his target if he has a well-balanced personality. Each person solves problems in his or her own unique way. Regardless of how resourceful he is in dealing with challenges, life's situations invariably involve tension. For coping with the day to day challenges of life one must have sound mental health. Present study was undertaken to study the mental health of the Adolescence in terms of locality (rural and urban). This study was based on sample of 200 students (100 boys and 100 girls) of class Xth from secondary Schools of Jammu. Mental health battery developed by Arun Kumar Singh and Alpana Sen Gupta was used by the investigator for the collection of data from class Xth students belonging to rural and urban locality. The collected data was analysed by the researcher with the help of statistical techniques like mean, standard deviation, standard error of mean, standard error of difference of mean and critical ratio. The results of the study revealed the significant difference in the mental health of rural boys and rural girls. Boys belonging to rural locality have good mental health as compare to mental health of girls belonging to rural locality. No significant difference was found in the mental health of boys and girls belonging to urban locality. Significant difference was also found in the mental health of adolescence boys and girls belonging to rural and urban locality. Urban boys and girls possess good mental health as compared to rural boys and girls.*

**Keywords:** Mental health, rural and urban, boys and girls, Comparison and challenges of life.

## 51. Women and Education

**Preeti Devi**, Assistant Professor of Education, Govt. Degree College Doda, J&K India

Women education refers to every form of education aims at improving the knowledge and skill of women and girls. It includes general education at school, College and university level as well as professional, technical, vocational and health education etc. it encompasses both Literary and Non Literary education.

During the vedic period, women in India had access to education, but over a while they have gradually lost the right. The need for women education goes back to times of Independence Savitirao Phule and Jyoti Phule were advocates for women's education ad set up an Institution for girls in 1848. During the time of Independence, the female literacy rate was at a meager 8.6%.

According to 2011 census the female Literacy rate in India is 65.46 %  
**Though it has seen a rise, India has not met the world average at female Literacy rate.**

The Govt. over the years had introduced many schemes to promote Women's education in India like, Beti Bachao Beti Padhao, Yojana, Sarva Shiksha Abhiyan, Rashtriya mahila kosh, mahila shakti Kendra etc. In modern age women rights are being recognised, most importantly their right to receive education.

There were many Prominent Indian eminent Persons like Raja Ram Mohan Roy and Ishwar Chandra Vidyanagar etc. who had emphasised women education in India. Women need to be given equal opportunities as Men, especially when it comes to education women education will help to eradicate the discrimination and stigma that women face today. The right to education. Is granted to every Indian citizen. We need to ensure that learning is available for all and not just for men. Spread of education in rural areas. Is vital as urban areas to empower women all over the country women education. Is necessary for the growth of any country.

**Keywords** – Gradually, spread, Literacy, Opportunities, discrimination

## 52. The Role of C. F. Andrews in shaping St. Stephen's College, Delhi- A Study of Undergraduate Education

**Priyanka Mathew**, Doctoral Scholar, ZHCES, JNU, New Delhi, India

In this article we shall briefly look at Gandhi, Tagore and C.F. Andrews. All these men influenced India with their ideas, teachings and activities. C. F. Andrews directly shaped St. Stephen's College, Delhi. Gandhi and Tagore indirectly gave birth to new ideas that moulded the College indirectly through their interactive sessions with the College. Moreover, the participation of these great men in the Indian Freedom Struggle gave a certain direction to St. Stephen's College, Delhi. Most of the College according to David Baker (1998) was nationalist in a moderate sense. At the same time, Lala Hardayal and Sucheta Kriplani, the alumni of the College gave a certain fervour to the Indian National Movement with their efforts. Thus, the College should be seen holistically.

**Keywords:** Teachings, Nationalist, Moderate, Alumni, Holistically

## 53. The Socio-Cultural Context: Vygotskian Perspective to Early Childhood Education

**Samrah Khan**, Research Scholar IASE, Jamia Millia Islamia, New Delhi India

The early years of a person's life are the most crucial years in terms of development, learning and socialization. ECCE should be considered as the most important developmental milestone in the later Educational, Psychological, Sociological and Emotional development. ECCE from a very early age can have extremely important consequences, including decreased grade repetition, dropout, aggression and violence. The NEP 2020 emphasizes on the socio-cultural approach to learning in the early years and so does the Vygotskian approach. 100 years back Vygotsky firmly believed that a child learns the best in its immediate **socio-cultural** context and in his own **nativelanguage**. The present study was conducted to study the impacts of integration of this approach in the ECCE programmes of different kinds of setups and to check its effectiveness on the learning outcomes of the children. The results were analysed after interviews of teachers, parents, heads, classroom and school observations etc. Results indicated that

majority of teachers untrained for teaching young kids. The curriculum focuses mainly on rote learning and written languages. English is the key for assessment of learning outcomes. Play which is psychologically and developmentally the most important factor of learning for young kids has no or very less importance in the ECCE programmes. The shortage of resources and the large student-teacher ratio is another barrier for learning. Professionally trained and dedicated teachers will definitely bring up the skilled, interactive, healthy and happy kids which will ultimately lead to a developed and prosperous society.

#### **54. Online learning through Mobile Phones: The stance of Economically marginalised Sapera families from an Urban Village of Delhi, India**

**Shiney Vashisht**, Ph.D. Research Scholar, IASE, Department of Teacher Training & Non-formal Education, Faculty of Education, Jamia Millia Islamia, Delhi

**Prof. Fauzia Khan**, IASE, Department of Teacher Training & Non-formal Education, Faculty of Education, Jamia Millia Islamia, Delhi

With the advent of COVID-19 global pandemic, it became obligatory for educational institutions, across the globe, to continue teaching- learning through online mode. While some countries were well equipped with this methodology, a developing country like India was far from ready; courtesy lack of resources and training. After the state-imposed lockdown in March 2020, teaching- learning in India was continued through mobile phones. For a country like India, where poverty is prevalent throughout, this methodology somehow became a saviour, as well as a problem.

As a part of Doctoral research, some economically marginal families of Sapera community, residing in an urban village of Delhi (India), were interviewed during the early days of online schooling. After a year these families were reinterviewed for understand their stance on the efficiency and outcomes of online learning through mobile phones. This paper discusses

the pros and cons of online learning, with a special focus on educational continuity, drop-out, and problems faced by both parents and students.

**Keywords-** Online learning, Mobile learning, Sapera Community, COVID-19 pandemic, Drop-out

### **55. Does Intelligence Affect Music Perception Ability in Children?**

**Shiuli Maity**, Ph. D. Scholar, Department of Education, The English and Foreign Languages University, Hyderabad

Intelligence is required to complete any task effectively. Children require intelligence to understand music perception. The study examined the relationship between intelligence and music perception ability in children at elementary level. For this Experiment, 32 children including 16 girls and 16 boys were selected as participants. Out of 32 children 16 were exposed to formal music classes and 16 did not have formal musical exposure. All the participants responded to a music experience questionnaire at the beginning of the study. Children's Intelligence skill was examined by administering standardized 'test of "g" culture fair- scale 2, form A' developed by R. B. Cattell and A.K.S. Cattell. To understand children's music perception, Short- Profile of Perception Skills (PROMS-S) was administered. The study was quantitative in nature. A significant positive correlation was found between working memory and different components of music perception. Result of the study, educational implications and scope for future research were discussed in this paper.

**Keywords:** Intelligence, Music-Perception, Music experience questionnaire, "Test of 'g' culture fair-scale 2, form A" and PROMS-S.

## **56. The Role of Mass Media and Information Technology to Redesign the Teaching-Learning Process Based on the Current Scenario of Coronavirus Pandemic**

**Sinoj Antony**, Research Scholar, Lovely Professional University Phagwara, Punjab, India

**Ishfaq Ahmad Trambo**, Lovely Professional University Phagwara, Punjab, India

The educational system is the backbone of every society and nation, without a proper educational system none can achieve proper growth and development. The nature of the educational system and its influence on social and individual growth has undergone tremendous changes over a period. The interaction between teacher and students is an important process in an education system, this interaction is known as the Teaching-Learning process and it is social interaction. The teaching-learning process is a channel of communication through which the individual can attain knowledge, values, beliefs, views, habits, attitudes, skills, and social acceptance. Social growth and development can be only attained through a proper and effective teaching-learning process. Today, especially based on the worldly stricken pandemic, COVID-19, the traditional concept of the teaching-learning process has been undertaken with incredible changes and views. According to the present situation, mass media and information technology have a great influence to shape the current educational system and its parameters. Professional educators and facilitators must redesign an effective teaching-learning process to achieve true educational goals and mold the responsible citizens of the future. In this paper and presentation, we focus on the role and influence of mass media and information technology to bring certain changes in the traditional views of the teaching-learning process, which affect certain social and individual relationships.

**Keywords:** COVID-19, Mass Media, Information Technology, Teaching Learning Process, Online Education

## 57. Educational Challenges of Transgender Community: An Exploratory Study

**Srimoyee Poddar**, Research Scholar (Department of Education), Regional Institute of Education Bhubaneswar, Odisha, India

Today in our country and throughout the world transgender people are marginalized section and are not considered equal to the other population. Thus the purpose of the present research is to explore the educational problems of transgender community in Kolkata and to analyze the factors leading to educational problems of transgender community in Kolkata. The researchers have analyzed the data with the help of content analysis. 20 transgender persons from Kolkata were selected for research. The sample was selected through non-probability snow-ball sampling technique. The study was exploratory in nature and the data were collected through semi-structured interview schedule consisting of eight dimensions to understand the objectives in depth. The study revealed that in the present situation transgender people are facing admission problem in educational institutes, lack of financial support for education, drop-out problem from regular education, lack of support services for education, stagnation at secondary classes, social exclusion, less vocational inputs in school, identity crisis, lack of conducive school environment, lack of conducive classroom environment. The study recommended that it is better to have conducive environment in the educational institutes and start awareness program from the school level to reduce stigma attached with transgender persons.

**Keywords:** Transgender Community, Educational Problems, Exploratory Study, Marginalized Section, Conducive Environment

## **58. Efficacy of Educational Games in Mathematics Learning – A Study**

**Sumati Sethi**, Research Scholar, Department of Education and Education Technology, University of Hyderabad, India

**Dr. A S Jalandharachari**, Assistant professor, Department of Education and Education Technology, University of Hyderabad, India

Constructivism articulates that learning is possible at optimum level when learners construct knowledge than takes information passively. Nowadays children learn a lot through games and activities which lead to construct their own concepts in turn produces concrete knowledge for them. Science and technology escalated greater standards and opportunities in innovations and experimentations in teaching and learning activities besides day to day activities. Greater proportion of teachers is trained than before, various novel educational tools are designed to make the learning process more motivated and interesting. Among those games are the most effective educational tools in learning mathematics in general and primary classes in particular. This is a conceptual paper and purpose of this study is to examine the efficacy of educational games in mathematics learning at school level on the basis of different reviews related to this concept. The study also explores the mathematics teachers' perspectives on expending educational computer games in mathematics education and the effects of computer games on mathematics achievements.

**Keywords:** Educational Achievements, Educational Games, Mathematics Learning, School Students and Teachers Perspectives.

## **59. National Education Policy 2020, Knowledge Transfer and Technology in Education: Towards A Complete Learning Environment**

**Syamili S**, Research Scholar in History, Department of Kerala Studies, University of Kerala, Kariavattom, Thiruvananthapuram, Kerala, India

Education is fundamental for realizing full human potential, developing an equitable and just society, and encouraging national development. Providing universal access to quality education is the key to India's continued ascent, and leadership on the global platform in terms of



economic growth, social justice and equality, scientific advancement, national integration, and cultural preservation, universal high-quality education is the best way forward for developing and maximizing our country's rich capacities and resources for the good of the individual, the society, the country, and the world. This paper attempts to plan out a framework for thinking about technology and education. In particular, it looks at the concepts of knowledge and knowledge transfer from the perspective of the goals that motivate their specific forms of combination into a learning environment.

**Keywords:** 1. Knowledge 2. The sources of its legitimation 3. Online teaching and collaboration 4. Learning environment 5. National Education Policy 2020

## **60. Digital Games: An Innovative Learning Approach**

**T Sahaya Mary**, Research Scholar, Department of Education, Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu, India

In recent years, the importance of interactive media technology has grown in our everyday lives. Children use this device for a several purposes, including playing games. The variety of games has grown as a result of technological advancement. Digital games are the first thing that comes to mind. Students want to learn through play, and digital games provide them with an excellent vehicle to do so. Individuals' lives are enriched by mathematics. Game-based learning can be used in the classroom as a teaching tool to help students learn mathematics more effectively. Digital game-based learning allows students to fully engage with the content and learn through interaction and simulation. This article discusses the importance of educational games in learning and suggests ways to learn through digital games. The benefits and drawbacks of interactive game-based learning are also discussed here.

**Keywords:** Digital Games, Digital Game-based learning, Mathematics

## 61. Gender Equality and Equity in NEP 2020

**Teresa Wahengbam**, Research Scholar, Department of Education, Manipur University

The paper will highlight the provisions laid down by the New Education Policy 2020 with regards to gender and education. Women have the same right to education as men, so thus the other gender i.e transgender. Educated women can make informed choices and form a far better range of options. Educating women saves lives and builds stronger families, communities and economies. An educated female population increases a country's productivity and fuels economic growth. As the same, today transgender too have also been empowered and holds a respectful position in the society. The importance of sexuality education in addressing gender issues cannot be undermined. It can help reduce gender-stereotypes, enable students to understand the diverse gender identities, and can prove crucial in combating high dropout rates for the vulnerable groups. The final text of the policy supports its promise of equity and gender equality in education more sincerely and consciously. Yet, a closer look at its recommendations, proposed equity-inducing initiatives, and use of vocabulary renders its intent of establishing gender equality weak and vague. Thus, the importance of the study is to address the need for equity and equality of all the genders (male/female/others) and thereby empowering all the genders in the field of education and to look closely the provisions and the probable implications enshrined by the NEP 2020 for achieving a knowledge superpower country.

**Keyword:** Gender, Equality, Equity, Provisions, NEP 2020

## **62. Teaching Fundamental Duties as a Part of curriculum: A Need of the Hour**

**Mrs. Rajput Shraddha Bhausingh**, Assistant professor (Law), Hidayatullah National Law University, Naya Rajpur, Chhattisgarh

*“The need for imagination, a sense of truth, and a feelings of duty-these three forces are the very nerve of education.”*

*-Rudolf steiner*

When it comes to the true heart of education, Rudolf Steiner says that it is built solely on imagination, reality, and duty. Education and children are the backbone of every country. If a country is to thrive, its children must be educated for them to uplift the nation with great pride. Education has advanced to a new stage because of liberalization, privatization, and globalization. However, the education we have for our children has both advantages and disadvantages. Are we giving our children the best education possible? My paper intends to highlight the concerns and value of instilling fundamental duties as part of the curriculum in this modern world.

**Keywords:** Duty, Education, Children, Nation, Curriculum

## **63. Humanities and Technology: A Study of Resistance to Computer-Mediated Teaching**

**Dr. Amitabh Vikram Dwivedi**, Faculty, School of Languages & Literature Shri Mata Vaishno Devi University, Katra, Jammu & Kashmir, India

Since the Covid-19 pandemic has started, teachers across the globe have been conducting online classes through Zoom/Google Meet, but some teachers are facing tremendous difficulty while conducting online teaching. Also, we have found a resistance toward computer-mediated teaching, particularly amongst the teachers of Humanities. Why these teachers are quite resistant to use computer-mediated teaching? This presentation deals with issues related to this resistance. Why do we have resistance to assist technology in teaching in a technological era? Is it justified? What factors contribute to faculty resistance? We understand that online teaching is

different from classroom teaching, and embracing technology is not that easy. The presentation will address challenges, and provide useful suggestions.

**Keyword:** Computer-mediated teaching; resistance; online teaching; Zoom; Google Meet

## 64. Quality Education

*Dr. Namra Munir, Education University Lahore, Pakistan*

What do we mean by quality education?

- ž Quality =effectiveness or efficiency. a standard education must be given to all. The content or syllabus must be same for all.
- ž improve with the passage of time.
- ž Quality Education Goals
  - Academic excellence
  - Improve academic standards
  - Applied learning
  - Lifelong academic skills
- ž Purpose of the Quality Education
  - To determine the educational needs of students.
  - To improve the quality of education
  - Make education assessable to everyone

## 65. Effective Teaching

*Dr. Rashid Minas Wattoo, University of Sialkot Pakistan*

The skills needed for effective teaching involve more than just expertise in an academic field. You must be able to interact with people and help them understand a new way of looking at the world. This is not an easy job! Although there are many different ways to teach effectively, good instructors have several qualities in common. They are prepared, set clear and fair expectations, have a positive attitude, are patient with students, and assess their teaching on a regular basis. They are able to adjust their teaching strategies to fit both the students and the material, recognizing that different students learn in different ways. As a teacher, you are a role model who sets

the tone for the class. If you are able to show enthusiasm and commitment, your students are more likely to reciprocate. Conversely, when you are negative, unprepared, or impatient, these qualities will be reflected in the attitudes of your students. Undergraduate students at Georgetown have high expectations of their instructors, and they also have many competing interests beyond the course you are teaching. Give them a reason to remember your class as an important part of their college experience!

## **66. Create Online Test in the new normal**

**Dr. Mona Taman**, Vice Chairman of the Future leader International Group, Professor of educational technology and e-learning General Coordinator of the Sheikha Fadia Al-Sabah Innovations Competition, Egypt

### **The Goals of the lecture**

- Designing electronic tests with high efficiency
- Eliminate the problem of cheating in electronic tests
- Follow-up and evaluation of students in distance education

### **Outlines**

- The most important electronic test design programs
- Program screen components
- Change test settings
- The test template format has changed
- Control the time and degree of each question
- Confidentiality control of the test
- Send the test to students
- Receive students' answers and evaluate them
- Correct the essay questions electronically

## **67. Early Childhood Education; Then and Now**

**Bandana Sodi**, Lecturer

The most remarkable period in a child's life are the early years of life as it inculcates 'sanskars' or basic values and social skills in a child. The foundations of all types of learning are laid during these years. Early childhood education aims at the holistic development of a child's social, emotional, and cognitive and physical needs in order to set a solid and broad foundation for lifelong learning and wellbeing. Good quality of early childhood education helps to reduce the chance of dropout and repetition and also improves learning outcomes at all levels of education. Early childhood education covers the inseparable elements of care, health, nutrition, play and early learning within a protective and enabling environment.

The focus of the present paper is the history of early childhood education in India, the present status of ECE, various policies and programs launched by the Government of India at the Central and State level.

**Keywords:** Sanskars, Values, Cognitive, Repetition, Nutrition

## **68. Technology for Teachers – A Boom**

**Dr Shalini Sharma**, Associate Professor in English, G.C.W Parade, Jammu

Technology has become an ever-increasing part of the English language classroom nowadays. It can expand the student's ability to read, write, research and learn, if we are willing to expand our classroom repertoire. This has enabled students to extend their reach to language learners through the Internet on one hand and also design innovative lesson plans on the other utilizing the latest technological teaching aids. Teachers from other countries are able to pass on the latest teaching techniques to their local counterparts and vice versa. Technology offers various powerful learning tools that demand new skills and understandings of students including multimedia and to engage students through virtual learning environments. English teachers have always used technology but the explosion in digital technologies has opened up new vistas. This paper tries to explore the possibilities for English teachers to look forward for new and

interesting ways to stimulate language learners. It also discusses major issues arising due to the evolving nature of technology.

**Keywords:** Repertorie, Multimedia, Virtual Learning, Vistas, Stimulate

## **69. Virtual Learning in Indian Higher Education: A Future Prospect**

**Dr. Dattatraya M. More**, Assistant Professor in English, Ujwal Gramin Mahavidyalaya, Ghonshi, Tq. Jalkot, Dist Latur. Maharashtra

V-learning is a substitute way to deal with the learning cycle which utilizes Information and Correspondence Technologies (ICT) to work together and impart in Higher Education (HE) environment. This contains specialized and mechanical skill that replaces the conventional study hall learning with online segment where learning measure is capable on the web. This investigation investigates the adequacy and proficiency of utilizing e-learning during the time spent instructing in advanced education in India. The strategy for using the data and correspondence innovation is profoundly significant in the Institutions and colleges who provide quality and affordable higher instruction at adaptable time. This paper underlines on the future viewpoint of Elearning in advanced education in India, where the interest for advanced education is comparable to the created nations. In 1980s E-learning was considered as valuable instrument for distance instruction alone in India. Yet, presently the situation has changed and e-learning is arising as the most inventive utilization of Internet that serves advanced education as well. This concentrate likewise portrays the how V-learning prompts higher pace of HE enlistment proportion.

**Keywords:** Higher Education, V-learning, ICT, etc.

## **70. English as a Second Language in Relation to Female Education: An Overview**

**Dr. Debarati Das**, Assistant Professor, Dept. of English, Handique Girls' College, Guwahati, Assam

Teaching of English as a second language in India is exaggerated by many factors and conditions across the globe. The way English is spoken shows a discrepancy from position to place and with echelons of fluency and wealth. In the colonial era, English was a precondition to be at the forefront, especially in the contemporary world of outsourcing, knowledge, and skill. English is debatably the most imperative craze the British left behind in India. The study of English language provided a common language for a region with a multitude of languages and dialects. The 86th Constitutional Amendment Act, 2001, has been a path breaking step towards the growth of education, especially for females. Improving girls' educational levels has been demonstrated to have clear impacts on the health and economic future of young women, which in turn improves the prospects of their entire community. Women also need to be given the opportunity to develop through formal education to be empowered to serve and profit from holding these public leadership roles.

**Keywords:** English, India, Second, Female, Language

## **71. Digital Media's Impact on Print Media**

**Dr. N Vijayanand**, Assistant Professor, Department of Business Administration, Mannar Thirumalai Naicker College, Madurai

The study's key goal is to figure out how internet media (e-Paper) affects print media (hard copy) newspaper revenue. As we all know, people used to rely heavily on newspapers to keep up with what was going on in the world. People used to wait for newspapers and even carried them with them wherever they went. However, as technologies advanced, smart phones became more prevalent in the industry, and news-related applications arose. This lowered people's enthusiasm for newspapers. The research looked at how modern technologies like Facebook, Twitter, Instagram, and other outlets have impacted print media (newspapers). The information was



gathered by in-depth questionnaires, and it reveals a decline in print media distribution among India's youth. The immersive behaviour of digital media (social media) is preferred by India's youth to reduce the time spent accessing news. The amount of time spent reading newspapers by teenagers has decreased to half of what it was previously. Even so, newspapers are mostly purchased from the older generation of subscribers.

**Keywords:**Digitalmedia, e-Paper, Online Newspaper, Printmedia, Socialmediawebsites.

## **72. New Education Policy 2020 and its Impact on Indian Education System**

**Dr. Rajeev Vashisht**, Assistant Professor, Dept. of Commerce, Rajdhani College, University of Delhi, New Delhi

*Education is fundamental to the development of human capital and a nation. It is a prerequisite to provide quality educational opportunities to the young generation because of their prominence in the development of the country. There was urgency for robust policy frameworks complement to 21st-century education requirements in alignment with the Sustainable Development Goal 4. Consequently, India has articulated National Education Policy 2020 after a prolonged interlude of 34 years for the holistic transformation of the education system. This comprehensive policy has undertaken reforms from early childhood education to higher education, adult education, teacher training & development, regulation, and governance. It is for the first time that the new policy pertains to the assurance of quality education to the future generation besides access and equity and will focus on how to develop critical and innovative learning skills amongst them. The policy has been contextualized upon five fundamental pillars of equity, accountability, access, quality, and affordability in calibration with SDG 4. Thus, the paper focuses on the alignment of NEP with the UN SDG 4 and answers the question of how NEP 2020 is going to change the education system in India through a discussion of some major interventions and challenges in the implementation of NEP 2020.*

**Keywords:** - Education; NEP-2020; SDG- 4, MHRD.

## 73. Environmental Education and Sustainable Development

**Dr. Shalini Sharma**, Assistant Professor in Environmental Sciences,  
Government College of Education, Jammu, J&K (India)

Sustainable development has been a key concept in debates on environment and also become a strong motive in guiding the thinking in the area of Environmental Education in recent years. However, the discussion about sustainable development and education for sustainable development is going on. This paper focused on the historical progress of environmental education through the disputatious concept of sustainable development. Over recent decades, global problems related to the degradation of natural resources and pollution have increased dramatically. The challenges and problems like handling and disposal of solid waste have emerged as third type of pollution. While environmental issues are now receiving greater support, measurers aimed at promoting population policies, social development, poverty reduction and other necessary measures for achieving sustainable patterns of development continue to be largely ignored by the general public. Environmental education is an interdisciplinary process with the goal of equipping people with the awareness, knowledge, attitude, skill, motivation and participation they need to help resolving environmental issues through sustainable development. The major goal of environmental education should be to help citizens in becoming environmentally knowledgeable and above all skilled and dedicated citizens willing to work individually and collectively towards achieving and maintaining a dynamic equilibrium between quality of life and quality of environment.

**Keywords:** Environmental Education, Sustainable Development, Natural Resources, Degradation, Pollution, Solid Waste.

## **74. Two Year Teacher Education Programme for the Preparation of Prospective Teachers: Concerns and Challenges in Indian Context**

**Dr. Sushma Bala**, Sr. Asstt. Professor, Deptt. of Education, GCOE, Jammu, J&K(UT), India

Teaching is an intellectual endeavour which involves love, anger depression, hope etc. Hargreaves (1994) claims that teaching involves “human nurturance, connectedness, warmth and love”. The quality and standards of an educational system largely depends on the quality, characteristics and commitment and beliefs of the teachers towards their teaching profession . The Ministry of Education document, “Challenge of Education : A Policy Perspective” mentioned, “Teacher performance is the most crucial input in the field of education. Whatever policies may be laid down in the ultimate analysis this have to interpreted and implemented by the teachers as much their personal example as through teaching –learning process “. The NPE,1986 similarly reiterated the status and position of teachers and suggested that the methods of teachers recruitment should be re-organised to ensure merit, objectivity and conformity with the functional requirements.

It is a basic fact that teaching is a fundamental duty of a teacher, therefore, and it has to be made effective in order to make a successful teacher .” Successful “ and “effective “ – these two terms may be used as synonymous in the context of good teaching .I.L. Mursell has, therefore aptly observed, “successful teaching is teaching that bring about effective learning.” The question is not what methods or procedures are employed, or whether they are old fashioned or modern, time-tested or experimental, conventional or progressive. All such considerations may be important, but none of them is ultimate, for they have to do with means, not ends. The ultimate criterion for success in teaching is results.”

Now the questions arises; by what kind of results should be success of teaching be judged? Such a criterion needs not only the knowledge, understanding, skills but also his/her attitude and beliefs towards teaching profession. Ideas, beliefs and theories about teaching and teacher development, their nature and methods , are numerous ,diverse , and often conflicting . Teachers are the single most important influence on the emotional, moral ,aesthetic and intellectual qualities of education . Thus

school improvement is closely linked to teacher development. The teacher is the real social –architect who can really shape the destiny of India by imparting need based education to the future generation of the society. Presently the number of secondary teacher training institutions is approximately more than 10000. But some fundamental question arises here such as- why there are so many teacher training colleges? And, are they really capable of providing quality teacher education. More than anything the quality of a nation's school is directly linked to the quality of its teachers. . The teacher should not feel that because he is a first class graduate or a post-graduate or he is a teacher with long experience to his credit, he can deliver a good lesson without any planning or preparation. He should think, rethink and plan his sequence of teaching point. Good teachers continue to plan their work and prepare their lesson afresh even if they teach the same subject to the same class for years. Pre-service teacher education programmes are the programmes for professional preparation of teachers and not the programmes of general, academic study. Accordingly, they provide for a comprehensive coverage of professional knowledge, understanding, attitudes, interests, values and skills along with functional orientation. It is an induction and initiation process with open ended design fostering initiative for further growth and equipping the trainee with the needed skills of self-directed learning through projects, individually tailored assignments etc. Success of any educational development depends on the quality of innovative and useful teacher education programme to a great extent.

Bocrates Chiseled up Socrates; Socrates groomed Plato' Plato was guru of the great Aristotle and Aristotle taught Alexander – The Great. What an amazing and great sequence of teacher-taught relationship.

Teachers are the builder of nation and whenever the nation was in need of some reliable shoulders to support, the teacher comes forward to provide the same. Generally speaking all those who are laden with the responsibility of safe-guarding the interest of a country- may it be Doctors, Engineers, Scientists, Economists, Statesmen or we can switch off from the big things like Kings and Emperors to a small employee of the system – all have been directly or indirectly shaped or moulded by a teacher. The teachers have a sacred responsibility for the total development of the

children in all the aspects professing democratic, secular and socialistic values in them.

**Keywords:** Prospective teachers, Teaching Profession, Challenges, Teaching, Teacher Education Programme.

### **75. *Bhartiya Bhasha* and NEP-2020: Scope & Challenges of Indian Sign Language**

**Kr. Abhimanyu Dev Singh Billawaria**, PhD Scholar, Nava Nalanda Mahavihara, (Deemed University, Central Ministry of Culture, Gov't of India), Nalanda

World Health Organization reports 63 million (6,30,00,000) people who are speech and hearing impaired in India, out of which only 1% are literate in Sign Language. The ration of speech and hearing candidate to ISL translator for healthy social inclusion is 4:1, but in India the ration is 2500:1 whereas in USA it is 10:1. Indian Sign Language (ISL) is a language used by hearing and speech impaired people not only to communicate among them and with rest of the people in India. But in India, handfuls of people are versed with Sign Language. NEP-2020 has recognized ISL as a complete language and working towards its standardization and including it towards mainstream academia. This paper attempts to explore the genesis, evolution and present status of Indian Sign Language and the role of NEP-2020. It also throws light on the fact that why ISL should be promoted and brought to mainstream for every individual of society. Interviews, newspaper articles, experts' comments, research articles and empirical observation forms the strong foundation of the argument.

**Keywords:** *Bhartiya Bhasha*, Indian Languages, Sign Language, Indian Sign Language, Indian, dialects, NEP-2020, social inclusion, social exclusion, Inclusion Policy, Government of India, India, WHO, education system

## 76. Educational Games as a Learning Method

**Ms. Jyoti Bala**, Research Scholar, Lovely Professional University, Jalandhar  
Punjab, India

“Games are not just filler in education. They have the ability to introduce, reinforce or even assess learning of a given topic “

**-Kara carrero**

The emergence of latest technologies in this day and age has made interactive contents more than an option to make the most of recent advances .The increasing use of latest tools in the field of education has become the most debatable topic among educational institutions and educators. Gaming is traditionally considered as interference to studies. Currently, it is playing a vital role in driving engagement and motivation among students to learn concepts in an interactive way. Educational Games (riddles, puzzles etc computerized, and traditional) can improve team work and interaction among students and help them to apply the concepts they have learned in real world. There are several fun and educational games for children of all age groups. One thing which is worth considering is whether such games are really helpful for children of their academic performance are there any consequences of technology in studies? Educational Games are widely used as a learning method to improve any simplify learning .By keeping the technological tools aligned with curriculum, educational games can directly impact their achievements. This study is aimed to discuss the use and implementation of educational games in modern teaching method, along with their benefits and possible use cases.

**Keywords:** - Educational Games, Gaming, Education technology, Learning Method

## 77. Industry 4.0 and Challenges in Technical Education

**Purushottam Balaso Pawar**, Lecturer, Mechanical Engineering  
Department, SVPM’s Institute of Technology and Engineering Malegaon, BK

Current curriculums of all Technical courses are designed considering the requirements of Industry 3.0. Concept of Industry 3.0 was introduced in around 1970 and it requires particular skill sets to be developed in fresh

graduates and it mostly focuses on workmanship. In this paper efforts have been taken to review requirements of Industry 4.0 and new courses need to be introduced so as to create competencies in fresh graduates in accordance with requirements of Industry 4.0. Current curriculum has been proved obsolete by many experts and it doesn't fulfil requirements of Industry in coming times. Technicians working in smart factories require knowledge of Artificial Intelligence, Machine Learning, Internet of Things, Programming, and other multidisciplinary areas. Newly introduced education policy 2020 has emphasised more on multidisciplinary skills but recent development in Industry needs advanced multidisciplinary knowledge and skills. Conventional curriculum and skills have been stated obsolete by Industry experts.

**Keywords:** Industry 4.0, NEP 2020, Technical Education, Multidisciplinary skills

## **78. Innovative Pedagogy in Teaching: Need of Present Scenario**

**Sarita Dogra**, Assistant Professor in Education, Govt. College for Education, Canal Road, Jammu

In order to fulfillment of predetermined objectives of education and thrust of learners towards learning, it is utmost important for teacher to adopt new methods and technology, which makes the learning process more effective and efficient. Education works like an engine for the growth and progress of any society or nation. It is not only restricted to impart knowledge, skills and moral values but it also act as a foundation for building human capital which breeds, drives and sets technological innovation and economic growth. Students always like learn in a lively delightful and entertaining way. The adoption of new pedagogy by teachers enables them to arouse their interest and arrest their attention towards learning and developing learning passion among them. A new paradigm of teaching and learning is needed to enhance the student's active participation, perception and cognitive development. We can say that there is need of transfer the textual learning contents to visual learning content. This transition will become effective only if the students learn through innovative and effective teaching methods.

**Keywords:** *Innovative, Teaching Methods, Technology, Passion, Paradigm*

## **79. Virtual Learning**

**Savita Sambyal**, Research scholar, Phagwara, Punjab

One of the major consequences of our response to the COVID-19 pandemic has been a disruption to traditional classroom learning and instruction. And yet, in many ways, the move to traditional learning has highlighted what's essential in the classroom (and what's not) . The technological revolution in the field of distance education facilitates two-way communication between the facilitators and learners. Thus the shift from one-way communication to two way communications remains the focus of modern distance education. Different technologies have been used for online learning such as e-learning, Internet learning, networked learning ,virtual learning, computer-assisted learning, web-based learning and distance learning. Virtual learning is designed to extend educational experiences. It does not try to replicate them. In virtual learning, students access resources and interact in ways they would not or could not in the physical classroom. This article includes some of the findings of the research and a discussion how the virtual classroom affected students active participation in e-learning activities.

This article also offers some suggestions that can be of use to instructors who teach through virtual medium.

**Keywords-** Traditional learning, e-learning, web based learning, learning resource, virtual learning.

## **80. Role of ICT in Educattion**

**Arti Mahajan**, Lecturer, Govt. Degree College, Akhnoor , Jammu & Kashmir, India

The present age is a digital age. It is difficult to think of any activity in our daily life that is not using Information and Communication technology. Technology has revolutionized each and every sphere of life. Our schools and classrooms are no exceptions. Innovations in the field of ICT have influenced the education sector up to a great extent. It helps in providing online content service. It constitutes a platform for organizing learning experiences by ICT developments. Students, teachers and educational



administrator and every stakeholder in education have been benefited by the integration of ICT in education. ICT helps in implementing the principle of life long learning. ICT increases variety of educational services and medium. It also promotes equal opportunities to obtain education and information. ICT develops a system of collecting and dissemination educational information. ICT promotes technology literacy of all citizens, especially for students. ICT helps in developing distance education with national contents. ICT promotes the culture of learning at school development of skills, expansion of optional education, open source of education etc. It supports schools in starting experience and information with others. The use of information and communication Technology has no doubt improved the quality of higher education in the past decade. The reason is that ICT contributes to better learning environment and improves the effectiveness set of activities that facilitates capturing, storage, processing, transmission and display of educational information by electronic means.

### **81. National ICT Policy In School Education**

**Miss. Pooja Rani**, Teaching Assistant (Geography), Bhaskar Degree College, Udhampur, Industrial Estate Dhar Road, Udhampur (J & K), India

Information and communication technology (ICT) are defined as all devices , tools , content resources , forums and services , digital and those that can be converted into or delivered through digital forms, which can be deployed for realizing the goals of teaching learning , enhancing access to and reach of resources , building of capacities , as well as management of educational system. In education, ICT play vital roles in facilitating teaching and learning. Worldwide research has shown that ICT can lead to an improved student learning and better teaching methods.

Information and Communications Technology (ICT) can impact student learning when teachers are digitally literate and understand how to integrate it into curriculum. The initiative of ICT Policy in School Education is inspired by the tremendous potential of ICT for enhancing outreach and improving quality of education. This policy endeavors to provide guidelines to assist the States in optimizing the use of ICT in school education within a national policy framework. Schools use a diverse set

of ICT tools to communicate, create, disseminate, store, and manage information.

**Keywords:** - ICT, Digital, Education, National Policy, Learning

## **82. A Study of the Use of Web Resources in the Teaching-Learning Process of English Language in the Colleges of Udupi District (Karnataka State)**

**Mr. Shridhar Bhat**, Assistant Professor of English, Dr. G. Shankar Government Women's First Grade College & PG Study, Centre, Udupi, Karnataka

The information revolution caused by the digital technology has brought about significant changes in the way English language is taught in colleges. The advent of ICT has given the process of education a new twist and shape as a result of which the role of the ELT teacher has also undergone significant transformation. The current paper examines whether the teachers of English language are ramping up their new roles incorporating technology in their teaching and if not, how they perceive the use of technology in teaching in the emerging educational scenario. Hence, in order to find out the extent of the use of web resources in the Teaching-Learning Process of ELT in the select colleges of Udupi District of Karnataka State and the attitude of teachers towards the integration of technology into teaching, this study was carried out in 16 colleges. The data was collected through questionnaire. The researcher visited each of the concerned colleges to ascertain the present status of the use of web resources and how technology affects the teaching learning process.

**Keywords:** ELT, ICT, Technology Integration, E-Learning, Web Resources

### 83. Women and Education

**Pinaki Bakshi**, Research Scholar, Eternal University, H.P, India

The one and only strongest weapon in the hands of women in today's time is education well said by Nelson Mandela. Malala Yousafzai also said 'Our books and our pens are the most powerful weapons'.

She also confessed that the thing that affected the most to the extremists was a girl with a book and pen. So undoubtedly by above mentioned quotations, it becomes crystal clear that how education has been the powerful dynamic force in the favour of women, by which they can conquer the world and can act as a legendary force in bringing a dire required change in our society. Women is inborn strong and extremely determined to her potentials and needs and getting education to be added in her profile can act as a perfect booster to her urge of becoming the force of bringing such a revolutionary change in her family, society and nation as well. Education is the most beautiful ornament hanging around a woman rather than a decorative piece of jewellery around her neck in the disguise of shackles and expectations that a society expects from her. My paper will throw light on the education as a requisite force for women to maintain her dignity and pride in the society and how it can affect her life and personality on the whole.

**Keywords:** Education, weapon, change, revolution, society.

#### **84. Tenebrosity of Partition in Shiv K. Kumar's *A River with Three Banks***

**Mrs. K Priya Mol**, Ph.D. Research Scholar in English,  
Reg. No: 17213164012027, Scott Christian College (Autonomous), Nagercoil,  
Kanyakumari, Tamil Nadu, India, Affiliated to Manonmaniam Sundaranar  
University, Abishekapatti, Tirunelveli, Tamil Nadu, India

**Dr. G Suhithar Baus**, Former Associate Professor, Department of English,  
Nesamony Memorial Christian College, Marthandam, Kanyakumari,  
Tamil Nadu, India, Affiliated to Manonmaniam Sundaranar University,  
Abishekapatti, Tirunelveli, Tamil Nadu, India

Brutalization is a social phenomenon which has attracted the attention of all in recent times. Brutalization or violence can occur in any place or in any form. Violence against women implies gender-based violence which would result in physical harm or sexual harm leading to adversities and long-lasting psychological impact. Dehumanization against humans on the basis of gender, religion, caste and creed is prevalent in every society where meek and voiceless become the victims of the debauchery men folk. The present study entitled "Tenebrosity of Partition in Shiv K. Kumar's *A River with Three Banks*" attempts to evaluate the violence and victimization of the women folk in the name of partition and patriarchy. The victims undergo psychological trauma which entirely disturbs their life and mind set. Terrible changes brought about due to partition of land dissolves the amicable relationships that exist between Hindus, Muslims and Sikhs and its ill effect is reflected mostly on the women folk who have been living as marginalized and voiceless creature in the male chauvinistic society.

**Keywords:** Brutalization, Violence, Sexual Assault, Trauma and Patriarchy.

#### **85. The Sacred Secrets of Indigenous People in Traditional India**

**Mrs. P A Padmavathi**, MPhil., B.Ed, Ph.D Scholar, Dept of English, Sri Ram  
Nallamani Yadava College, Tenkasi

The Indigenous people and local communities have created a wealthy traditional knowledge and cultural expressions which are still protected.

Their cultures, traditions, food habits and dress codes were not only unique but are treasure to us in this pandemic period. Traditions must be understood by the pupils of India which could be beneficial for our kids in this pandemic period. India is still a country of peasants. Agrarian development is extensive, but still with primitive technique. Though pupils learn via internet, mentors has the responsibility to teach them about the sacred secrets about indigenous people and their cultural habitats which may aware them from the pandemic diseases. This article analyse the secret traditions of people who are far away from us in technology but well to do in food habits, cultural habitats and all time occupations.

**Keywords:** Culture, Tradition, Indigenous, Technique, Habitats.

### **86. Marriage as misalliance in JaishreeMisra's *Ancient Promises***

**P Starlin Judith Venibha**, Research Scholar, Reg no: 18133164012042 ,  
St.Jude's College, Thoothoor, Affiliated to Manonmaniam Sundaranar  
University, Abishekapatti, Thirunelveli

**Dr. D L Jaisy**, Assistant Professor of English, St.Jude's College, Thoothoor,  
Kanniyakumari, Affiliated to Manonmaniam Sundaranar University,  
Abishekapatti, Thirunelveli

Jaishree Misra, one of the notable Indian women writers of the 21st century is of the view that love and faithfulness is the basement of all successful marriages. Marriage is considered as the perfect union of souls. In the marital bond it is the woman who is expected to adjust herself, for a husband is like a sheltering tree. She is an object a man who can manipulate. Woman indoctrinated to abide by the wishes of her husband. This becomes a major contributory factor for marital happiness. Women in India are nailed to the cross of matrimony. Misra portrays the mental sufferings of the protagonist Janu in *Ancient Promises*. As a girl of eighteen Janu, the protagonist felt in love with a Delhi boy, Arjun. She knew that her love affair with him would not lead to their marriage. At first, she could not understand the gravity of the problem and when her parents found her a partner, she protested. But soon she realized that she had no other means that to accept it. Janu was provoked when she came to know that, her marriage had been fixed with Suresh, he belonged to Maraar community in Kerala. She told her

parent that she wanted to continue her studies. But her parents were not ready to leave her. Women are annoyed when they find the married life totally different from the one they had enjoyed till then. Janu the protagonist of Jaishree Misra's *Ancient Promises* belongs to this category. The present study portrays the struggle behind the improper alliance of present day society.

**Keywords:** Victim, Alienation, Survival, Inferiority complex.



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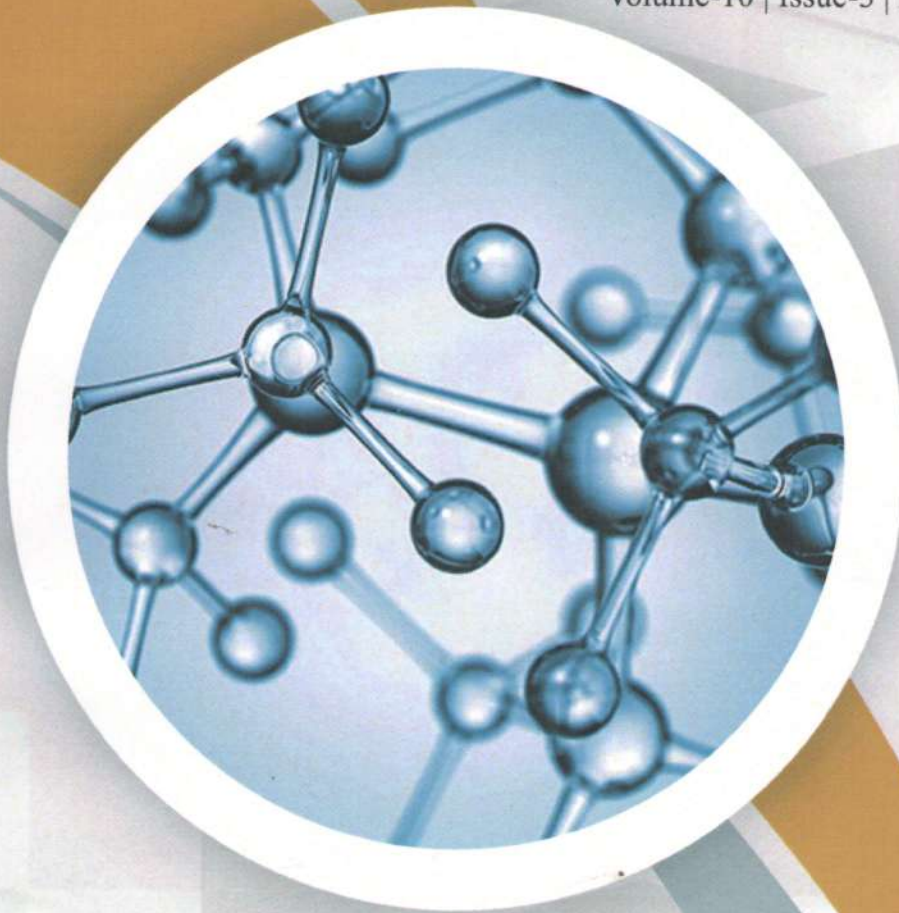
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MICROPROPAGATION OF MATURE *TERMINALIA CATAPPA* VARIETIES

## Forestry Science

**Farzana Tasneem**  
**MI\***

Research Scholar, Department of Biotechnology, Tumkur University.\*Corresponding Author

**Narasegowda P.N**

Department of Biotechnology, V. V. Pura college of Science, K R Road, Bangalore 560004.

## ABSTRACT

Micropropagation is used to multiply plants such as those that been genetically conventional plant breeding with the multiplying progeny. Plant tissue culture is a collection of techniques used to maintain or grow plant cells, tissues or organs under sterile conditions on a nutrient medium of known composition. Plant tissue culture is widely used to produce clones of a plant in a method known as micropropagation. Success of Plant tissue culture in recent years approaches have been used as an efficient tool for micropropagation of trees in short time. Propagation of woody trees through tissue culture has many advantages over conventional propagation with different methods like fast growth, season independent of production of the plant, germ plasm conservation and facilitating their growth. This review provides an overview of success achieved on in vivo work done for a number of important forest trees. Rapid culturing of producing clonal plants this review study of invitro work has been done for no of important forest trees [3]. Both the varieties were subjected, nodal explants were subjected with MS M. Growth hormones with the dilution of kinetin with 1-1.5 mg/ml and with the mixture of both Kinetin, BAP with the dilution of 1-3 mg/ml. Increase of time for 3-5 weeks the growth was 3-6 cm length. The study of micropropagation in both the varieties, all the values of the variables. Mean of at least 3 independent experiment. The MEAN±SEM and the extract number of experiments are given in legends. The Significant difference between control and each trial treatment was analysed using ANOVA showed statistical results as and ANOVA is  $p < 0.05$  is significant.

## KEYWORDS

*Terminalia catappa*, Micropropagation, Nodal culture, BAP, Kinetin.

## 1. INTRODUCTION:

Botanical derived medicinal plants play a major role in human society [4]. Plant extract has active ingredients [5] and extracts from the extraction of the medicinal plants contain several phytochemicals that can work alone or synergistically with others against various ailments. *Terminalia catappa* is an ornamental tropical tree belonging to the Family Combretaceae native to Southeast Asia in tropical regions of Asia, Africa and Australia. *Terminalia catappa* L has larger, glossy, dark green leaves, thicker branchlets, longer flower spikes and larger fruits. It is known by the common names such as Bengal almond, Country almond, False kamani, Indian almond, Malabar almond, Sea almond and Tropical almond [6]. The roots, stems, bark, leaves and fruits of these medicinal plants play an integral part in tackling diseases. The edible fruits from some of these plants are both nutrition, medicinally, nutritionally as well as pharmaceutically to human being. This plant is originally from Africa, Asia and Australia before spreading to other parts of the world. Due to globalization green revolution. It also causes significant litter on the ground [7]. *Terminalia catappa* featured high content of nutrients and polyphenols needed for biological metabolism and human health. In addition, heavy metals were also present at traces level indicating that these plants would be safe for medicinal uses [8]. Tropical almond can be consumed or used for preparing fruit salad, smoothie or for garnishing dishes. Oil can be extracted from the dried nuts which can be used for cooking. *Terminalia catappa* L is a Combretaceous plant, the extract of leaves and bark are reported for their anticancer, anti-HIV reverse transcripts, hepato-protective, anti-inflammatory, hepatitis, antidiabetic, as well as aphrodisiac. The leaves are used as food for the Tasar silkworm. The therapeutic potential of this plant is a primary importance to analyse its phytochemicals, secondary metabolites, antioxidant and antimicrobial activities, as it is vital in everyman's life throughout the history due to its usefulness either in the form of raw or processed or combined to drug find's application in pharmaceutical industries for health care [9]. The present study of the medicinal plant has been investigated in various pharmaceutical studies as it contains a variety of chemical component [10]

Micropropagation is the practice of rapidly multiplying stock plant material to produce a large number of progeny plants using modern plant tissue culture methods, an extremely effective tool. It is artificial process of producing vegetatively through tissue culture or cell culture techniques. This method is a production of cells from meristematic culture, callus culture, suspension culture, and embryo culture protoplast culture. A wide range of fruit ornamental and forest species are currently interested as for invitro propagation. The developed regeneration system is also used to developed regeneration system are

also used to optimize effective cryopreservation technique. This is widely used application of the tissue culture technology in agriculture and forestry. Plant tissue culture is a technique that has been developed technology around or more than 30 yrs. This process is an important technology in developing countries for the disease-free high quality planting material. This technique is used to produce large number of identical plants (clones) from a selected stock plant, propagation of rare species. Propagation of plants can be achieved through regeneration pathways that is axillary bud proliferation, somatic embryogenesis and adventitious bud formation [2,3]. The history of plant tissue culture and its applications have been reviewed and discussed.

Micropropagation is conventional plant breeding method. Multiplication is the taking of tissue samples produced during vegetative stage and increasing their number. Following methods are used for successful introduction and growth of plant tissue invitro. Plants can be propagated by sexual or asexual means clonal propagation or by the process of asexual reproduction by multiplication of genetic material. Identical copies of individual plants. Clone is used to represent a population derived from a single individual by asexual reproduction. In faster multiplication, large number of plants can be produced from a single individual in a short period possible to produce genetically identical plants. In this process sterile hybrids can be easily propagated in plants, tendrils. This method is expensive frequently unsuccessful. A handy technique for rapid multiplication of plants. Plant regeneration processes are called as organogenesis and somatic embryogenesis. Artificial seed propagation, study of genetic variability, production of disease-free plants. Totipotency of the cell has the genetic material capable of developing a pathway leading to the formation of an identical plant that is identical to the plant from which it is desired under control of the invitro of high intensity-controlled temperature and defined nutrient medium. This technique is used to establish and maintain virus-free plant stock, it is one of the conventional methods in the aseptic condition are essential to achieve success. In commercially vegetatively propagated plant species. A tissue culture technique used for plant propagation in which a part of tissue is taken from plant and grown in a laboratory to produce plantlets that are genetically identical to parents. National council of Italy said that identical cultures are identical to the parent. It is an innovative technique of high importance in Italy. Recent studies on medicinal plants are the most important source of life saving drugs for the population showed that the culture stimulates the development of axillary buds, apical dominance which allows massive elongation of shoots in gelled media. Objective of production for free stock, multiply plants, produce progenies which are genetically

genetic variability and recovery of distant parents, germplasm conservation and exchange of genetic material. Conservation of germplasm and also for propagation of forest trees is a major application of plant tissue culture. Micropropagation of tree species offers a rapid means of producing clonal planting stock of afforestation woody biomass production and conservation of elite and rare germplasm. This review provides an overview of the success achieved in work done for a number of important forest trees. In recent years use of tissue culture techniques for clonal propagation of forest trees has increased considerably by using juvenile as well as mature plant parts as starting material. Many tree species have been propagated successfully through nodal shoot proliferation from cotyledonary nodal explant of seedlings.

Micropropagation are being used by increasing number of research and commercial firms. Tremendous progress in plant tissue culture resulting in advances, successful and influenced by a variety of factors that are categorized either as environmental or hormonal-plant growth regulators factors, acclimatization and subsequent standard method of propagation for many species of economic importance and mass production scaled mechanized efficient and integrated systems of micropropagation will allow mass production of important in vitro plant products as flavorings, pharmaceuticals, health beneficial plant compounds. Sufficient literature is available on various aspects of tissue culture studies in important plant and desert trees. As an application of Micropropagation, the Plant tissue culture is sufficient for the production of millions of clones in a year using micropropagation. It would be great deal of time to produce an equal number of plants using conventional method has more scope and time. This technique of micropropagation is a good alternative for those plant species that show resistance to practice of conventional propagation. It is an alternative method of vegetative propagation in a short period. Any particular variety may be produced in large numbers and time to develop new varieties is reduced by 50% large number of plants are maintained in small spaces and storage of germplasm. Production of in vitro stock can be done at any time of the year. This technique is useful for seed production in certain crops as the maintenance of genetic conservation to a high degree is important for micropropagation. Somatic embryogenesis is the production of synthetic natural seeds.

#### Review of literature:

The main objective of tissue culture work was ascertaining the possibility of culturing the cell indefinitely. Plant biotechnology study reveals that having tissue culture as an important tool offers approaches for genetic improvement of any species. Micropropagation is a powerful tool for fast multiplication of selected genotypes at faster rates; therefore, it has been adopted in agriculture as well as in forestry. An innovative approach to tissue culture using meristematic cells like root and stem tips was reported [1]. A significant breakthrough in tissue culture was the discovery of Auxin [2]. Revised medium for rapid growth and bio-assays with tobacco tissue cultures is studied. Physiology of the Plant was conducted [2].

The history of plant tissue culture begins independently stated the cell theory and proposed the totipotency which states that the cells are totipotent in principle are capable of regenerating to give a complete plant. In vitro vegetative propagation methods were started with Ball [1946] pointed out exactly which part of a shoot meristem gave rise to a whole plant. Plant tissue culture is a collection of techniques used to maintain or grow plant cells, tissues or organs under sterile conditions on a nutrient culture medium of known composition. Plant tissue culture is widely used to produce clones of a plant in a method known as micropropagation, the success of plant tissue culture [1]. Several conditions about the requirements in media in experimental conditions which induce cell division proliferation and embryo induction and he is regarded as father of tissue culture [13].

Depends on the choice of the nutrient as required by the whole plant, growing in vitro are mainly heterotrophic, that is they cannot synthesize their own food as mass values of providing them with the macronutrients and micronutrients ( $\mu\text{mol/l}^{-1}$ ). Plants containing medicinal and medicinal properties have been known and used as sources of food, fodder, oils, medicines fuel, wood, fibres and timber by increasing population growth due to increased demand for pulp, paper, construction materials, farmlands and fuel, status of woody micropropagation forest trees are greatly affected. Plant is our wealth and

its conservation is important for economic ecological and scientific medicinal and ethical issues therefore, there is a great need to conserve forest ecosystem by agrotechnology in recent years approaches have been used as an efficient tool for micropropagation of trees in short time. Propagation of woody trees through tissue culture has many advantages over conventional propagation with different methods like fast growing season independent of production of the plant germ plasm conservation and facilitating their growth.

Micropropagation of tree species offers rapid means of producing clonal plants this review states that in vitro work done for number of important forest trees. [3] Cotyledonary node explants excised from 21-day old seedlings of *T. arjuna* produced multiple shoots were cultured on full strength of modified MS (1/2MS and Fe-EDTA). Proliferating shoot culture was established by reculturing the original cotyledonary nodes 88% shoots could be obtained well after 15hrs of pulse treatment with IBA [5]. The cotyledonary explants excised from 2-day old seedlings of *Terminalia arjuna* produced multiple shoots when cultured on full strength MS or modified M S Media with different concentration (0.1-1.0 mg/ml) of BAP maximum [4][7]. Shoots explants were recorded after 30 days of inoculants about 80% of the plantlet were successfully acclimatized [14]. The different techniques in plant tissue culture may offer certain advantages over traditional methods of propagation [15][16,17].

Micropropagation of mature *Terminalia catappa* (Indian Almond) a medicinally important forest tree reported on efficient in vitro propagation of *Terminalia catappa* using nodal segments of a 15-year-old mature tree nearly 75% of the plantlet could be acclimatized within 5 weeks and successfully established this is the first report on micropropagation of *Terminalia catappa* which can be applied for further genetic transformation assays and pharmaceutical purposes [2].

An efficient and improved in vitro propagation method has been developed for *Terminalia bellarica* a medicinally important tree from nodal explants of 10 years old mature tree. Shoot multiplication was influenced successive transfer of mother explants for differentiation and subculture with excised shoot on fresh medium of MS Medium containing 2.22  $\mu\text{M}$  BAP was found to be the shoot multiplication. Further enhancement in morphogenetic response when excised shoot clumps on MS medium supplemented with 2.22  $\mu\text{M}$  BAP, 1.16  $\mu\text{M}$  Kn and 0.5  $\mu\text{M}$  IAA. Plantlets rooted in vitro as well as ex vitro were acclimatized successfully under the green house condition. Plant production serves as a more economical option present method is used for large scale commercial production of this medicinally important tree. The trial investigation to the effects of coconut milk on stem and root cuttings of *Terminalia catappa* there was a significant interaction between cutting type and coconut milk should be used for vegetative propagation programs of species. Rapid in vitro micropropagation protocol of *Terminalia bellarica* was achieved by nodal explants when placed on medium supplemented with 0.5mg/l, 6-BAP showed 100% shoot bud with 4.5-0.56 shoot length per explants. The nodal segments from micro shoot obtain from induction medium were cultured on MS medium supplemented with different concentration of hormones like BAP, NAA. These cultures were placed in green house for primary hardening. After four weeks plants were transferred from green house to net house where the plants exhibited gradual acclimatization to outdoor conditions. Nodal segments obtained from 15 day old aseptically grown seedlings were used as explants, shoot multiplication was achieved on MS medium containing BAP and Kn. The maximum number of shoots was obtained with 3.5 mg/l BAP+0.5 mg/l Kn. Best rooting was observed on medium containing quarter strength MS salts, 0.8% agar and 1.0 mg/l IBA. Plantlets were hardened initially in culture room conditions and then transfers to mist house. Maximum callus induction response was observed on M S medium supplemented with 0.25 mg/l, 2, 4-D + 0.3 mg/L Kinetin within 4 weeks from leaf petiole. Maximum callus induction response was observed on medium supplemented with 0.25 mg/ml of 2,4D +0.3 mg/ml of kinetin within 4 weeks from leaf petiole.

The result of this study in the leaf architectural characters are of great help in plant taxonomy and systematic most especially in dealing with sterile plant specimens [9]. The micropropagation of *Terminalia bellarica* from mature tree M S medium gave best shoot bud proliferation system in incorporation of antioxidants and PVP, the mother plant confirmed true type clonal explants. The study reported that *Terminalia bellarica* from nodal segments of a 30 years old tree.

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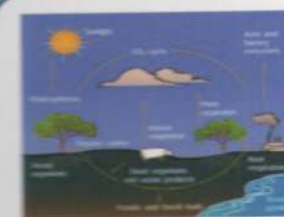
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## Assessment of *Terminalia catappa* varieties using RAPD and SSR Markers

Farzana Tasneem M.I

Assistant Professor, HOD, Dept of Biotechnology, Surana College, South end Circle Bangalore-04

### Abstract

DNA marker study was used to evaluate the genetic diversity in two varieties of *Terminalia catappa* sample collected from different places of Bangalore city. It is a large tropical tree found in tropical regions of Asia, Africa, Australia belongs to the family Combretaceae. The parts of the plant have a wide spectrum of medicinal uses, commonly fruits are used as a medicine for urinary tract infection and the seeds are a rich source of protein. The leaves are antibacterial, antifungal, preventing ageing, imparts longevity, immunity, and body resistance against diseases. The leaf samples were subjected to DNA isolation by using CTAB method and further PCR amplification was done to molecular markers study by RAPD and SSR analysis. The amplification accomplished by using 4 primers (OPA-11, OPC-5, OPA-9 and OPD-5). The dendrogram was constructed based on the binary data generated from the RAPD markers. The clustering of *Terminalia* genotypes was carried out using Jaccards coefficient, which resulted in the formation of two clusters. Cluster one consisting of genotypes 1 and 2 where as cluster 2 consists of genotypes 3 and 4. A dendrogram was also constructed by using the binary data generated from scoring the gels of SSR amplified bands. Three main clusters were formed genotypes 1 and 3 formed the first cluster with more genetic similarity values. Whereas the genotypes 2 and 4 formed the second cluster with higher dissimilarity values than the first cluster indicating the presence of variation and genotypes 2 and 4 clustered with genotypes 1 and 3. In conclusion, the study of molecular characterization of PCR based RAPD and SSR markers by using primers for the two varieties of *Terminalia catappa* showed difference in genetic diversity, which provides the information for the study as diagnostic markers in herbal drug preparation.

**Key words:** *Terminalia catappa*, RAPD, SSR, CTAB, Genetic diversity.

### Introduction:

*Terminalia catappa* is an ornamental tropical tree belonging to the family Combretaceae, native to the tropical regions of Asia, Africa, and Australia. It is known by the common names Bengal almond, country almond, false kamani, Indian almond, Malabar almond, sea almond, and tropical almond. It is a large deciduous perennial tree reaching a height of between 15-25 m and about 9 m in width with symmetrical canopy and characteristic pagoda shape (Edward and Dennis, 1964 and Mitchell, 1964). It is cultivated in Nigeria as a shade tree and for its fruits. The seeds are eaten as fruit as well as for medicinal uses (Oni and Bada, 1982). The greenish yellow leaves are clustered in axillary spikes, small and inconspicuous and usually commences flowering within 2-3 years of out planting but this may vary with site and genotype. *Terminalia* species showed the clustering of species for morphological studies (Vishal .P et.al., 2009). Different factors contributed to genetic structure of *Terminalia catappa* on geographical scales (Arjuna ratnayaka 2015). Characterization of molecular markers is highly sensitive and effective technology therefore molecular markers can be employed to characterize the present genetic markers (Tharachand C et.al., 2012). Plants produces DNA of good quality and quantity which can be used as PCR based studies (B.O. Oboh et.al., 2009). RAPD-PCR is means of creating a biochemical fingerprint of an organism and is used to analyze the genetic diversity of an individual by using random primers. RAPD successfully discriminates among all species therefore providing an easy and rapid tool for investigation (Ranade 2001). Microsatellite is a track of repetitive DNA in which certain DNA motifs ranging from 2-13 base pairs are repeated typically 5-50 times. Microsatellites occur at thousands of locations within organisms genome leading to high genetic diversity (Maryam sarawath et.al., 2005 and Shasikala 2015).

The review states the various methods used for plant genomic DNA. The renaissance in herbal medicine to detect morphology of DNA (Chen et.al., 2014). Modified CTAB technique for Isolation of DNA from some medicinal plants this method gives the purity range. Research Techniques made simple Polymerase Chain Reaction (PCR) it is used in forensic medicine to identify criminals and it provides information for sophisticated analysis of genes and the genome. (Lilit Garibyan et.al., 2013). Review mainly focuses on authentication of ayurvedic herbal medicines by DNA based fingerprinting methods to prevent intentional and adulteration or substitution of targeted ayurvedic medicinal herbs (Santosh Kumar .P 2014). Due to the use of RAPD as Molecular markers for Taxonomic and systemic analysis of plants. Phytochemical and Antimicrobial Studies on *Terminalia catappa* by using RAPD Technique and (SSR) markers (Salim Khan et.al., 2009). DNA profiling role of DNA and the database in forensic investigation (S. Pannerchelvam et.al., 2003). DNA-based simultaneous identification of three *Terminalia* species Targeting Adulteration and to identify approaches are advancing the conventional (Sonalsharma, and Neeta Shrivastava 2016).

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