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Volume II

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PREFACE

We are delighted to publish our book entitled ***"Advanced Research in Material and Chemical Science Volume II"****. This book is the compilation of esteemed articles of acknowledged experts in the fields of Chemical Science, Material Science and Nanotechnology.*

This book is published in the hopes of sharing the excitement found in the research and study of chemical and material science. Chemical and material science can help us unlock the mysteries of our universe, but beyond that, conquering it can be personally satisfying. We developed this digital book with the goal of helping people achieve that feeling of accomplishment.

The articles in the book have been contributed by eminent scientists, academicians. Our special thanks and appreciation goes to experts and research workers whose contributions have enriched this book. We thank our publisher Bhumi Publishing, India for taking pains in bringing out the book.

Finally, we will always remain a debtor to all our well-wishers for their blessings, without which this book would not have come into existence.

- Editorial Team
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CONTENTS

SYNTHESIS STRATEGIES OF MoO_3 NANOSTRUCTURE-BASED ELECTRODES FOR SUPERCAPACITOR APPLICATION: A STATUS REVIEW

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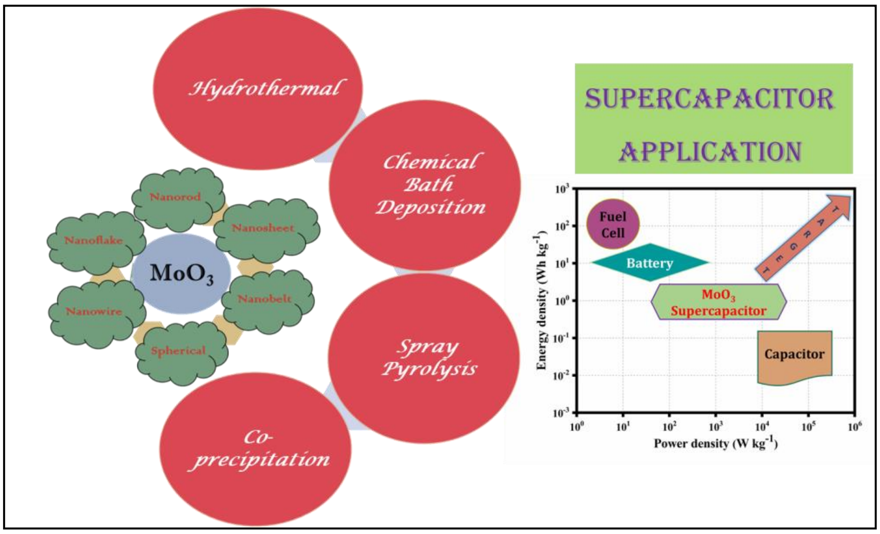
Abstract:

An emerging novel energy storage device-supercapacitors can store electrical energy and deliver quickly whenever needed. Supercapacitors hold potential to replaces batteries and conventional capacitors, due to its relatively higher energy density, power density, fast charge discharge rate, cycling stability. The performance of supercapacitor mainly depends on the nature of electrode material, so researchers focused on the developing electrode material. In this perspective, metal oxides with more active site are considered as competent candidate for enhanced supercapacitive performance. In this review concise description of synthesis of MoO_3 targeted via numerous strategies such as hydrothermal, chemical bath deposition, spray pyrolysis and co-precipitation has been discussed. This discussion highlights the future opportunities of MoO_3 electrode material for the supercapacitorapplication.

Keywords: MoO_3, Nanostructure, Supercapacitor, Synthesis strategies.

Graphical Abstract:



1. Introduction:

The demand for energy is increasing day by dayfor the development of the human population and rapid industrialization.So, there has been an urgent priority to develop and scale up environmental-benign, sustainable, clean energy harvesting and their associated efficient storage devices. As electronic gadgets become essential and obligatory part of our life, it is necessary to develop high performance energy storage devices to keep them charged throughout the day with using less power. Electrochemical capacitors (ECs), also called supercapacitors, play a crucial role in satisfying the demand energy in accomplishing our day-to-day necessities. In both academia and industry, supercapacitors have grabbed more attention due to its distinct characteristics such as higher power densities (compared to battery), higher energy density (compared to conventional capacitor), fast charge-discharge rate, long cycle life ($>10^6$ charge–discharge cycles) (Suprimkumar D Dhas *et al.*, 2021; Lohar *et al.*, 2021). Depending on their charge storage mechanism, supercapacitors are briefly categorized as electrochemical double-layer capacitors (EDLCs), pseudocapacitors and hybrid-capacitors. In literature many research groups have focused their attention on the transition metal oxides (TMO) such as NiO(Pore *et al.*, 2021), V_2O_5(M. D. Patil *et al.*, 2021), MoO_3(Zhao *et al.*, 2020), MnO_2(Zhang *et al.*, 2021), CuO (A. S. Patil *et al.*, 2017) etc. as efficient electrode materials, which store charge faradaically (pseudo-capacitors). Amid, MoO_3 is a competent candidate for energy storage devices, due to its low cost, non-toxicity, ease of synthesis, unique layered structure, high electrochemical activity and environmentally benign nature. There are several reports on MoO_3thin films that have presented novel scientificand technological applications in various fields likegas sensors (Mane *et al.*, 2016), supercapacitor(Gurusamy *et al.*, 2021), Li-ion battery(Udayabhanu *et al.*, n.d.), electrochromism(Santhosh *et al.*, 2020), optoelectronic devices(Adewinbi *et al.*, 2021)and many others.

The n-type semiconducting MoO_3 has a wide band gap of 2.8-3.6 eV(Malik *et al.*, 2021).The nanocrystalline MoO_3shows polymorphism: thermodynamicallystableorthorhombic α-MoO_3 phase, two meta-stable phasessuch as monoclinic (β-MoO_3) and hexagonal (h-MoO_3) (**Fig. 1**).All these phases constructed by using cornerstone MoO_6 octahedron as central pillars. The unique layered orthorhombic α-MoO_3 phase is formed by edges and corners sharing zigzag chain of MoO_6 octahedra. This stacking layered building blocks connected through van der Waals forces. The cornersharing MoO_6 octahedra in monoclinic β-MoO_3 form a distorted cube, while in hexagonal h-MoO_3 building blocks connect through the cis-position(Song *et al.*, 2007; L. Zhou *et al.*, 2010). The gaps present in peculiar crystalline layered structure of MoO_3 are favorable for intercalation/deintercalation of electrolyte ions and molecules into the bulk electrode, also provide shorter diffusion paths.

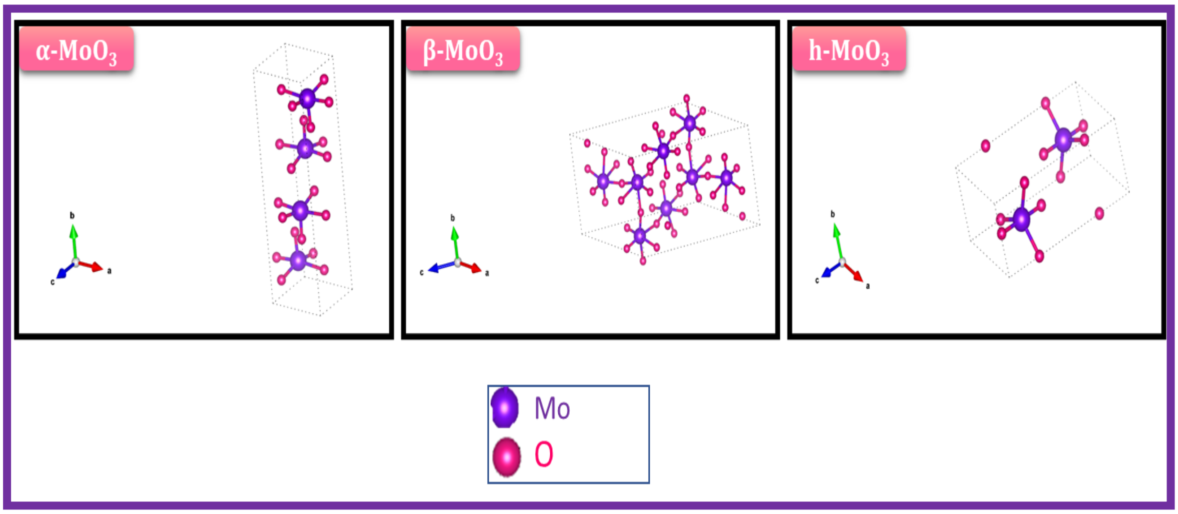


Figure 1: Crystal structure of α- MoO_3, β- MoO_3, h-MoO_3
[JCPDS Card # 00-005-0508, 00-047-1081, 00-021-0569 respectively]

Thus, in recent years numerous efforts have been made to develop nanostructure MoO_3 electrode material with high surface to volume ratio, in order to boost the supercapacitive performance.The unique structures of MoO_3 are probably advantageous for the charge storage mechanism. These painstaking efforts are reflected in an increasing number of publications on MoO_3 nanostructure electrodes for supercapacitor application (**Fig. 2**). Keeping eye on this, present review article drafted in line journey of MoO_3 nanostructure synthesis approach for supercapacitor application.

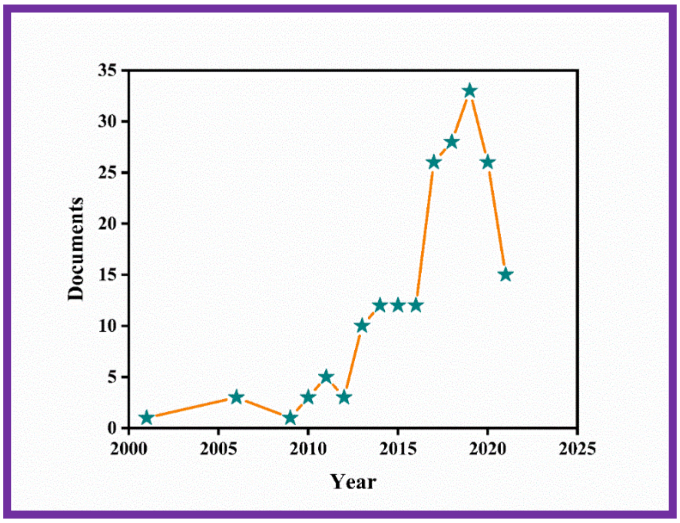


Figure 2: Number of publications on $MoO_3$for supercapacitor application per year [Source: Scopus; TITLE-ABS-KEY (MoO_3 AND supercapacitor)]

2. Synthesis strategies for MoO_3 electrode materials:

The morphology and structure of metal oxides are important characteristics for enhancing its functional properties. These parameters are controlled by using different synthesis strategies, or different precursors, or different environmental conditions like temperature, pH, concentration etc. of electrode materials (Zappa *et al.*, 2018). Till today, a variety of synthesis strategies have been employed to fabricate MoO_3 electrode materials.Some synthesis methods are described here briefly:

2.1 Hydrothermal Method

A hydrothermal method is a solution-based synthesis route most commonly employed for high-purity nanomaterials preparation.Hydrothermal method relies on morphology-controlled synthesis of nanomaterials ata wide rangeof temperature and pressure(S D Dhas *et al.*, 2021; Gan *et al.*, 2020). The process is carried out in a sealed container placed in a furnace. This method forces hydrolysis of reactant precursors for crystallization, and simultaneously resist introduction of contaminants from the growth environment in order to produce high purity nanomaterials (Suvaci& Özel, 2021). The powdered products obtained as a result of hydrothermal treatment are high purity, controlled morphologies and desirable particle size, essential phase stability. These novel properties of as-obtained products are beneficial in both laboratory and industry to tackle the technological challenges and meet the advanced productive requirements and efficient skills. In literature many researchers have synthesized nanostructured MoO_3 and its composite via hydrothermal route and their path breaking finding have been presented in **Table 1**.

Table 1: A detailed overview of supercapacitive performance of nanostructured MoO_3 and MoO_3 based composites synthesized via hydrothermal route

Material	**Precursor**	**Temp. ^{0}C/ hrs**	**Morphology**	**Substrate**	**Electrolyte**	**Performance**		**Ref.**
						capacitance	**Stability (%)/ no. of cycles**	
MoO_3 nanostructure								
α-MoO_3	Molybdic acid	180 / 6	Nanorods	Glassy carbon electrode	1M H_2SO_4	30 F/g @ 5 mV/s	-/100	(Shakir *et al.*, 2010)
α-MoO_3	sodium molybdate	160 / 12	Nanobelts	Nickel foam	0.5 M Li_2SO_4	302 F/g @0.1 A/g	90/500	(Li & Liu, 2013)
α-MoO_3	Mo powder	180 / 48	Nanobelts	ITO	1M H_2SO_4	8.8 F/g @20 mV/s	-	(Mendoza-Sánchez *et al.*, 2013)
MoO_3	AHM	180 / 20	Nanobelts	Nickel foam	0.5 M Na_2SO_4	256.83 F/g @ 5 mV/s	-/200	(Pal & Kumar Chattopadhyay, 2018)
α-MoO_3	AHM	180 / 20	Nanobelts	Nickel foam	6 M KOH	445 F/g @0.5 A/g	58/1000	(Wen *et al.*, 2019)
MoO_3 -based nanostructure								
PPy/ MoO_3	AHM	180/ 24	Nanorod	-	1 M H_2SO_4	687 F/g @1 A/g	83/3000	(Wu *et al.*, 2016)
MoO_3/$NiMoO_4$	Mo powder	200/24	Nanobelts	Nickel foam	3 M KOH	1307 F/g @1 mV/s	171/10000	(Xingyan Zhang *et al.*, 2018)

MoO_3/GF//PANI/(MnO_2-RGO)/PANI	Molybdenum chloride ($MoCl_3$)	150/12	rectangular nanocrystals	Nickel foam	PVA/KOH	146 F/g @1 A/g	82/5000	(Ghosh & Yue, 2018)
MoO_3/GF//MoO_3/GF						136 F/g @1 A/g	85/5000	
$MoO_3/TiO_2/Ti_3C_2T_x$	AHM	180/24	Layered	Nickel foam	1 M KOH	162 F/g @2 mV/s	91/8000	(Q. Zhao *et al.*, 2018)
MoS_2/MoO_3/PPy	Sodium molybdate	200/10 min	Core shell	activated carbon cloth	2 M H_2SO_4	527 F/g @5 mV/s	-	(Indah Sari & Ting, 2019)
MoO_3/MnO_2	AHM	180/24	Nanorods	carbon paper	1 M NaOH	352 F/g @1 mV/s	82.2/3000	(Cao *et al.*, 2017)
MoO_3/ GA@PPy	$MoCl_5$	170/1.5	Spherical	glassy carbon electrode	1M HCl	1788 F/g @1 A/g	89.3/1000	(Xin *et al.*, 2020)
$MoO_3/Ti_3C_2T_x$	AHM	180/24	Layered	Nickel foam	1 M KOH	151 F/g @2 mV/s	93.7/8000	(Zhu *et al.*, 2016)
MoO_3/ rGO	AHM	200/24	Nanorod	Nickel	1 M Na_2SO_4	486 F/g @1 A/g	92/1000	(Prakash, *et al.*, 2019)
MoO_3/Pd	AHM	200/24	Nanorod	Nickel	1 M Na_2SO_4	501 F/g @1 mA/g	94/1000	(Prakash *et al.*, 2019)

NiO@Ni(OH)$_2$-α-MoO$_3$	molybdenum chloride	160/12	nanosheets and nano spherical	Nickel foil	1 M KOH	445 F/g @1 A/g	97.3/3000	(Manibalan *et al.*, 2021)
MoO$_3$/ppy	Mo powder	180/12	Core shell nanobelts	Carbon	1 M Na$_2$SO$_4$	285 F/g @0.5 A/g	-	(Du *et al.*, 2018)
MoO$_3$–MWCNTs	MoO$_2$	180/6	nanowires	glassy carbon electrode	1 M NaOH	178 F/g @20mV/s	55/100	(Shakir & Sarfraz, 2014)
Fe$_3$O$_4$-rGO- MoO$_3$	Sodium molybdate	180/24	Nanoparticle	Carbon cloth	2M LiCl	1666.50 F/g @2.5 A/g	95.01/5000	(Khan *et al.*, 2020)
MoO$_3$ NPs						952.38 F/g @2.5 A/g	92.5/5000	
PANI// MoO$_3$	Mo powder	220/14	Nanobelts	Ti mesh	0.1 M Fe$^{2+/3+}$/0.5 M H$_2$SO$_4$	197 F/g @ 1 A/g	109/1000	(Meng *et al.*, 2020)
MoO$_3$					0.5 M H$_2$SO$_4$	1243 F/g @2 mV/s	-	
MoS$_2$/MoO$_x$	Sodium molybdate	200/10	nanoflowers	activated carbon cloth	1 M H$_2$SO$_4$	230 F/g @ 5 mV/s	128/1500	(Sari & Ting, 2018)
MoS$_2$/MoO$_3$	AHM	190/8	Nanosheets	-	0.5 M NaOH	287.7 F/g @ 1 A/g	97.4/1000	(Vattikuti *et al.*, 2018)

PANI/MoO_3/ACC	AHM	180/20	Layered	activated carbon cloth	1 M H_2SO_4	1050 F/g @ 0.5 A/g	71/2000	(Ling *et al.*, 2018)
MoO_3/ACC			Microrods			296.7 F/g @ 0.5 A/g	91/600	
α-MoO_3/graphene	AHM	120/12	Nanoflakes	Graphite		360 F/g @ 0.2 A/g	100/1000	(J. Zhou *et al.*, 2015)
h- MoO_3/AC	AHM	180/12	Rod shaped	stainless steel (SS)	1 M Na_2SO_4	211 F/g @ 2 mV/s	79/5000	(Sangeetha *et al.*, 2020)
MoO_3–MWCNT	MoO2	180/10	nanowires	-	1 M Na_2SO_4	210 F/g @ 5mV/s	95/2000	(Shakir *et al.*, 2011)
MoO_3@SnO_2	Sodium molybdate	180/24	Nanobelts	Nickel foam	0.5 M Na_2SO_4	584.3	86.2/2000	(S. Wang *et al.*, 2017)
Ni doped MoO_3	Sodium molybdate	180/20	Nanobelts	Nickel foam	1 M Na_2SO_4	~60 F/g @ 10 mV/s	-	(Xia Zhang *et al.*, 2018)
Cu doped MoO_3			Nanobelts			~50 F/g @ 5 mV/s	-	
Mn doped MoO_3			Nanobelts			~47 F/g @ 5 mV/s	-	
Co doped MoO_3			disordered sheet			~30 F/g @ 20 mV/s	-	
Cr doped MoO_3			disordered sheet			~10 F/g @ 5 mV/s	-	

2.2 Chemical Bath Deposition (CBD) Method

Among various wet chemical synthesis techniques, CBD is the simplest, cost effective method widely used for producing functional electrode materials at relatively lower temperature. Thin film formation using CBD method occurs via two types of growth mechanism: ion-by-ion growth and cluster-by-cluster growth(Chodankar *et al.,* 2014). In literature three reports are available on synthesis of MoO_3 thin films using CBD method for supercapacitor application.Pujari et al.(Pujari *et al.,* 2016) synthesized hexagonal microrods of MoO_3 at relatively low temperature (343 K) and studied its supercapacitive properties in Na_2SO_4 electrolyte. Kariper *et al.,*(Kariper & Meydaneri Tezel, 2019), placed molybdate ions into the active sites (holes and cracks) on the surface of enzymes using bio-chemical bath deposition technique for the first time. Later,Yu et al.(Yu *et al.,* 2020), fabricated PANI//MoO_3roll-type asymmetric supercapacitors on carbon fiber. This assembled asymmetricsupercapacitor widened the potential range (1.5 eV), which resulted in higher energy and power densities and found application in wearable systems.

2.3 Spray Pyrolysis Method

In spray pyrolysis technique, a precursor solution is sprayed or injected through a nanoporous nebulizer onto the hot substrate in the furnace at a given temperature. Theseprecursor droplets vaporize vigorously anddecompose to form the final desired material on the surface of the substrate. MoO_3 thin films are synthesized using spray pyrolysis techniques for various potential applications like gas sensing (Mane & Moholkar, 2018),resistive switching memory devices (Rasool *et al.,* 2020),photochromism (Afify *et al.,* 2017).However, reports on synthesis of sprayed MoO_3 electrode material for supercapacitor application are scanty (Deokate *et al.,* 2021), sprayed α-MoO_3 on conducting FTO substrate. Synthesized nanosheet type α-MoO_3 electrode shows capacitive behavior with a specific capacitance of 1249 F/gand cycling stability of 85% even after 5000 cycles.

2.4 Co-precipitation method

Co-precipitation method is another pathway to synthesize nanostructured MoO_3, offer several advantages like simple manufacturing, controlled particle size and morphology, energy efficient, and can operate at lower temperature. The co-precipitation method simultaneous nucleation, growth, agglomeration processes that occur on the surface of the substrate (Rane *et al.,* 2018). Although many researchers across the globe reported the co-precipitative synthesis of

MoO_3 for various applications like industrial wastewater treatment, photodegradation of dyes (Ama *et al.,* 2018; Tariq *et al.,* 2020) etc., no single report available for supercapacitor application. Tian *et al.* (Tian *et al.,* 2017) have synthesized needle like $CoMoO_4$ via chemical co-precipitation in hydrothermal condition, and observed that the presence of Mo in $CoMoO_4$ indirectly affect the electrochemical performance of electrode material.

3. Effect ofmorphology on supercapacitive performance:

The surface morphology of electrode material plays an important role in its potential application. Designing the different morphologies of electrode material could result of different synthesis parameters. Nanoscale morphologies of electrode materials have larger surface area to volume ratio, which provide more active area for diffusion of electrolyte ion and leads to enhance the supercapacitive performance (Simon & Gogotsi, 2020). MoO_3 nanostructures are morphology rich material, designed in 1-dimentional nanobelts (Mane & Moholkar, 2017; Mo *et al.,* 2020; L. Zhou *et al.,* 2010), nanorods (Shakir *et al.,* 2010; Swathi *et al.,* 2020); 2-dimentional nanosheets (Sen *et al.,* 2019; Vattikuti *et al.,* 2018; Wang *et al.,* 2020), nanoflakes (J. Zhou *et al.,* 2015); 3-dimentional nanoflowers (Sari & Ting, 2018) and many others (Du *et al.,* 2018; Manibalan *et al.,* 2021; Xin *et al.,* 2020). To take benefit of this, in past few years, particular research attention paid towards different morphologies, to boost the electrochemical properties.

4. Conclusion and future outlook:

This book chapter imprints some efficient strategies to fabricate MoO_3electrode material for supercapacitor application. It covers an up-to-date progress on synthesis of MoO_3 via hydrothermal, chemical bath deposition, spray pyrolysis and co-precipitation. The environmentally friendly, low-cost, scalable, simple and easy synthesis route make the electrode material fill the practical lacunas in academic research and industrial production. From the literature study, author believes that more research focus should be highlighted on the novel deposition techniques for MoO_3 nanostructure and its potential application in the field of energy storage. Further, to explore full capability of the electrode materials, it is necessary to optimize synthesis parameters like temperature, pH, concentration etc., and material properties. To meet the rising demand of energy storage devices, some researcher doped or make composite of electrode with other potential candidate, while some researcher paid their attention on hybrid capacitors. These encouraging results open up the challenges to develop MoO3 electrode for improving overall supercapacitive performance.

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GREEN SYNTHESIS OF NANOPARTICLES USING *MANILKARA ZAPOTA* PLANT EXTRACTS: A REVIEW

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Abstract:

Nanotechnology plays a crucial role like other fields like engineering, medicine and pharmacy, which comprise the materials that exist at the nanoscale (1-100nm) with one or more dimensions. For several research and commercial purpose, nanoparticle is synthesized by numerous methods. Among them green synthesis method utilize plants, fungus, bacteria and algae as a source for the ecofriendly and cost effective nanoparticles production. Therefore, this review paper considers various nanoparticles synthesized from different parts of *Manilkara zapota* plant to determine its antidiabetic, anti-inflammatory, antibacterial, antifungal, antioxidant, anticancer and antiarthritis activities. *Manilkara zapota*comes under the family Sapotaceae and is widely recognized all around the global for its medicinal importance. This review article provide a way to investigate the potential of *Manilkara zapota* plant in an exceedingly nanoscale level.

1. Introduction:

Nanotechnology arrived as a new field of research which includes synthesis and development of numerous nanoparticles and nanomaterials [1]. Nano is a Greek word means "Dwarf"- extremely small, of about 10^{-9}[2]. The nanoparticles are having distinctive characteristics, such as different shape, size and structure. They possess uniform or irregular surface variations, some of them are crystalline or amorphous in nature [3].

Synthesis of nanoparticles is mediated by different methods such as green, physical and chemical. Physical methods such as Molecular beam epitaxy, Thermal evaporation, High vacuum pulsed laser deposition etc., are used [4]. Chemical methods such as wet chemical,

chemical and direct precipitation, Electrode position, microwave assisted combustion, Spray pyrolysis, Chemical micro emulsion, etc., are used [5]. But these methods uses toxic and hazardous chemicals, it will affect the environment and the human being [6]. To avoid this now-a-days green synthesis methods are used for the efficient synthesis of metal nanoparticles like Gold, Silver, Zinc oxide, Copper and others. In green synthesis the plant extracts are widely used due to their availability and easy handling processes [7].

Manilkara zapota, *P. Royen*, or *Achrassapota*, comes under the family Sapotaceae [8]. Sapodilla is a resultant of the Zapotilla, a Spanish word which represents small Zapote (a soft edible fruit) [9]. The fruit is widely known as Sapodilla, Chikoo or Sapota. Origin of sapodilla is in Mexico and is innate to America. But it is also grown in various countries of Asia including India for different purposes [10]. It is large, evergreen and globrous tree with a milky juice [11]. And the height is 30m with a diameter upto 1.5m. The leaves are very simple, glabrous, peak thick to just acuminate, oblong and gathered at the leaf tips. Flowers appear green in colour, solitary, bisexual, 6 sepals, and 6 corolla lobes and havea brown pubescent peduncle [12].

Fruit is brownish in colour and taste sweet and juicy with scented. It looks like a globular berry which isovoid and outer layer is with rough brown skin and inside it has 1-12 shining, black or brown seeds (frequently 5) [9]. The plant parts are very useful in traditional medicines like Ayurveda. These leaves, fruits, flowers are used for curing bronchitis, cough, cold, diarrhea and dysentery. It's bark and seeds are used for febrifuge, aperients, astringent and diuretic tonic. It has a natural energizer like fructose/sucrose enriched with minerals, vitamins, dietary fibers which are also used to prevent micronutrient malnutrition [14]. It is widely cultivated in tropical conditions across so many countries for aids like eatable fruits, wooden, fluid, etc. [15]. Synthesis of various nanoparticles using *Manilkara zapota* plant extracts has been reported in this present study.

2. Taxonomy:

Sapotaceae family which is having an ecologically diverge family of 800 species and 65 genera, shrubs and trees are also included in this family [15]. With the combination of milky latex and alternate (spiral) leathery leaves with parallel secondary and tertiary veins, they can be easily confessed by these characteristics [16]. 30-32 species of *Manilkara* genus are most important commercially and economically used as a basis of wooden, fruits and fluid [15].

Table 1: Toxonomy of *Manilkara zapota*

Kingdom	Plantae (plants)
Sub kingdom	Tracheobionta (vascular plants)
Super division	Spermatophyta (seed plants)
Division	Magnoliophyta (flowering plants)
Class	Magnoliopsida (dicotyledanae)
Sub class	Dilleniidae
Order	Ebenales
Family	Sapotaceae
Genus	*Manilkara Adans* (Manilkara)
Species	*Manilakara zapota* (L.) van Royen

Vernacular names:

Table 2: *Manilkara zapota* have a number of vernacular/common names [16]

Country/Language	Vernacular/Common Name
Brazil	Sapoti, Sapotilha
Bahamas	Dilly
Cuba	Sapota, Sapote
Puerto Rico	Nispero
Thailand	Lamoot, Lamut, Lamut-farang
English	Sapodilla
Indonesia	Sawu
India	Chickoo, Chicku, Chiku
E1 Salvador	Muyozapot
Mexico	Chicopote, Chicozapote
West Indies	Nasebery
Dutch West Indies	Sapatija, Sapodilla plum, Sapodille
French West Indies	Sapotille, Sapotillier
Singapore	Ciku
Malaysia	Chikoo
Surinam	Mispu, Mispel, Mispelboon
Sinhala	Sapodilla, Rata mee
Virgin Island	Mespel

Synonyms:

In literature large number of synonyms is used such as *Manilkara achras (Miller) Fosberg, Manilkara zapotilla (Jacq) Gilly, Achraszapotilla Nutt, Achras mammosa L., Achras zapota L varzapotilla Jacq, Achras sapota L., Sapota achras Miller, Sapota zapotilla (Jacq) Coville* and *Sapota zapotilla (Coville)* [17].

3. Botanical description:

Sapodilla is a dense tree with milky latex known as chicle.

Branching system: (sympodial type).

Size: It reaches up to 20-30 metres in height [16]

Roots: Sapodilla roots show shallow-root system. The roots up to 75cm absorb 66% moisture from the soil.

Leaves: When it is young they are pink in colour and become evergreen. It is spirally arranged (7- 12x2-4cm in size) and the subordinate veins branched with the midrib.

Flowers: Flowers are bell-shaped, small (10mm in diameter), bisexual, either singly or in bunches in the leaf axil near the branch tips.

Fruit: The fruit of sapodilla is a brown in colour (5-10 cm in width). When the berry is unripe it is very hard latex it becomes soft and juicy on maturity.

Seeds: Some sapodilla fruits are seedless but normally it produces 3-12 seeds per fruit. In some cases the fruits are seedless. It is rigid with brown or black in colour on white margin. Hydrocyanic acid is present in seeds, so it should be removed before eating the fruit and it also contains some phytochemicals like achras saponin, saponin, bitter sapotinine and sapotin [15].

Reproductive biology: It is an out breeding species. Here, cross pollination occurs because it is self-incompatibility. It is pollinated by insects. Pollinators of sapodilla are *hermitia* spp. *Oecophylla smaragdina, Thrips hawaiiensis* and *Haplothrips tenuipennis*. Honey bees also collect nectar. The seedlings start bearing fruits after 5-8 years, while the grafted varieties flower earlier (2-3 years from planting). Flowering and fruiting occur throughout the year; it takes about 4 months for fruits to mature[18]

4. Green synthesis of nanoparticles using *Manilkara zapota* plant extracts:

Biosynthesis of nanoparticles from the various plant parts extracts is an easy, cheap, environment friendly, single step protocol and does not require high pressure, energy, temperature or the use of highly toxic chemicals [19]. Time and costly equipment consumption is less and its end product obtained from its source is also pure [4]. It was validated that the manufacturing of metal nanoparticles with the extracts of plant could be completed in the metal salt solution within minutes at room temperature, relying onthe nature of the plant extract [7]. Plants are maximum favored supply of NPs synthesis because they lead to stable large- scale production of nanoparticles which vary in size and shape [20]. Nanoparticles were synthesized by using different elements of flora such as leaves, roots, stems, seeds, rhizomes, bark, fruits, flowers, etc, as their extract is wealthy in phytochemicals like polysaccharides, polyphenolic compounds, proteins, enzymes, alcoholic compounds, vitamins, amino acids, alkaloids, flavones, terpenoids secreted from the plantplay a dual role as reducing agents and capping agents which produce a stable and shape-controlled nanoparticles [21]. Varies parts of *Manilkara zapota* plant are reported to facilitate the synthesis of nanoparticles, as it can be seen from the table 3.

Table 3: Green synthesis of nanoparticles using *Manilkara zapota* plant extract

S.No	**Plant part taken for Extraction**	**Nanoparticles**	**Size(nm)**	**Shape**	**Reference**
1.	Seeds	Silver	20	Spherical	22
2.	Leaf Stem	Silver	94.2-207.2 254.3-452.1	Small and Round Hexagonal and spherical	23
3.	Leaf	Silver	70-140	Granular, rough	24
4.	Leaf	Silver	70-140	Granular and spherical	25
5.	Leaf	Silver	24	Spherical	26
6.	Sapota fruit waste	Silver	8-16	Spherical	27
7.	Seeds	Silver	-	-	28

5. Characterization of Nanoparticles:

It is important to acquire more evidence about properties and applications that focusing on toxicological studies. For the characterization of nanoparticles namely composition, morphology, coating and size various types of techniques is used [29]. UV-Vis spectroscopy, Near Infrared (NIR), Fourier Transform Infrared Spectrometry (FTIR), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Atomic force microscopy (AFM), X-ray diffraction (XRD), High performance liquid chromatography (HPLC) and associated methods with atomic spectrometry, including the single particle inductively couple plasma mass spectrometry (SP-ICP-MS) and flow field-flow fractionation inductively couple plasma mass spectrometry (AF4-ICP-MS) are widely used in the process of characterization. Other techniques might be used to analyze other characterization of nanoparticles namely electrical conductivity, resistivity and capillary electrophoresis among other. While adopting a specific technique for characterization we should deliberate the complexity of the matrix, the analyte concentration and the physicochemical characteristics. In some cases, for the characterization even separation and /or sample dilution techniques may be used [30].

6. Pharmacological Studies:

Antioxidant activities:

Antioxidants are chemical compounds that inhibit the initiation or propagation of oxidizing chain reactions by delaying the oxidation of certain molecules [31]. For the survival of cells, Oxidative metabolism is an important process which effects in the formation of free radicals and other reactive oxygen species (ROS). Too much of free radicals can destroy so many enzymes such as superoxide dismutase, catalase and peroxidase and it leads to destruction and even cell death (e.g., apoptosis) by oxidizing membrane lipids, cellular proteins, DNA and enzymes thus stops cellular respiration. To protect food materials from oxidative degradation, antioxidants are extensively used [32]. The synthetic or natural antioxidants are available as exogenous antioxidants. Medicinal plants are serving as an important source for a wide type of natural antioxidants [33]. Antioxidants particularly carotenoids (xanthophylls and carotenes), polyphenols (anthocyanins, flavonoids, phenolic acids, lignans and stilbenes) and vitamins C and E are some of the example [34].

Mathur and Vijayvergia observed *in vitro* antioxidant activity of AgNPs from stem and leaf of *Manilkara zapota L.* by DPPH assay and reducing power assay. The characterization of AgNPs was done by UV-Vis spectroscopy and Scanning electron microscopy. Results showed that the AgNPs plant extracts could prevent the formation of free radicals and reduce oxidative stress revealed that it have potent antioxidant activity [23].

Antimicrobial activity:

Nanotechnology is also beneficial in treating infections caused by bacteria [35]. Morphological and physicochemical characteristics of the nanometals have been used in antimicrobial activities. The nanoparticles that are too small carry toughest bactericidal effect

[36]. Metal nanoparticles such as silver (Ag), zinc (Zn), titanium (Ti), copper (Cu), Gold (Au), possess antimicrobial activities with effectiveness and ranges of activity, that is known and used for decades [37].

AgNPs synthesis of sapota fruit extract affords a simple and effective way for nanoparticle synthesis. The spherical AgNPs formed were of 8-16nm in size, presented face centered cubic crystal structure and straight forwardly they are optimized using UV-Visible spectroscopy, characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD) and Transmission electron microscopy (TEM). The AgNPs were found to be reasonably stable and possess worthy antibacterial properties against Gram positive and negative microorganisms [27].

Aqueous seed extract of *Manilkara zapota L*were used to synthesize AgNPs. The synthesized AgNPs were characterized by Ultraviolet visible (UV-vis) spectrometer, energy dispersive X-ray Analysis (EDX), Dynamic light scattering (DLS), and Transmission electron microscopy (TEM) and the size of AgNPs are 5-35nm. The as-synthesized AgNPs showed excellent antimicrobial and significant antibacterial activity against wide range of Gram positive, negative bacteria and fungus against five Candida species [22].

Plant seeds of *Manilkara zapota* (Sapodilla) were taken to synthesize silver nanoparticles. Characterization is done by UV-Vis spectroscopy. Synthesized silver nanoparticles possess antibacterial activity and were determined and found that silver nanoparticles have significant antibacterial activity against *Bacillus subtilis, Bacillus licheniformis* and *Bacillus fusiformis* [28].

Antidiabetic activity:

In recent years the medicinal drug potent plants are used to synthesize the antidiabetic nanoparticles to serve as a dual protectiveas a reducing and stabilizing agents [38]. The combination of the biological activities of medicinal plant and metal nanoparticles are notably appealing [39]. This helps us to treat diabetes in an exceedingly more practical means. And additionally they have capability to enhance drug delivery system of exiting artificial medications for enhanced antidiabetic treatment [40].

The *in vitro* antidiabetic activity was carried out using Alpha amylase assay of AgNPs stem and leaf of *Manilkara zapota* L. Characterization was done by UV-Vis spectroscopy and Scanning electron microscopy. It inhibit alpha amylase enzyme, thus lowering postprandial glucose and control diabetics. This suggests that the plant parts of *Manilkara zapota* L. have potent antidiabetic property [23].

Anticancer activity:

Drug delivery systems based on tumor targeted nanoparticles assisted to develop novel anticancer treatment, efficient drug delivery and to enhance immunogenicity of cancer vaccines [41, 42]. To diagnose cancer at an early stage, nanoparticlescan be used [43].

Biosynthesis of silver nanoparticles (MZLAgNPs) employing leaf extracts of *Manilkara zapota* (L.) under optimized condition. MZLAgNPs can be characterized using UV-Vis spectroscopy, FTIR, XRD and FESEM analyze shown that the particles were largely spherical approximately 24nm in size. MTT assay, fluorescence and scanning electron microscopy, annexin V-FITC, clonogenic assay, scratch assay, flow-cytometry, cell cycle distribution, RTq-PCR and western blot analysis were used to assess their cellular effects. The therapeutic potential of biogenic MZLAgNPs as an effective agent for killing carcinoma cells by apoptosis without disturbing the growth of normal human WBCs and RBCs [26].

Acaricidal activity:

Acaricides and repellents are pesticides designed to control harmful species of mites and ticks [44]. They are regarded as the easiest method for control but they have several drawbacks like toxicity, cost, waiting time and acaricide resistance [45]. Excess use of these pests causes resistance and serious effects on non target organisms and human health concerns. An alternative source for chemical control of dust mites is usage of plant extracts. Plants are considered as a good source to control microscopic arachnids since they have less effect on non-target organisms or to the environment [46].

Silver nanoparticles leaf extract of *Manilkara zapota* used to resist *Rhipicephalus (Boophilus) microplus*. The AgNPs are spherical and oval in shape and size of 70-140nm. The characterization of AgNPs was done by UV-Vis spectrum, scanning electron microscopy (SEM), Fourier transform infrared and X- ray diffraction [25].

Feeding deterrent activity:

Pests are any animals, plants or microorganisms that compromise our food, health or comfort [47]. Pest damage in warehouse and grain stores normally effects in irretrievable resources wasting and huge economic losses. Currently, synthetic chemical pesticides serve as the main method to control stored- product insects [48]. Synthetic pesticide is a chemical serve as a killer or a repellent to reduce, destroy and kill pests which includes insects, fungi, wild plant and other undesirable organisms which have an effect on human health, agricultural crops, and the environment [49]. Botanical pesticides are taken into consideration as an eco friendly and sustainable strategy to control pest damage. Botanical pesticidesare partially substituted by synthetic pesticides which seemed to be easy to handle and long lasted [50].

Manilkara zapota aqueous leaf extract of is used to synthesize silver nanoparticles (AgNPs) with the shape of spherical and oval, the size of 70-140nm and their characterization is carried out by UV-Vis spectrum, Scanning electron microscopy, FTIR analysis and XRD pattern. The synthesized AgNPs have the probable and ideal eco-friendly approach to destroy the house fly, *Musca domestica* (Diptera: Muscidae) [24].

7. Conclusion:

The above review showed that nanoparticle synthesized from *Manilkara zapota* plant extracts shows efficient biological significance like antioxidant, anticancer, antidiabetic, antimicrobial, acaricidal and feeding deterrent activities. It paves a novel way of research that in a nanoscale level, we can get the biological properties of plants in a more efficient manner. For future research purpose we can use this plant to synthesize more number of nanoparticles and analyze their medicinal properties which is further gave as a new platform to treat many biological problems.

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NANOTECHNOLOGY AND THEIR APPLICATIONS

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Abstract:

Nano science and advancement is the current day world thought which relies upon the investigation of little atom inside the size degree no short of what one estimation assessed from 1 to 100 nanometers. Nonmaterial are material science based approach to manage nanotechnology. In Nano scale size all materials have a critical generous surface zone to volume extent. This single brand name clears course for new quantum mechanical effects. On account of these effects the range of the atom diminishes, which causes a change in the electronic properties of the solid. Exactly when the range of the material will be scaled down scale, there will not be any impedance of the quantum sway. Nevertheless, the effect will start its play when the material will be Nano-sized. There will be changes in the physical and substance activities of the material. At the point when the material changes from huge scope to Nano-scale likewise, it is grasped that there is an extreme change in properties. These movements can be outstandingly unique and can be used for an arrangement of employments. This paper gives an investigation of various nonmaterial and their applications. Nanotechnology is new wildernesses of this century. The world is confronting extraordinary difficulties in fulfilling rising needs for essential items (for example Food, water and energy), completed products (e.g., cellphones, vehicles and planes) and administrations (for example asylum, medical services and business) while diminishing and limiting the effect of human exercises on Earth's worldwide climate and environment. Nanotechnology has arisen as a flexible stage that could give productive, practical and earth satisfactory answers for the worldwide supportability challenges confronting society. As of late there has been a fast expansion in nanotechnology in the fields of medication and all the more explicitly in focused medication conveyance. The application of nanotechnology to address worldwide difficulties like water sanitization, clean energy advancements, ozone depleting substances, materials supply and usage, and green assembling and science are in progress. Shrewd conveyance of supplements, bio-partition of proteins, fast inspecting of natural and compound toxins and Nano embodiment of nutraceuticals are a portion of the arising subjects of nanotechnology for food and horticulture.

Keywords: Nanotechnology, Nanomaterial, drug delivery

1. Introduction:

The term nanomaterial incorporates all nano sized materials that can be built or found in nature. Nanotechnology can be depicted as the innovation of composite utilitarian frameworks at the nano size of the materials. Nanotechnology manages creation and control of the matter on a nuclear, sub-atomic and supra molecular level. Supramolecular structure is vast atoms which are conglomerated with littler particles. Nanotechnology is going to cut a corner in wide and broadened field of science including miniaturized scale manufacture, semiconductor, surface science, medicine and natural science and so forth as appeared in Fig 1.

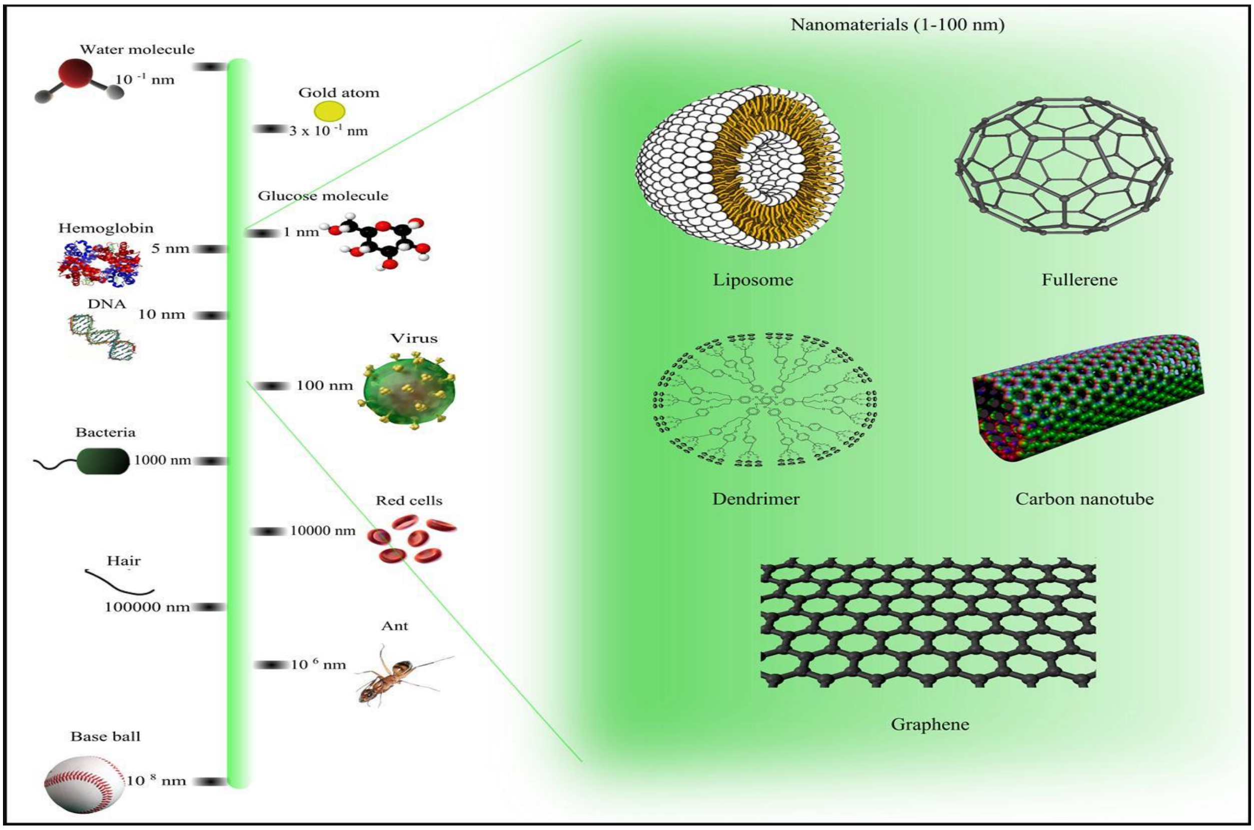

Figure 1: Natural Nanomaterials (Source: en.wikipedia.org)

They are imperative since they show one of kind properties which are essentially not quite the same as their traditional mass partner. The National Nanotechnology Initiative (NNI) depicts the property of nanomaterials as "At the nanoscale, the synthetic, the physical and organic properties of materials contrast in principal and significant courses from the properties of individual particles or mass matter and atoms.Nanotechnology, introduced almost half century ago, is one of the most active research areas with both novel science and useful applications that has gradually established itself in the past two decades.Not surprisingly, it is observed that expenditure on nanotechnology research is significant. The U.S. National Nanotechnology

Initiative (NNI) expenditures exceed $1 billion each year, with the President's 2008 budget forNNI at $1.5 billion. However, the research is mainly moving forward motivated by immediate profitable return generated by high value commercial products [1].According to a study by the Canadian Program on Genomics and Global Health (CPGGH), nanotechnology in construction ranked 8 of 10 applications that most likely have impact in the developing world [2].

2. Literature survey of nanomaterials:

Khademolhosseini *et. al* [3] portrayed that as of late use of nano/bio materials for upgraded oil recuperation (EOR) has been inspected by couple of analysts, however there exists vague ideas about synchronous infusion of nano-particles/biomaterials. In this manner, in this study they investigated heavy oil removal systems utilizing synchronous infusion of nano silica/bio-surfactant in a glass micro model. To better outline the impact of nano/bio material diverse flooding situations containing refined water, nano silica/refined water, biosurfactant/refined water and nano silica/biosurfactant/refined water have been directed.Test results showed that concurrent nearness of nanoparticles and bioproducts have collaboration on each other and in view of IFT decrease, enhancing the portability proportion and expanding the infused liquid consistency; the oil recuperation can be accomplished around 58%. Moreover, nanoparticles can play as an inhibitor to maintain a strategic distance from asphaltene precipitation.

SudiptaNaskar *et. al* [4]clarified that bond based cement can be supplanted by low calcium fly-cinder based geopolymer concrete with respect to the unfavorable impact of the assembling of conventional Portland concrete on environment. These days, nano innovation has an essential part in the field of development businesses. It has been seen that few properties of bond based cement are affected by various nano materials. As low calcium fly-slag based geopolymer cement is an alternate choice for bond based cement, nano materials may likewise have impact on it. A trial program has been taken up on low calcium fly-fiery debris based M25 review geopolymer concrete having 16 (M) grouping of activator fluid. Diverse percentage of nanomaterials viz. nano silica, carbon nano tube, titanium di-oxide were used to investigate the impact of nano materials on geopolymer concrete. Geopolymer concrete with 1% titanium dioxide demonstrates calculable change in compressive quality despite the fact that pH remains almost same in all cases.

Hongjian Du *et.al* [5] examined the strength properties of cement containing nano-silica at measurements of 0.3% and0.9%, individually. Because of the nano-filler impact and the pozzolanic response, the microstructure became more homogeneous and less permeable, particularly at the interfacial move zone (ITZ), which drove to reduced penetrability. Tests on the strength properties checked the useful impacts of nano silica. The channels for unsafe operators through the concrete composites were incompletely filled and blocked. The pore size dissemination additionally demonstrated that the extensive slender pores were refined by the nano-silica, because of the consolidated commitment of the nano-filler impact and the pozzolanic response.

Mukharjee *et.al* [6]gave examination that arrangements the investigation of compressive quality and attributes of the Interfacial Transition Zone (ITZ) of cement containing reused totals and nano-silica. For this reason, compressive quality at 7, 28, 90 and 365 days are resolved for completely normal and reused total cement blends made with or without nano-silica. Notwithstanding above, Vickers miniaturized scale hardness test and backscattered-mode filtering electron minute investigation is conveyed to describe ITZ of cement blends. The consequences of study portrayed that full supplanting of normal coarse totals with reused ones have noteworthy impact on compressive quality and ITZ attributes of cement. Be that as it may, compressive quality and microstructure of cement blends enhances with the fuse of nano-silica.

3. Nanotechnology basics:

Nanotechnology is the creation of materials and devices by controlling of matter at the levels of atoms, molecules, and supramolecular (nanoscale) structures [7]. It is the use of very small particles of materials to create new large scale materials [8].To better understand the difference among various scales, Table 1 shows the categories of scales and its related topics[9].

Table 1: Scales vs. Topic Areas

Scales	**Relates Topics (not inclusive)**
10-2	Quantum Mechanics Molecular Dynamics
10-3	Nano mechanics Molecular Biology Biophysics Elasticity
10-6	Plasticity Dislocation
10-9	Mechanics of Materials
10-0	Structural Analysis

Nanotechnology is not a new science or technology. It was believed first introduced by Richard P. Feynman in his lecture at the California Institute of Technology in 1959. However, the research on this has been very active only in recent two decades. This is because the development and application of nanotechnology are relying on the development of other related science and technology such as physics and chemistry that are commonly new to break through at that time. Most promising developments of nanotechnology are fullerene (a new form of carbon, C60) and carbon nanotubes [10]. In Figure 1, are "a grapheme sheet rolled into a cylinder with specific alignment of hexagonal rings."[10].

4. Classification of nanomaterials:

Nanomaterial's can be characterized principally into two sorts: Natural nanomaterial and misleadingly manufactured nanomaterial.

A. Natural nano materials: These incorporate nano materials that exist in natural frameworks; eg: viruses (capsid), substances in our bone network, and so forth as appeared in Fig. 2.

B. Artificial nano materials: These are the ones that are created by various analyses. They can promote sub-isolated into 4 classes:

1. Carbon Based: These nano materials are made for the most part out of carbon, most regularly taking the type of an empty circles, ellipsoids, or tubes. Circular and ellipsoidal carbon nano materials are alluded to as fullerenes, while tube shaped ones are called nanotubes (carbon nanotubes (CNTs). These particles have numerous potential applications, including enhanced movies and coatings, more grounded and lighter materials, and applications in gadgets.

2. Metal Based: These nanomaterials incorporate quantum specks, nanogold, nanosilver and metal oxides, for example, titanium dioxide. A quantum spot is a firmly pressed semiconductor precious stone involved hundreds or a great many molecules, and whose size is on the request of a couple of nanometers to a couple of hundred nanometers. Changing the span of quantum dabs changes their optical properties.

3. Dendrimers: These nanomaterial's are nanosized polymers worked from spread units. The surface of a dendrimer has various chain closes, which can be custom-made to perform particular concoction capacities. This property could likewise be valuable for catalysis. Likewise, in light of the fact that three-dimensional dendrimers contain inside depressions into which different atoms could be set, they might be valuable for medication conveyance.

4. Composites: Composites consolidate nanoparticles with different nanoparticles or with bigger, mass sort materials. The composites might be any mix of metal based, carbon based or polymer based nanomaterials with any type of metal, fired, or polymer mass materials.

Figure 2: Natural Nanomaterial's (Source: nanoyou.eu)

5. Shapes of nanomaterials:

As per the measurements nanomaterial's can be isolated into zero dimensional, one dimensional, two dimensional and three dimensional nanomaterial's as shown in Fig.3

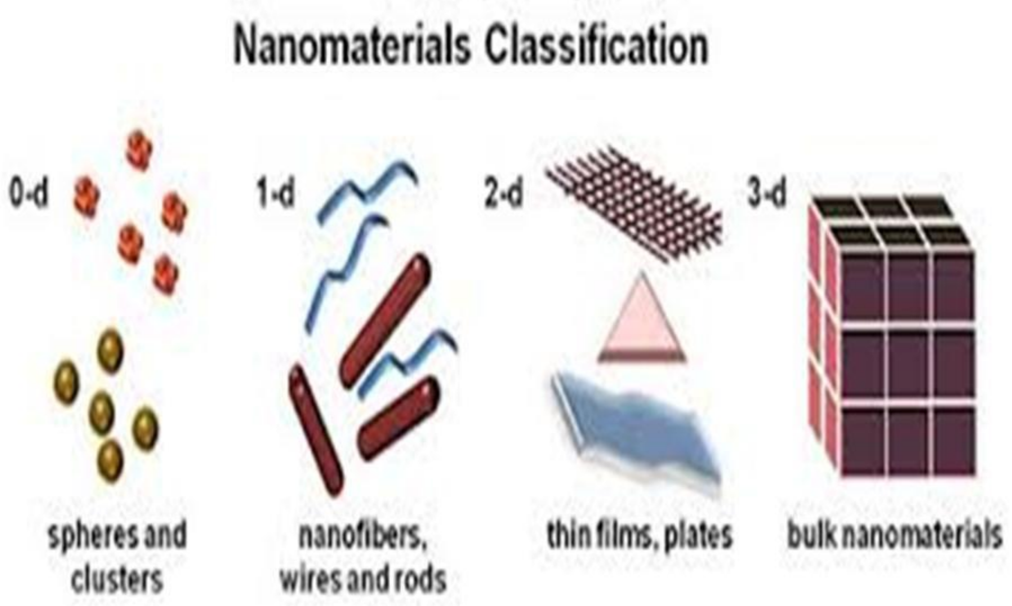

Figure 3: Different dimensional Nanomaterials (Source: nanoyou.eu)

A. Zero dimensional (0-D): These nanomaterial's have Nano- measurements in all the three bearings. Metallic nanoparticles including gold and silver nanoparticles and semiconductor, for example, quantum specks are the ideal case of this sort of nano particles.

The majority of these nano particles are round in size and the breadth of these particles will be in the 1-50 nm range 3D squares and polygons shapes are likewise found for this sort of nanomaterials.

B. One dimensional (1-D): In these nanostructures, one measurement of the nanostructure will be outside the nanometer range. These incorporate nanowires, nanorods, and nanotubes. These materials are long (a few micrometer long), yet with measurement of just a couple nanometer. Nanowire and nanotubes of metals, oxides and different materials are couple of case of this sort of materials.

C. Two dimensional (2-D): In this sort of nanomaterial's, two measurements are outside the nanometer range. These incorporate distinctive sort of Nano movies, for example, coatings and meager film-multilayers, nano sheets or nano-dividers. The region of the nano movies can be expansive (a few square micrometer), however the thickness is dependably in nano scale range.

D. Three Dimensional (3-D): All measurements of these are outside the nano meter range. These incorporate mass materials made out of the individual pieces which are in the nanometer scale (1-100 nm).

6. Properties of nanomaterials:

A. Magnetic properties:

- Magnetic nanoparticles are utilized as a part of a scope of uses like imaging, bioprocessing, refrigeration and in addition high stockpiling thickness attractive memory media.
- The extensive surface region to volume proportion results in a considerable extent of particles having diverse attractive coupling with neighboring molecules prompting contrasting attractive properties.
- Bulk gold and platinum are non-attractive however at the nano size they go about as magnetic particles. Au nanoparticles get to be ferromagnetic when they are topped with the fitting particles, for example, thiol.
- Giant magneto resistance(GMR) is a marvel saw in Nano scale multilayers comprising of solid Ferro magnet (Fe,Co,Ni) and a weaker attractive or non-attractive support (Cr,Cu).It is typically utilized in information stockpiling and detecting [11].

B. Optical properties:

- In little nano bunches the impact of diminished dimensionality on electronic structure has the most significant impact on the energies of most elevated involved sub-atomic orbital (HOMO) which is valence band and the least vacant sub-atomic orbital(LUMO),essentially the conduction band.

- The optical emanation and adsorption happens when the move of the electrons happen between these two states.
- Semiconductors and numerous metals indicate vast changes in optical properties, for example, shading, as an element of molecule size.
- Colloidal tension of gold Nano particles have a dark red shading which turns out to be dynamically more yellow as the molecule size increments. Gold circles of 10-20 nm display red shading. Gold circles of 2-5nm display yellow shading. Gold circles of >20nm show purple shading. Thus, Silver particles of 40nm display blue shading. Silver particles of 100nm display yellow shading. Crystal molded Silver particles red shading. Other properties which may be affected by reduced dimensionality include photo catalysis, photoconductivity, photoemission and electroluminescence.

C. Electronic properties:

- The changes which happen in electronic properties as the framework length scale is diminished are connected mostly to the expanding impact of the wave-like property of the electrons (quantum mechanical impacts) and the shortage of diffusing focuses.
- As the span of the framework gets to be practically identical with the de Broglie wavelength of the electrons, the discrete way of the vitality states gets to be obvious by and by, in spite of the fact that a completely discrete vitality range is just seen in frameworks that are restricted in every one of the three measurements.
- In certain cases, directing materials get to be covers beneath a basic length scale, as the vitality groups stop to cover. Attributable to their inherent wave-like nature, electrons can burrow quantum mechanically between two firmly nearby nanostructures, and if a voltage is connected between two nanostructures which adjusts the discrete vitality levels in the DOS, resounding burrowing happens, which unexpectedly builds the burrowing current
- Conduction in exceptionally restricted structures, for example, quantum spots, is extremely touchy to the nearness of other charge transporters and consequently the charge condition of the speck.
- These Coulomb bar impacts result in conduction forms including single electrons and thus they require just a little measure of vitality to work a switch, transistor or memory component.

- All these wonders can be used to deliver drastically distinctive sorts of segments for electronic, optoelectronic and data handling applications, for example, full burrowing transistors and single-electron transistors.

D. Chemical Properties:

Synthetic properties of nanomaterial additionally change at Nano scale. As the rate of surface particles in nanoparticles is expansive contrasted and mass articles, thusly reactivities of nanomaterials are more than mass materials. The accompanying are the portion of the compound properties are:

- The dominance of surface is a noteworthy explanation behind the adjustment in conduct of materials at the Nano scale. As up to half of the considerable number of atoms in nanoparticles is surface molecules, properties, for example, electrical transport are no more controlled by strong state mass marvel.
- The atoms in nanomaterial have a higher normal vitality than molecules in longer structures, in view of the bigger extent of surface particles. For instance, synergist materials have a more prominent compound action per molecule of uncovered surface as the impetus is lessened in size at the Nano scale.
- Defects and polluting influences might be pulled in to surfaces and interfaces, and connections between particles at those little measurements can rely on upon the structure and nature of synthetic holding at the surface.
- Molecular monolayers might be utilized to change or control surface properties and to intercede the connection between nanoparticles.

7. Contemporary scenario of nanotechnology development in India:

The Indian nanotechnology activity is a multi-organization exertion and has solid likeness with US multi-office model. The key offices that have embraced real activities for limit creation are the Department of Science and Technology (DST) and Department of Information Technology (DIT). Different offices demonstrating significant association are the Department of Biotechnology (DBT), Council of Scientific and Industrial Research (CSIR), Ministry of New and Renewable Energy, Ministry of Health and Family Welfare, Indian Council of Agricultural Research, Indian Space Research Organization, Department of Atomic Energy, and Defense Research and Development Organization. Nanotechnology as an unmistakable territory of government examination support began with NSTI (Nano Science and Technology Initiative) in the Xth arrangement period (2001-2006) with an allotment of rupees 60 crores (approx. USD 12 million). NSTI was started and executed by the DST [12].

- NSTI helped in setting up units for creating research greatness in Nano science, habitats for nanotechnology each went for application advancement and two national instrumentation/portrayal offices. On the whole, fourteen national foundations, including seven IITs and ten colleges have been bolstered under the NSTI.
- Different exploratory divisions/organizations likewise have their own assignments for Nano science and innovation programs/exercises as appeared in Fig 4. They have guided center to target key zones: for instance DIT (Nano electronics), DBT (Nano-Medicine), CSIR (Energy, Metrology, and Nano medicine/Pharmaceutical), ARCI (Water, Textile, Smart Materials), NIPER (Nano-Pharmaceutical, Toxicology.

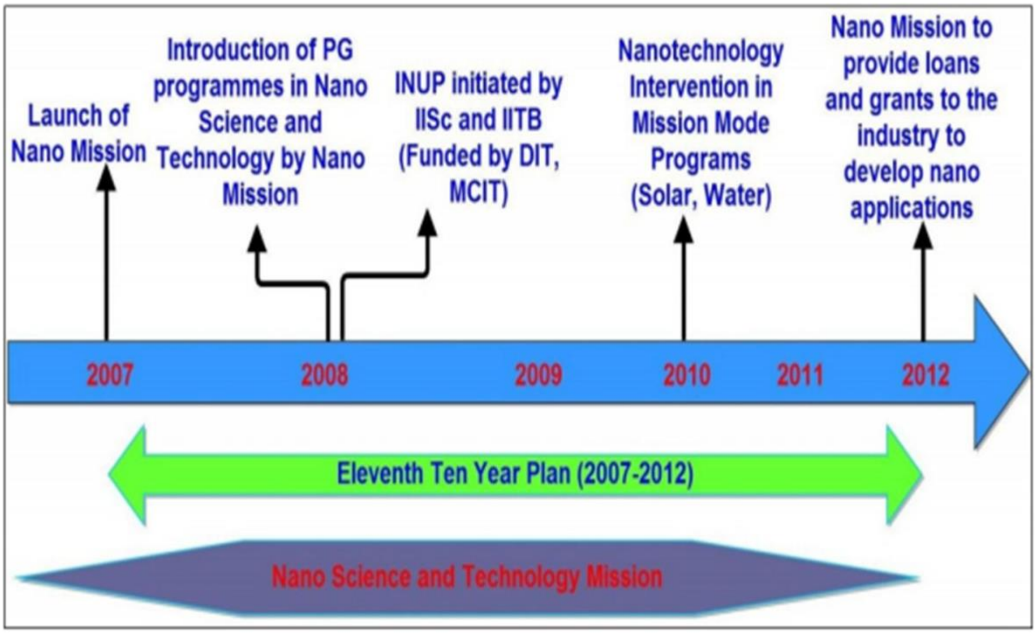

Figure 4 : Major Initiatives in Nanotechnology 2007-2012 (Source: http://www.nistads.res.in/)

8. Applications of nanotechnology:

At nanoscale, materials have novel properties like increased strength, resiliency, electrical conductivity [13,14]. One of the most common examples of Nano device is the iPod Nano which uses microscopic memory chips for increasing the storage capacity. Life sciences combined with nanotechnology has given rise to Nano biotechnology that has been given insights in to disease processes, hence identifying more efficient biomarkers and understanding the mechanism of drug action[15]. Abraxane® a chemotherapy agent created by Abraxis is another lively example. Bioscience is usedto destroy the tumor cells. The chemotherapy is delivered directly into tumour cells because tiny particles penetrate cell membrane easily [16]. Nanomaterial's are used in treating glaucoma patients also. Many vaccines like hepatitis and malaria are also utilizing nanotechnology[17]. Nanomaterial vaccines are used to produce greater immunity to pathogens by delivering medications directly to specialized dendritic cells in the immune system[18]. Glucose levels are being monitored with the help of patient monitoring devices. Miniature biochips detect increase in glucose level[19].

8.1 Drug Delivery System:

At present, 95% of all new therapeutic system have poor pharm kinetics and less developed biopharmaceutical properties[20]. There is no such medicinal system that delivers drug and distribute therapeutically active drug molecules to the site of action or inflammation without any side effects [21]. These problems are overcome by nanotechnology drug delivery systems which possess multiple desirable attributes. Nano medicine has a size such that it can be injected without occluding needles and capillaries which enables targeted drug delivery and medical imaging[22]. Thus Nano sized liposomes, micelles, Nano emulsions, Nano gels are used for this purpose.

8.2 Implications of nanotechnology:

Implantations of Nano transmitters and Nano sensors within individuals have opened gates for monitoring and treating them at the microscopic level with the use of Nano devices.But this crosses traditional bounderies of care in the hospitals as persons can get the treatment done while siting in their homes[23].Pateients at home could have access to date transmitted from biochips which will moniter the diseases like hypercholesterolemia, alerting them when critical levels are obtained. Patients and clinicians would need to have throughout knowledge of device interfaces as all body metabolisms will be regulated by these devices. The day may not be far than insurance deny us as money due to monitoring our health at cellular level in early stages[24]. Nanotechnology will make us over dependent on devices. Inaccurate and errors with monitoring devices will be very challenging to detect. Advocates will be needed by everyone for safe and ethical use of nanomaterial[25]. Monitoring methods would be needed to assure that devices are checked and calibrated within safety limits. Hence if these implications can be managed nanotechnology is the biggest boon to mankind.

8.3 Targeted drug therapies for treatment of cancer:

If scientists can load their cancer-detecting gold nanoparticles with anticancer drugs, they could attack the cancer exactly where it lives. Such a treatment means fewer side effects and less medication used. Nanoparticles also carry the potential for targeted and time-release drugs. A potent dose of drugs could be delivered to a specific area but engineered to release over a planned period to ensure maximum effectiveness and the patient's safety[26].These treatments aim to take advantage of the power of nanotechnology and the voracious tendencies of cancer cells, which feast on everything in sight, including drug-laden nanoparticles. One experiment of this typeused modified bacteria cells that were 20 percent the size of normal cells. These cells were equipped with antibodies that latched onto cancer cells before releasing the anticancer drugs they contained. From manufacturing to medicine to many types of scientific research, nanoparticles are now rather common, but some scientists have voiced concerns about their negative health effects. Nanoparticles' small size allows them to infiltrate almost anywhere [27].

That's great for cancer treatment but potentially harmful to healthy cells and DNA. There are also questions about how to dispose of nanoparticles used in manufacturing or other processes. Special disposal techniques are needed to prevent harmful particles from ending up in the water supply or in the general environment, where they'd be impossible to track.

8.4 Gene-Silencing Nanoparticles:

The researchers attach a protein (transferrin) that normally delivers iron to cells so that it delivers short interfering RNA (siRNA) molecules to cancer cells. The main function of RNA is protein synthesis within a cell. siRNA molecules are a class of RNA molecules that interfere with the expression of particular genes[28]. The researchers encased the siRNA payload with sugar-containing polymers to create Nano sized particles. Attaching transferrin molecules to the outer surface of a nanoparticle is one of the methods used to target nanoparticles to cancer cells. The nanoparticles will seek out cancer cells that overexpress the transferrin receptor.The gene-silencing siRNA nanoparticles are injected into the bloodstream and pass through blood vessels into the surrounding tissue. When the siRNA nanoparticles enter the tumor cells, acidic substances cause the nanoparticles to release the siRNA. The siRNA shuts down (silences) particular genes by leading to the degradation of the RNA transcripts of these genes throwing a monkey wrench into the cellular machinery and halting the multiplication of cancerous cells. To test their approach they tried it on laboratory mice with Ewing's sarcoma tumors. They designed the siRNA to target a specific growth promoting gene that is only active in Ewing's sarcoma tumors, the EWS-FLI1 gene[29]. Their siRNA inhibits expression of EWS-FLI1, this shuts down part of the cellular machinery in the cancerous Ewing's sarcoma cells so they should stop multiplying. This treatment technique should have fewer side-effects than traditionally administered chemotherapy (which affects all dividing cells in the body, both healthy and cancerous) since the nanoparticles are doubly targeted to the cells that overexpress the transferrin receptor and have the EWS-FLI1 gene—i.e., the tumor cells. The ingested siRNA nanoparticles only exert their effect in cells that contain the EWSFLI1 gene—i.e., they have no effect when taken in by normal cells. After three consecutive days of treating 50 mice, they observed, "strong, but transient, inhibition of tumor growth. However, when used over longer durations (twice-weekly injections up to four weeks), the results were striking. Long-term treatments with this delivery system markedly inhibited tumor growth, with little or no tumor growth in many animals.[30]"

8.5 Nanomaterial Applications utilizing Carbon Nanotubes:

Applications being created for carbon nanotubes incorporate adding antibodies to nanotubes to frame microorganisms sensors, making a composite with nanotubes that curve when electric voltage is connected twist the wings of transforming airplane, adding boron or gold to nanotubes to trap oil slicks, incorporate littler transistors, covering nanotubes with silicon to make anodes the can expand the limit of Li-particle batteries by up to 10 times..

8.6 Nanomaterial Applications utilizing Graphene:

Applications being created for graphene incorporate utilizing graphene sheets as electrodes as a part of ultra-capacitors which will have as much stockpiling limit as batteries yet will have the capacity to revive in minutes, joining strands of DNA to graphene to frame sensors for fast ailment diagnostics, supplanting indium in level screen TVs and making high strength composite materials.

8.7 Nanomaterial Applications utilizing Nano composites:

Applications being created for Nano composites incorporate a nanotube-polymer Nano composite to frame a framework which speeds up substitution of broken bones, making a graphene-epoxy Nano composite with high strength-to-weight proportions, a Nano composite produced using cellulous and nanotubes used to make an adaptable battery.

8.8 Nanomaterial Applications utilizing Nano fibers:

Applications being created for Nano fibers incorporate fortifying the generation of ligament in harmed joints, piezoelectric Nano fibers that can be woven into dress to deliver electricity for mobile phones or different gadgets, carbon Nano fibers that can enhance the performance fire retardant in furniture.

8.9 Nanomaterial Applications utilizing Nanoparticles:

Applications being produced for nanoparticles incorporate convey chemotherapy sedates specifically to growth tumors, resetting the resistant framework to anticipate immune system maladies, conveying medications to harmed districts of supply routes to battle cardiovascular illness, make photo catalysts that create hydrogen from water, lessen the expense of delivering energy components and sun based cells, tidy up oil slicks, water contamination and air contamination. Look at our Applications of Nanoparticles page to perceive how nanoparticles are being utilized.

8.10 Nanomaterial Applications utilizing Nanowires:

Applications being created for carbon nanotubes incorporate utilizing zinc oxide nanowires as a part of an adaptable sun oriented cell, silver chloride nanowires to disintegrate natural atoms in contaminated water, utilizing nanowires produced using iron and nickel to make thick PC memory - called "race track memory.

9. Conclusions:

Nanotechnology has brought a revolution in manufacturing materials, creating a vast number of new devices, drug delivery systems and monitoring and diagnosing systems. But the implications if this technology are very diverse, impacting consumers, clinicians and the practice of informatics. A major area of concern for health care providers is the ethical use of nanomaterials. Nanotechnology has brought a new era in healthcare but the challenges are to develop it by overcoming various difficulties and implications. New opportunities have provided us with a powerful tool in the field of genomics, proteomics, molecular diagnostics and high throughout screening. Nanoparticles have the properties to become the most versatile materials for developing diagnostics. Advances in nanotechnology will provide a good inside view of our human systems. It has a bright future with the emergence of several promising approaches for delivery of therapeutics agent and imaging using the advantage of nanoscale carriers. Future studies will now be addressing a no. of challenges faced in Nano medicine application. Greater funds are being allocated for clinical and preclinical studies but still are studies are lacking in safety data that includes toxicity studies. Also the cost of Nano medicine should be in acceptable range so that it is successful in clinics. Nanotechnology is being applied at all stages of drug development, from formulations for optimal delivery to diagnostic applications in clinical trials. Actual utilization of nanotechnology novel drug delivery techniques lag behind because of perception that such technologies could delay products due to technical or regulatory reasons. So oral drug delivery remains a preferred option. Further the cost factor becomes a hindrance in its daily use.

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POTENTIAL IMPACT OF NANOTECHNOLOGY

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Abstract:

Nanotechnology is regarded as the technology of the future; which holds the promise for the better future of our society and is capable of revolutionizing the global economy. Nanotechnology is an interdisciplinary approach involving physics, chemistry, biology, material and environmental science. A Nano technique is the study at atomic and molecular level where the size ranges in between 1nm to 100nm. The miniaturization of materials at nano scale generates unique and novel features in the materials. The concept of nanotechnique was given by an American physicist Richard Feynman in 1959.Using nanotechnology, the materials can be made stronger, durable, flexible, with high degree of electrical and thermal conductivity which can retain their properties at varying pH and temperature. Nano engineered materials make superior house holds products like air purifiers, water purifiers, stain removers, filters, sensors, etc. Nanotechnology has a great use in almost every sector of life and is contributing a lot in IT, medicine's, aerospace, environmental, and energy sector to make highly efficient smarter and smaller materials. In a broader sense it can be defined as the science or technology involved in the designing, synthesizing, and characterisation of new materials and devices in the nano range. The nano engineered materials are synthesized artificially in the laboratory to exhibit peculiar chemical and physical properties in comparison to their bulk counterparts. This paper presents an insight on somewonderful breakthroughs in nanotechnology including electronics, medicine, environment, space etc.In future nanotechnology is going to be a toolkit for different industries with the help of which nanomaterials with exclusive properties can be formed.

Keywords: Nanotechnique, Nanoscale, Applications, Properties, Characterisation

Introduction:

Nanotechnology is a technique which works at molecular level to create large structures with potent and novel properties. Nanotechnology is diverse field that covers a vast array of devices and tools derived from the fusion of all the facets of science. It encompasses macro properties at micro level. The enhancement in their properties is generally due to their large surface area which increases their catalytic activity and reactivity. Nanotechnology is almost ready to revolutionize many technology and industrial sectors. Described below is just a reflection of rapidly growingimportanceand applications of nanotechnology in different aspects of life.

Electronics:

Nanotechnology in electronics offers faster, smarter and slimmer devices. The technology increases the efficiency, enhances the durability and reduces the power consumption. It is used in many electronic devices such as mobiles, computers, laptops, cameras and sensors. Nowadays nanotechnique is used to increase the density of memory chips so as to manage large amount of datas. Besides being small and allowing more transistors to be packed into a single chip, the uniform and symmetrical structure of nanotubes allows a higher electron flow and faster frequency. Nanolithography is the technique used for the fabrication of chips. Reducing size of devices is the need demand of era and to achieve this nanotechnique is playing a pivotal role. So in coming years we can definitely predict that the, big things are going to be really small.

Nanotechnology is also considered as an industrial revolution for the telecommunication industry and has led to tremendous development and innovation in this sector. The use of wireless communication system is growing with a pacy rate because of various advantages like wireless communication, less power consumption and improved quality. Presently, a lot of research is going on to synthesis wireless sensors, logistic devices, and environment monitoring systems.

Medicine:

Nanotechnology is playing a very vital role in medicinal sector. The use of nanomaterials is proving to be a boon for the diagnosis and treatment of critical diseases. The nanomaterials because of their micro size are helping for both in vivo and in vitro biomedical analysis. The fusion of nanotechnology with chemistry has led to the development of many nanomedicine’s, nanocatalysts and nanodevices which are proving their importance in the field. Nanoparticles are being used to diagnose certain critical diseases like lukemenia, hereditary complications, cancer, etc. by inducing them in the body of patients with special techniques. Recent studies shows that nanotechnology is also being used to reproduce or fix the raptured and broken tissuesunder the banner of Tissue Engineering. Nanomedicine’s are yet another fabulous example of nanotechnology in which the medicine’s are given in the powdered form. Due to this they acquire large surface area and are highly effective for the patients. Presently many clinical trials are going on around the world to harness the optimum potential of nanomedicine’swhich could include the successful treatment of some deadly diseases.

Energy:

Nanotechnology is considered to have multidimensional applications in the field of energy and fuels. It provides the potential to enhance energy efficiency of different energy sources due to its novel properties. The technology is being applied in solar cells, batteries, electrodes and other equipment’s to enhance their activity.

The epoxy containing carbon nanotubes (CNTs) is being used to make windmill blades which are much stronger and lesser in weight than the normal ones. Researchers are working on to prepare graphene layers mixed with nano metal chalcogenides to increase the binding energy of hydrogen to the graphene surface, resulting in a higher amount of hydrogen storage is graphene layered tankers. Other researches have shown that sodium borohydride nanoparticles can effectively store hydrogen and other inert gases at the room temperature. Piezoelectric electric nanofibres have been synthesized in many European countries that are flexible enough to be woven in the clothes, which can turn the sunlight into electricity to power the cellphones, smartwatches and other electronicgadgets**.** Scientists at Rice universityare working on the electrical conductors containing CNT's that would have nearly zero resistance and maximum conductance (current) than the wire currently used in transmission grids; and this is definitely going to change the scenario of power problem across the globe.

Thus, nanotechnology is going to completely change the face of energy sources like gas turbines, solar cells, thermo electrics, fuel cells, electrical motors in the near future.

Space:

Nanotechnology is showing its importance in the field of aerospace. The technology is being used to manufacture lighter, stronger and resistive spacecraft’s, rockets and solar sails. The benefit of such a light structured rockets and spacecraft’s would be enormous as it will increase the speed and reduce the fuel consumption by manifolds. Researchers are also excited about the possibilities of space elevators which can accelerate the space exploration by reducing the cost dramatically. In a research it has been found that using CNT a solar sail has the capability to travel at about 40,0000km/sec. which is approximately 15% of the speed of the light. This sail with this speed can reach Mars in few hours.

Space travel to other planets and stars is going to be feasible with these fast moving and advanced nano solar sails. Presently, materials such as graphene and metal composite polymers containing Titanium[Ti], Thallium[Th], platinum[Pt]and many more are being used in manufacturing of spacecraft's, rockets and satellites. Lots of research is going on to replace the conventional materials with these advanced nanomaterials which have a high degree of tensile strength and are only 1/10 of the weight of the steel. In coming years nanosenors are going to monitor the life support system inside the spacecraft ensuring that even trace of chemicals and contaminants if any in the interior environment should be at a safer level for space passengers. MIT's space laboratory is using nanotechnology to develop high performance devices that will greatly improve astronaut's ability and health on space flights.

Environment:

Nanotechnology has potential environmental benefits and can act as panacea for many environmental problems and disorders. Nanotechnology can be used in different ways to improve the environment; this includes cleaning the pollution, reducing the contaminants and chemicals and making the alternative from of energy more cost effective. One example of this is the use of Ag nano clusters as catalyst to reduce the polluting by products of industries. Photo catalytic copper oxide [CuO] nanoparticles have been used to break down oil spills in the biodegradable compounds. Nanofiber catalyst made of manganese oxide [MnO] removes volatile organic components from industrial smoke. Iron [Fe] nanoparticles having large surface area and reactivity are used to detoxify carcinogenic chlorinated hydrocarbons in groundwater.

Nanotechnology offers numerous opportunities to prevent, protect and reduce environmental pollutants. Researches have shown that nanomaterials of rest (ferric oxide) can be used to remove arsenic [As] from the water using the magnetic property. Nanofibres, nanosenors and nanoadsorbents are used for decontamination of fresh water. Thus nanotechnology has the potential to improve the current environmental scenario and is going to be the potent tool for environment conservation.

Conclusion:

As Richard Feynman said in 1959 that, "there's plenty of room at the bottom "is absolutely true as very little has been done in the field of nanotechnology. There's a lot of scope and possibilities in this sector which can be highly beneficial for the mankind and create a wonderful planet for the coming generations. Nanotechnology is a carrier for the mankind to advance into the next era. Nano chemists are leaving no stone unturned to exploit the wonderful benefits of nanomaterials in the field of medicine, energy, space, environment and many more. In coming decades we are going to explore a wide range of nanomaterials with astonishing features having the tagline: **smaller but smarter.**

Today nanotechnology impacts human life every day with the limitless benefits which are diverse in nature. Nanotechnology is ubiquitous and pervasive and is going to explode the next industrial revolution. At this junction the world is at the optimal time to take advantage of this technology with lots of sense and responsibilities. There is need for the collaborative efforts from the industry, public groups and government to find economically viable strategies to promote the future technology i.e. nanotechnology by protecting the environment and human health.
So, let’s welcome the **micro era with macro hopes**

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RECENT PROGRESS ON COPPER-CATALYZED CROSS-DEHYDROGENATIVE COUPLING FOR C(SP^3)-C(SP^2) BOND FORMATION THROUGH C–H FUNCTIONALIZATION

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Abstract:

Cross-Dehydrogenative Coupling (CDC) reactions mainly undergo through the formation of a new bond between two different molecules andthe elimination of a hydrogen atom from each molecule. The copper-Catalyzed cross-dehydrogenative coupling reactions have secured a prominent position to synthesize a wide range of complex compounds due to their sustainable nature, low toxicity, eco-friendliness, catalytic versatility and coast effectiveness. The present chapter emphasizes the recent progress on synthesizing important organic compounds involving copper-Catalyzed cross-dehydrogenative coupling to construct C(sp^3)-C(sp^2)by C−H functionalization.

Keywords: Cross-coupling reaction, Synthesis, Copper Catalyzed, Cross-dehydrogenative coupling, C−H functionalization.

Introduction:

The transition metal-Catalyzed methodologies have played a significant role in synthetic organic chemistry (Stanforth, 1998; Nakamura and Yamamoto, 2004; Patel *et al.*, 2014). In the last decade, cross-coupling reactions for the formation of carbon-carbon and carbon-heteroatom bonds via direct activation of C–H bonds under cross-dehydrogenative coupling offer an atom cost-effective and sustainable alternative to classical cross-coupling procedures (Peng *et al.*, 2019; Kim and Li, 2020). The number of scientific publications and patents relating to the cross-dehydrogenative couplingreactions for synthesizing various important organic and heterocyclic analogues has been increasing continuously, Forthe past ten years (Figure-1).

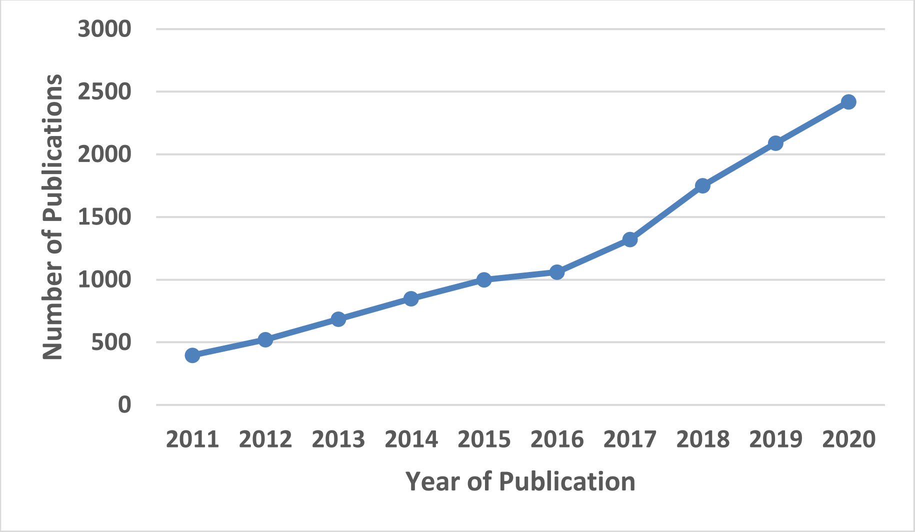


Figure 1: Recent research progresses on Cross-Dehydrogenative Coupling

The cross-dehydrogenative coupling reactions are used to construct carbon-carbon bonds between C(sp^3)-C(sp^3), C(sp^3)-C(sp^2), C(sp^3)-C(sp), C(sp^2)-C(sp^2) and C(sp^2)-C(sp) atoms (Wen *et al.*, 2012; Ding *et al.*, 2014). Different types oftransition metal catalysts such as Palladium, Ruthenium, Zirconium, Nickel, Copper, Iron, Cobalt etc., are widely used in cross-dehydrogenative coupling and have found wide applications in heterocyclic chemistry (Beletskaya and Cheprakov, 2004; Li and Li, 2006). The cross-dehydrogenative coupling reactions do not require anypre-functionalization (Girard *et al.*, 2014). They frequently undergo in the presence of hydrogen atom acceptors such as O_2, DDQ, peroxides, hypervalentiodine, or TEMPO, reagents etc. (Baeten and Maes, 2017; Guo *et al.*, 2017).

Copper-mediated cross-coupling reactions have received substantial attention in organic synthesis due to their economic and greener reaction protocols (Zhang *et al.*, 2012; Bhunia *et al.*, 2017). This chapter briefly describes recent advances reported in various Copper-Catalyzed cross-dehydrogenative coupling reactions for the C(sp^3)-C(sp^2) bond formation through C−H functionalization.

Copper-Catalyzed CDC for C(sp^3)-C(sp^2) bond formation:

The general scheme for the construction of carbon-carbon bond in Copper-Catalyzed cross-dehydrogenative coupling reactions involves eliminating H_2 molecule in the presence of suitable oxidant (Figure-2) (Li, 2009; Yeung and Dong, 2011).

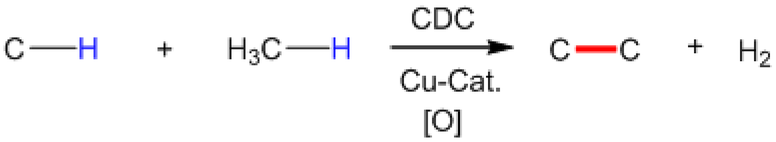


Figure 2: General scheme for Copper-Catalyzed cross-dehydrogenative couplingfor C-C bond formation

Wu and co-workers (Figure-3) introduced $Cu(OAc)_2/(^tBuO)_2/Py$ Catalyzed cross-dehydrogenative coupling of aromatic sp^2 C–H bonds and unactivated aliphatic sp^3 C–H bonds. The synthetic protocol displayed high efficiency and good functional group tolerance (Wu *et al.*, 2015).

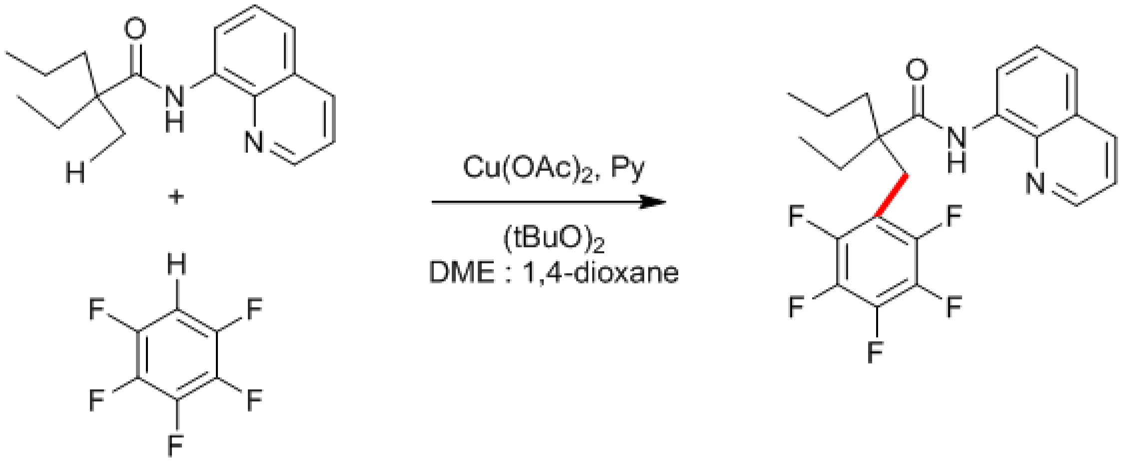


Figure 3: Copper-Catalyzed cross-dehydrogenative coupling of 2-ethyl-2-methyl-N-(quinolin-8-yl) pentanamide with pentafluorobenzene

Romo-Pérez *et al.* (Figure-4) developed CuBr/DDQ mediated cross-dehydrogenative coupling reaction using a widevariety of nucleophiles such as nitroalkanes, dialkyl malonates, alkynes, dialkyl phosphites, carbonyl compounds, pyrrole, andindoles.(Romo-Pérez *et al.*, 2015)

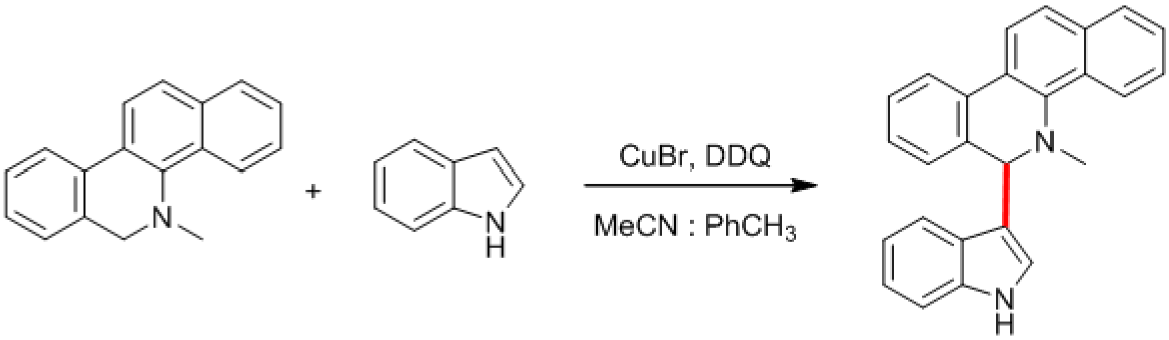


Figure 4: Copper-Catalyzed cross-dehydrogenative coupling (CDC) of 5-methyl-5,6-dihydrobenzo[*c*] phenanthridinewith indole

Zhang *et al.* (Figure-5) reported the synthesis of various 2-benzylindoles by Copper-Catalyzed regioselective cross-dehydrogenative C(sp^3)-C(sp^2)coupling of *N*-pyrimidylindoles with benzylic. They used $Cu(OAc)_2$as a catalyst, di-tert-butyl peroxideas a mild oxidant, and benzaldehyde as an effective additive (Zhang *et al.*, 2015).

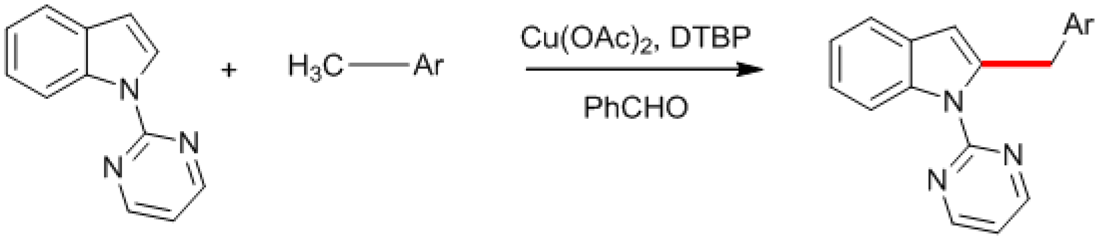


Figure 5: Copper-Catalyzed cross-dehydrogenative coupling of *N*-pyrimidylindoles with benzylic

Qin *et al.* (Figure-6) demonstrated a novel Cu-Catalyzed direct implanting of a benzyl group into simple enones under mild andneutral reaction conditionsin the presence of $Cu(tfacac)_2$, Salicylic acid and TBP throughthe construction of C(sp^3)-C(sp^2)bond (Qin *et al.*, 2015).

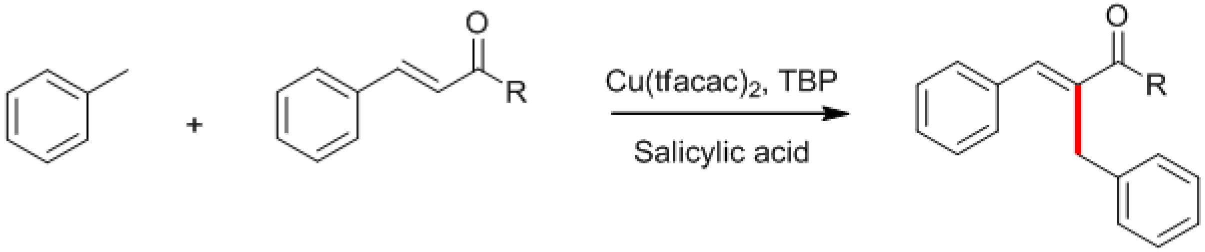


Figure 6: Copper-Catalyzed cross-dehydrogenative coupling of benzyl group with enones.

Baral *et al.* (Figure-7) described the $Cu(OTf)_2$Catalyzed cross-dehydrogenativecoupling reaction of quinone derivatives withthe various cycloalkanes by using TBHP (Baral *et al.*, 2016).

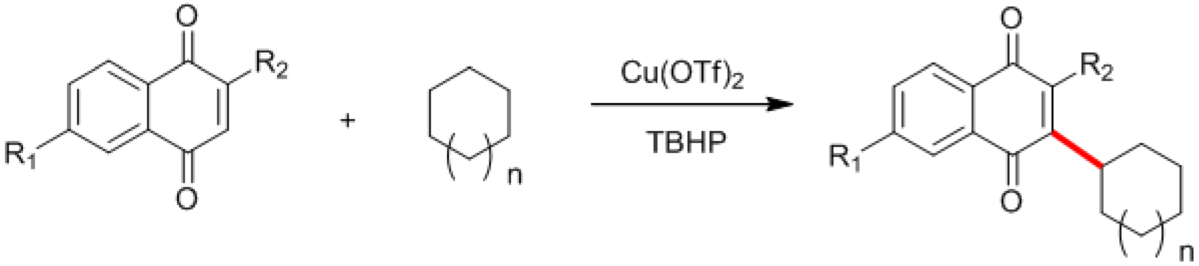


Figure 7: Copper-Catalyzed cross-dehydrogenative coupling of quinones with cyclicalkanes

Cai and co-workers (Figure-8) developed Cu(OTf)$_2$Catalyzed cross-dehydrogenative coupling reaction of thiazoles with THF in the presence of potassium persulfate.They performed a DFT and KMC Study of Cu-Catalyzed CDC of thiazoles and THF (Cai *et al.*, 2016).

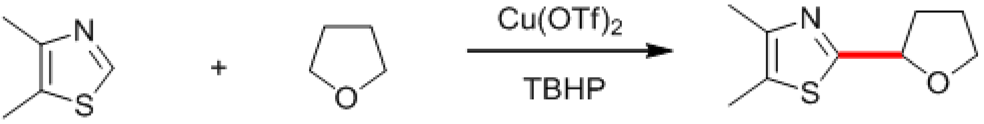


Figure 8: Copper-Catalyzed cross-dehydrogenative coupling of thiazoles with THF

Chua *et al.* (Figure-9) described the construction of the C(sp^3)-C(sp^2) bond between hydrogenated graphene and tetrahydrothiophen-3-one through a cross-dehydrogenative coupling reaction using Cu(OTf)$_2$ asthe catalyst and DDQ as the oxidant (Chua *et al.*, 2016).

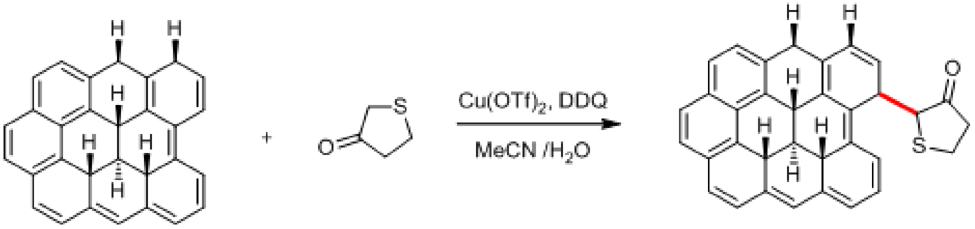


Figure 9: Copper-Catalyzed cross-dehydrogenative coupling of hydrogenated grapheme with dihydrothiophen-3(2*H*)-one

Storr *et al.* (Figure-10) introduced the CDC synthesis of substituted halodiarylmethanes using stoichiometric copper(II) bromide and di-tert-butyl peroxide(DTBP) (Storr *et al.*, 2016).

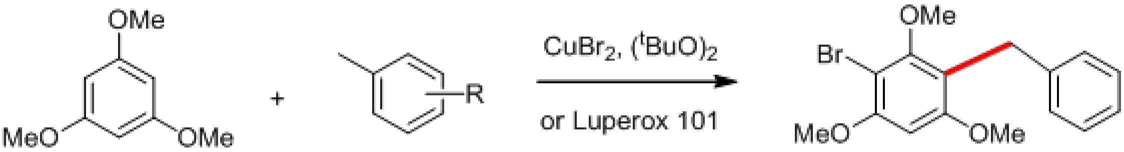


Figure 10: Copper-Catalyzed cross-dehydrogenative coupling of alkoxybenzenes with toluenes

Xu and co-workers (Figure-11) developed an efficient synthetic route to construct a C-C bond between indolederivatives and fluorinated alcohol using CuBr,dicumyl peroxide and t-BuOH/TFE catalytic system (Xu *et al.*, 2016).

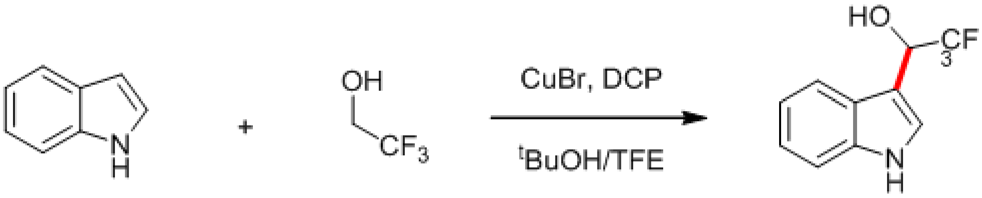


Figure 11: Copper-Catalyzed cross-dehydrogenative coupling of *N*-heterocycles with fluorinated alcohols

Sarkar *et al.* (Figure-12) developed a new general method for synthesizing acridine-1,8-diones through C(sp^3)-C(sp^2) bondCDC coupling of enamino-ketones using an efficient CuBr, CH_3CN and air catalytic system (Sarkar and Mukhopadhyay, 2016).

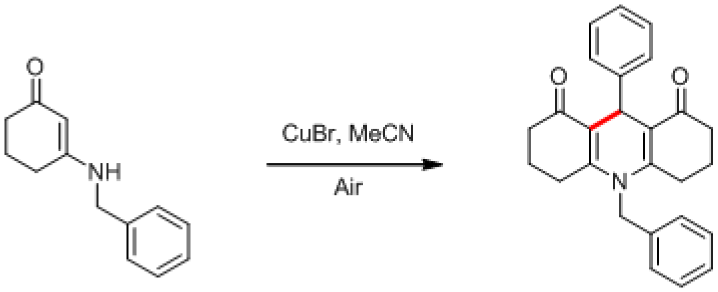


Figure 12: Copper-Catalyzed cross-dehydrogenative coupling of enamino-ketones

Hurst *et al.* (Figure-13) reported an inexpensive Cu(2-ethylhexanoate)$_2$ Catalyzed radical cross-dehydrogenative coupling approach to acridanes and related heterocycles from readily available 2-[2-(arylamino)aryl]malonates (Hurst and Taylor, 2017).

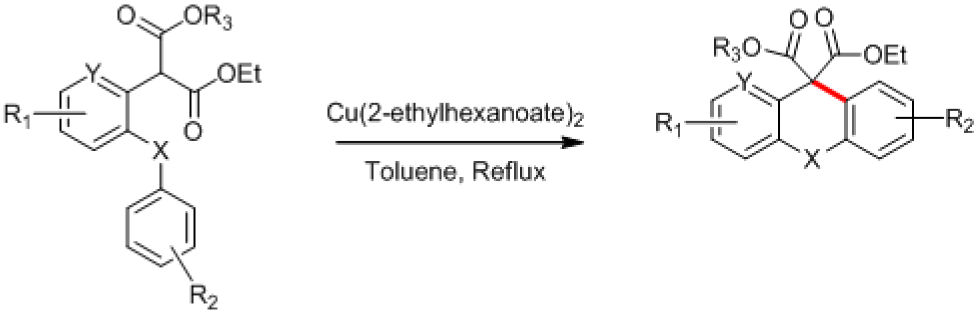


Figure 13: Copper-Catalyzed cross-dehydrogenative coupling of acridanes

Zhu *et al.* (Figure-14) reported externaloxidant free copper-Catalyzed oxidative C(sp^3)-C(sp^2) type cross-dehydrogenative coupling of *N*-arylglycine esters with 2-arylimidazo[1,2-*a*]pyridines. They introduced Cu(OTf)$_2$ mediated catalytic system inMeCN solvent using air as an oxidant (Zhu *et al.*, 2018).

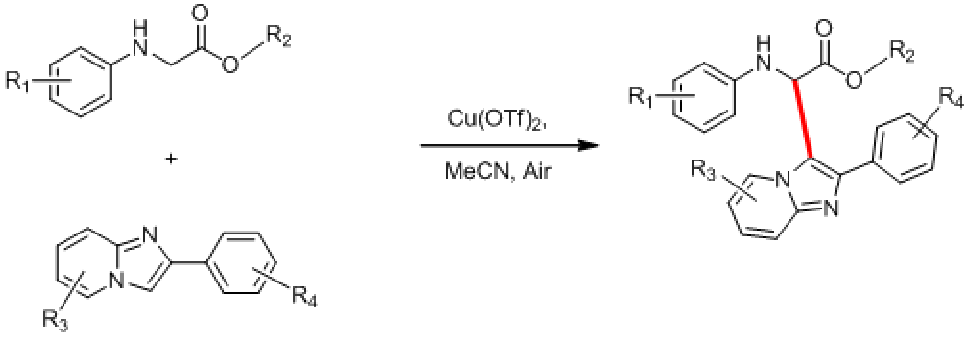


Figure 14: Copper-Catalyzed cross-dehydrogenative coupling of *N*-arylglycine esters with 2-aryl imidazo[1,2-*a*]pyridines

Hurst and co-workers (Figure-15) established a novel synthetic methodology for the synthesis of spirocyclic oxindoles. They have developed an efficient $Cu(OAc)_2H_2O$ catalytic system in the presence of atmospheric oxygen and used tolueneas a common solventfor the construction of $C(sp^3)$-$C(sp^2)$ type carbon-carbon bond (Hurst *et al.*, 2018).

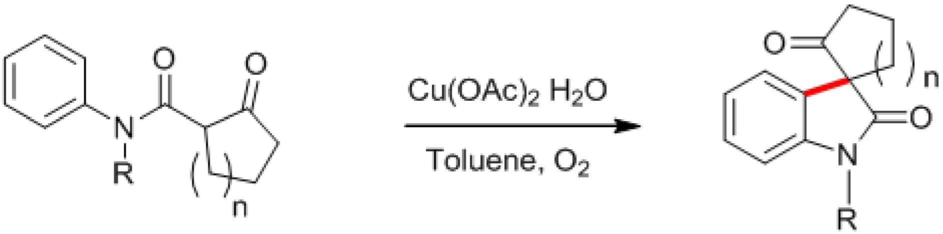


Figure 15: Copper-Catalyzed cross-dehydrogenative coupling to prepare satavaptan scaffolds

Gorman *et al.* (Figure-16) developed a cyclization procedure to prepare 4-carboxy-quinolin-2-ones from linear anilides via a one-pot cross-dehydrogenative coupling using Cu(2-ethylhexanoate)$_2$,*N*,*N*-Diisopropylethylamine, mesitylene and air catalytic system (Gorman *et al.*, 2019).

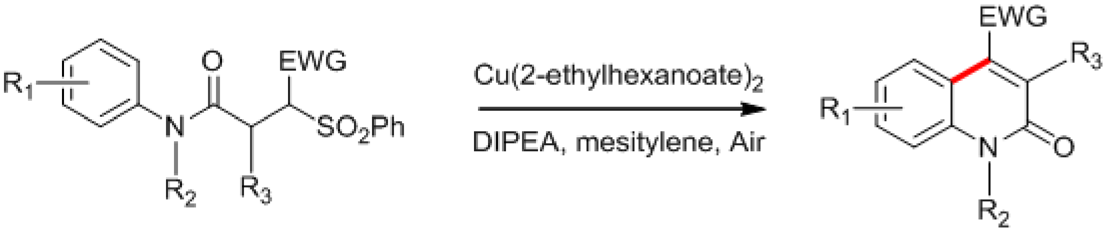
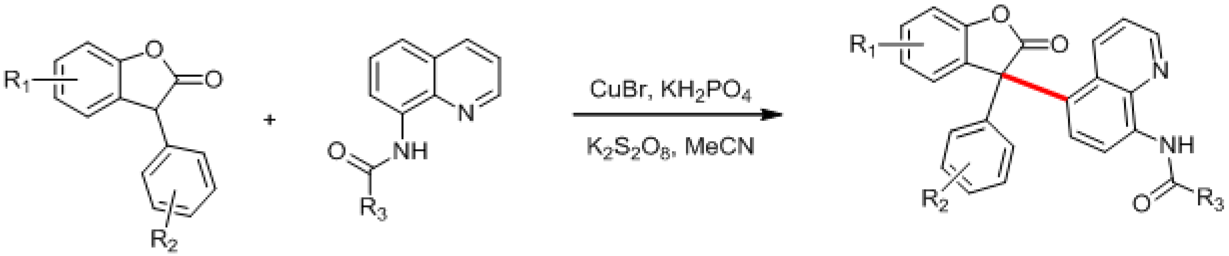


Figure 16: Copper-Catalyzed cross-dehydrogenative coupling to prepare4-carboxy-quinolin-2-ones

Tang *et al.* (Figure-17) introduced Cu-Catalyzed protocol for cross-dehydrogenative coupling of benzofuranones with indoles, quinolines, thiophene, and carbazoles, which furnishes highly functionalized 3,3-diaryl benzofuranones bearing a three aryl quaternary carbon centre atthe C3 position in good yields.(Tang *et al.*, 2019)



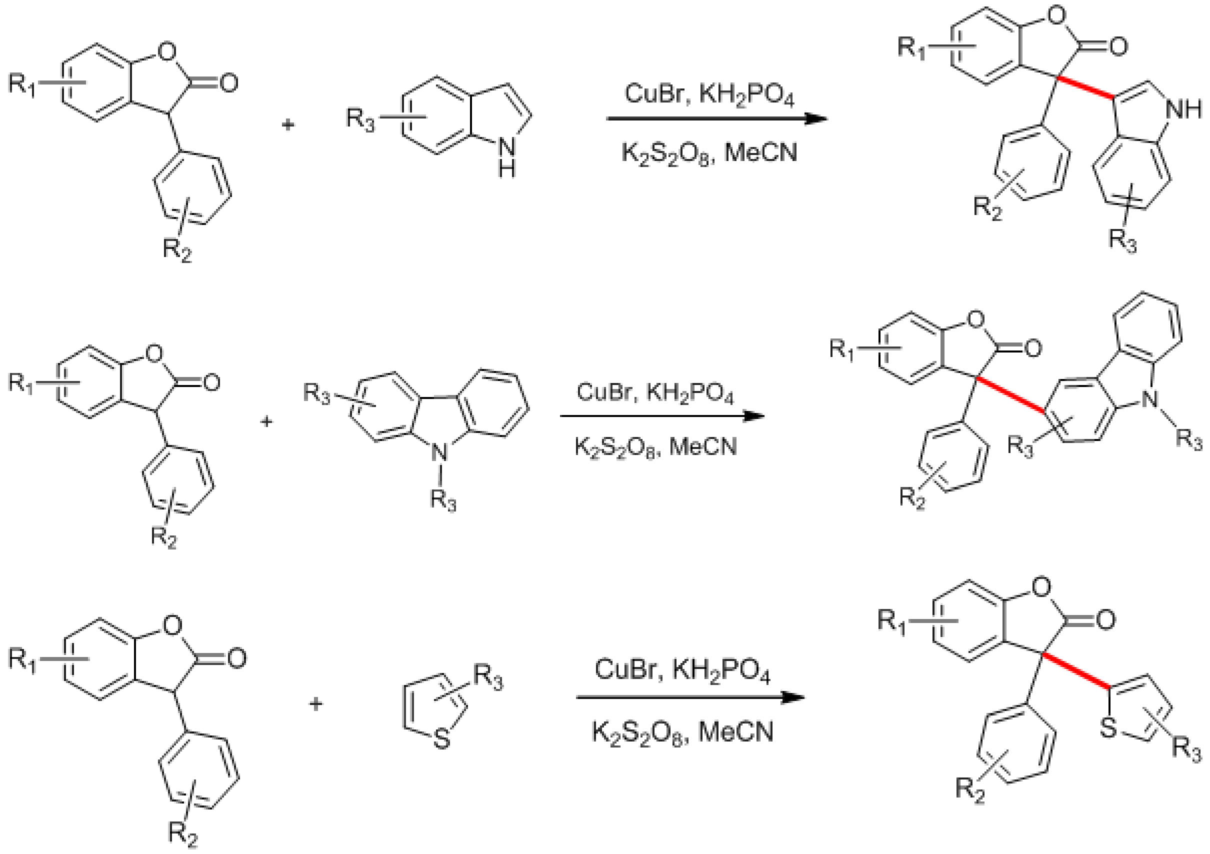


Figure 17: Copper-Catalyzed cross-dehydrogenative coupling benzofuranones with indoles, quinolines, thiophene, and carbazoles

Zhu *et al.* (Figure-18) introduced an efficient cross-dehydrogenative coupling reaction in the presence of $Cu(OTf)_2$, $MnO_2$and 4,4′-di-tert-butyl-2,2′-bipyridine in DMF solventto facilitateC(sp^3)-C(sp^2)bond in various heteroarenes, such as imidazo[1,2-*a*]pyridine and dimethylglycine (X. Zhu *et al.*, 2021).

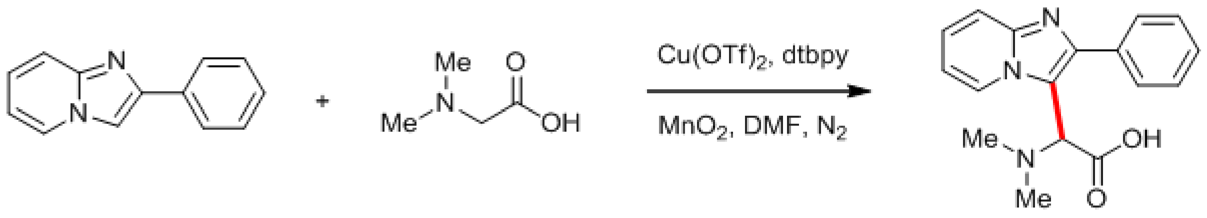


Figure 18: Copper-Catalyzed cross-dehydrogenative coupling 2-phenylimidazo[1,2-*a*] pyridine with 2-(dimethylamino) acetic acid

Treacy and co-workers (Figure-19) developed cross-dehydrogenative C(sp^3)-C(sp^2) coupling between the alkane andelectron-deficient olefin using an efficient $CuCl_2$/LiCl/TBACl catalytic system inMeCN solvent (Treacy and Rovis, 2021).

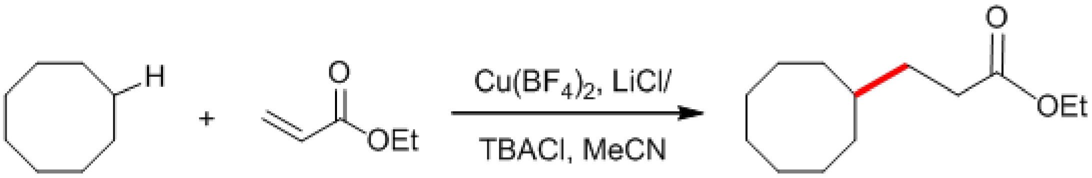


Figure 19: Copper-Catalyzed cross-dehydrogenative coupling of cyclooctanewith ethyl acrylate

Liu *et al.* (Figure-20) reported a novel dehydrogenative coupling reaction of *N*-fluorocarboxamides with polyfluoroarenes forming C(sp^3)–C(sp^2) bonds enabled by efficient Cu($CF_3COCHCOCH_3$)$_2$/*t*-BuONa/bpy catalytic system in trifluorotoluene solvent (Liu *et al.*, 2021).

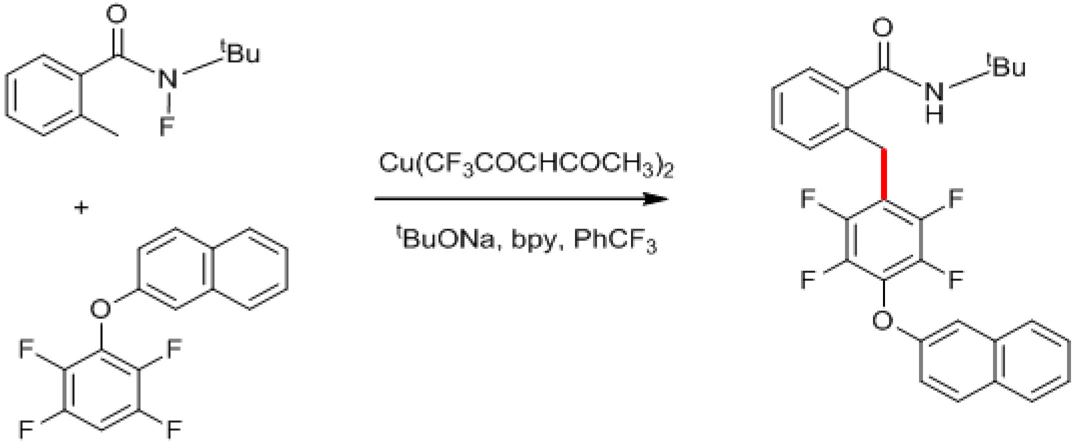


Figure 20: Copper-Catalyzed cross-dehydrogenative coupling of *N*-fluorocarboxamides with polyfluoroarenes

Conclusion:

Copper-Catalyzed cross-dehydrogenative coupling reactionshave secured an important place in synthetic organic chemistry due to their straightforward, mild and eco-friendly reaction conditions as well as cost-effectiveness. The present review will be helpful to the organic chemists in academia and industrial R&D sectors to understand the challenges related to the recently reportedCopper-Catalyzed Cross-Dehydrogenative coupling for C(sp^3)-C(sp^2) bond formation through C−H functionalization as well as the future potentials.

Acknowledgements:

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LANGMUIR-BLODGETT (LB) TECHNIQUE AND ITS IMPORTANCE

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Introduction:

In everyday life we often observe the phenomenon of spreading of oil on the water surface. It always forms a thin layer of about few nm. Sir Benjamin Franklinin 1774 first showed some scientific interest on the formation of the monolayer film onto water surface and experimentally described the phenomenon of spreading of oil at the pond of Clapham where he noticed the effect of oil on the “stilling of waves” [1]. A German lady Agnes Pockels, in her kitchen first performed a scientific experiment on monolayer film anddetermined the factors whichchange the area of the surface in case of different oils [2, 3].The thickness of the film spread on water surface was first calculated by Lord Rayleigh and thickness was nearly of the one molecule [4].

In last two decades, Irving Langmuir first performed systematic studies on floating monolayers of fatty acids, esters andalcohols on water. From his experimental study it was confirmed that the surfactant molecules consist of two parts one is hydrophilic part and another is hydrophobic part. Another important part he confirmed that the molecular area only depends on the hydrophilic part of the molecule not on hydrophobic part [5]. Irving Langmuir received the Nobel Prize in the year 1932 in Chemistry for his contribution to surface chemistry. On the other hand, Katherin Blodgett first gave theprocess of transfer of monolayer films onto a solid substrate from the air-water interface and he received Nobel prize in the year 1934. Based on their investigations now-a-days such types of monomolecular films are called Langmuir-Blodgett (LB) films.

Langmuir-Blodgett technique allows the preparation ofmaterials with high degree of control on the structure at the molecular level. Due to the control organisation of the molecules the thin films of these materials show considerable potential for different technological applications such as molecular electronics devices [6-8], molecular switching behaviour [9], optoelectronic devices [10-14] and also for the construction of different biological sensing devices [15-17]. In LB technique the monolayer film formed at the air-water interface used as a model system to study the different phenomena*in vitro*. Brewster Angle Microscope and

Fluorescence Imaging Microscope are used to study these phenomena. After transfer of the monolayer film onto solid substrate and by repeating this process we get the multilayer film. The organisation of the assembly of molecules onto solid substrate can be changed by considering different parameters such as temperature and pH of the subphase, molarratio of the sample, surface pressure etc.

Ideal LB compatible materials:

1. **Amphiphilic Materials**

For the preparation of ultra- thin films using Langmuir-Blodgett technique amphiphilic molecules are the most suitable which have two parts one part is hydrophilic part and another is hydrophobic part. Hydrophilic part is the water loving part and hydrophobic part is the water hating part.

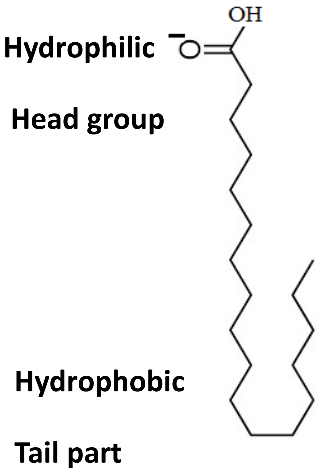


Figure 1 (a): Structure of saturated fatty acid

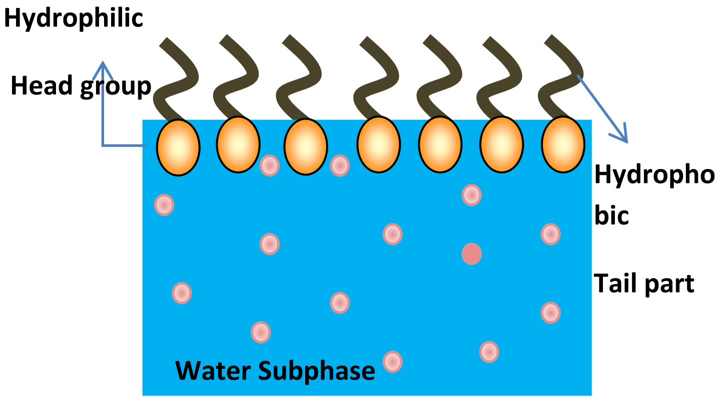


Figure 1 (b): Amphiphilic molecules arranged on air-waterinterface

Due to the presence of the hydrophobic part amphiphilic molecules are not soluble in water but soluble in organic solvent and capable of forming ideal Langmuir monolayer. They are known as surfactants. There are so many important types of surfactants such as soaps, phospholipids, protein, fatty acids, amines and various substances with long alkyl chains connected to polar head groups. The long chain -CH2- part of these molecules that's hydrocarbonpartis responsible for the repulsion of water (water hating) whereas the polarhead group (-COOH or -OH etc) has sufficient affinity for water (water loving) to attach themolecules. The most commonly used materials for Langmuir-Blodgett technique are stearic acid (SA), arachidic acid (AA),octadecylamine (ODA) etc, esters, amines, alcohols and various biomolecules such as phospholipids, protein, Cholesterol etc.

2. **Non-amphiphilic Materials**

Some molecules which have no hydrophobic part are called non-amphiphillic molecules. These non-amphiphilic molecules can also form stable Langmuir monolayer on mixing with a building matrix of long chain fatty acid or some optically inert polymer matrices namely polymethylmethacrylate (PMMA) or polystyrene (PSt). Some non-amphiphilic molecules are 2-(4-biphenylyl)-6-phenyl benzoxazole (PBBO), 1,4-bis(3-quinolyl)-buta-1,3-diyne (DQ), phthalocyaninate, bathophenanthroline (BPH) and behenic acid (BA). Such types of molecules have interesting physical and physico-chemical properties and have their vast technological applications in thin film science.

3. **Water soluble Materials**

For the technological importance Langmuir monolayer of varioustypes of water soluble cationic and anionic molecules such as different dyes, namely Rhodamine, Acridine Orange, Safranine, Congo Red, Porphyrins, Pthalocyanines, Oxazines andtheir derivatives, Proteins, Enzymes, DNA etc.[18-20] areprepared at the air-water interface and correspondingmono- and multi-layered LB films are transferred onto solid substrate. In this case a complex Langmuir monolayer is formed due to the electrostatic interaction of water-soluble molecules with the another oppositely charged molecules say stearic acid (SA), arachidic acid (AA), octadecylamine (ODA), dipalmitoyl phosphatidylcholine (DPPC) and also several others.In recent years such types of complex Langmuir monolayers have attracted great interest in the architecture and molecular engineering with desired structural and physical properties [21, 22].

4. **Ionic nano-particles (NP)**

When Ionic nano-particles (NP) are dispersed in the aqueous subphase of the Langmuir trough they can adsorbed onto a template monolayer of oppositely charged molecules and thus form a stable organo-NP hybrid monolayer. There are several NPs like metallic nano particles namely Ag, Au [23], metal oxide nano particles namely ZnO, CaO [24-26], metal sulphide nano particles namely ZnS, CdS [27-29] and others like ZnSe [30], CdSe [31], carbon nano tubes [32], and nao-clay platelets [33]. These nano particles have the unique capability to adsorb and intercalate the water-soluble molecules including various dyes and other biologically important molecules namely proteins, enzymes, DNA etc. The hybrid Langmuir monolayer formed by such types of nano-particles have their important applications in various technological fields.

5. Clay minerals: Nano clay platelets

Clay minerals have permanent colloidal size, unique structural charge and layered structure. Due to the presence of cations / anions between the interlayer spaces clays are charged particles. For these reasons theyshow a variety of physical and chemical properties and they are eco-friendly and non-hazardous in nature. There are different clay minerals such as montmorillonite, saponite, hectorite, laponite, kaolinite etc.

Clay minerals are easily adsorbed into the organic materials and are used to construction the hybrid organic/inorganic nano composites as they have unique material properties like colloidal size, layered structure and nano scale platelet shaped dimensions [34, 35]. Organo- clay hybrid LB filmshave vast applications in sensors development, electrode modifiers, and pyroelectric materials [36].

These hybrid films are prepared by incorporating charged or neutral organic molecules into the clay surface or interlamellar space of the clay surface. Cation exchange capacity (CEC) is the number of exchangeable cations, which is usually expressed in micro-equivalents per gram (μeqg^{-1}). It depends on surface area, the type of exchangeable cation and the pH value. Due to these properties the organic molecules are either adsorbed onto the clay surface or enter into the inter laminar space of clay surface resulting in the formation of organo-clay hybrid system[37]. There are different parameters which control the monolayer formation of several molecules in Langmuir-Blodgett technique and also the transfer of stable film onto solid substrate.

1. Surface pressure

Due to surface tensionthe liquid molecules always try to reduce its surface area at the liquid/gas interface. When the surface tension of a liquidis higher it less spreads out. In liquid, molecules have excess free energy called surface tension and is defined by

$$\gamma=(\delta G/\delta A)T,P,n$$

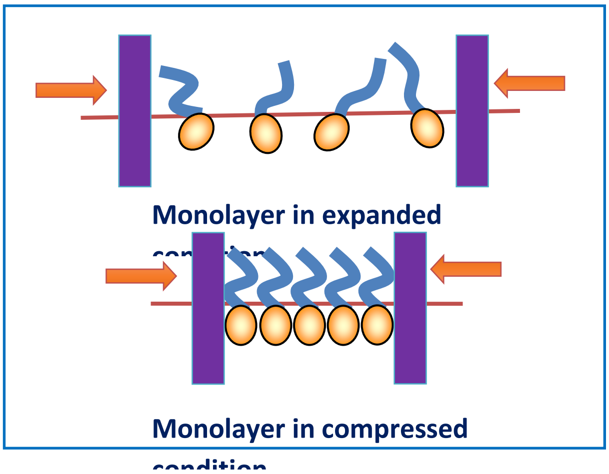


Figure 2: Schematic of compression of amphiphilic molecules by a movable barrier at air-water interface

Where G is the Gibbs free energy of the system, A is the surface area. The temperature T, the pressure P and the composition n are held constant. Water is mostly used as subphase in LB experimentsbecause it has a high value of surface tension of 74 mN/m at 20°C and normal atmospheric pressure. The energy required to expand the surface isothermally by unit area is called surface energy and it is numerically equal to the surface tension. Various surfactant molecules like fatty acids, esters etc. when spread at the air-water interface, they have the tendency to come close to each otherand cause the expansion of the interface which lowers the surface tension of water. When the volatile solution (solvent like chloroform) of the amphiphilic moleculespreads on the water surface they quickly try to cover the available surface area and a monolayer is formed (Figure 2). The chloroform evaporates after some time and then amphiphilic molecules lie at the air-water interface of the Langmuir Trough. At the initial stage the intermolecular distance between the molecules is large due to the large available area at the air-water interface and the intermolecular interactions between the molecules become weak.In this case the monolayer can be considered as a two-dimensional gas. Under these circumstances the monolayer has the small effect on the surface tension of water. When area of the monolayer is reduced by the compression of the barrier the molecules come in contact and exert a repulsive force on each other. As a results surface tension decreases with respect to the surface tension of pure water surface (γ_0). Surface pressure is measured by the reduction of the surface tension of the pure liquid by the amphiphilic molecules i.e.

$$\pi = \gamma_0 - \gamma$$

Where γ_0 is the surface tension of the pure liquid and γ is the surface tension of the monolayer surface.

2. Formation of Langmuir monolayer and monolayer phases

When some organic amphiphiles are spread on the water subphase of the Langmuir trough and surface pressure is increased by compressing the barrier, a stable Langmuir monolayer is formed. Due to the highly ordered organisations of the organic molecules a well-organized mono- and multi-layered structures of organized molecular assemblies are formed at the interface.When the number of molecules on the water surface is sufficiently small, the surface tension does not change noticeably, i.e. the surface pressure remains zero. By reducing the area available per molecule and simultaneously recording the surface pressure, we get the surfacepressure versus area per molecule isotherm (π-A isotherm) at a constant temperature. From theπ-A isotherm some valuable information about themonomolecular film can be obtained and also one can be sure whether the material of interest is suitable for LB film fabrication or not.

Figure 3 shows an idealized (π-A)isotherm with distinct three phases in the curve.The discontinuities in the π-A isotherm curve confirm the presence of the different phases in the monolayer at the air-water interface. Depending on the nature of the material, temperature and different microenvironment of the subphase, the shape of the (π-A) isotherm also changes. The different types of forces between the hydrophilic head groups, the length of the hydrophobic part of the amphiphilic molecules influence the formation of the Langmuir monolayer at the air-water interface [38].

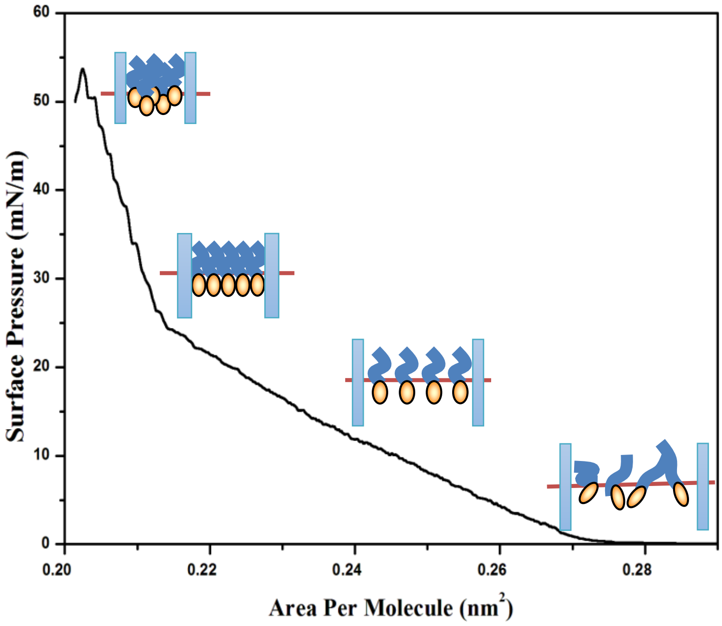


Figure 3 A: graphical representation of a surface pressure –area per molecule isotherm at the air-water interface

Different types of Langmuir monolayer prepared at the air water interface:

Depending on the chemical and physical properties of the materials used, different types of Langmuir monolayer can be prepared at the air-water interface. These are discussed in brief in the following sections.

1. Mixed Langmuir monolayer

Apart from the amphiphilic materials as compatible for the formation of conventional stable Langmuir monolayer, different non-amphiphilic and even water-soluble organic materials also form stable Langmuir monolayer [39]. In case of non-amphiphilic molecules some inert building matrix, namely long chain fatty acid or an optically inert polymer matrix are required for the formation of a stable Langmuir monolayer at the air-water interface and can be easily transferred onto solid substrate to form mono- and multilayer mixed Langmuir Blodgett (LB) films. The properties of the materials are often modified in mixed thin films as compared to the bulk. The interesting phase behaviour of the mixed Langmuir monolayer may be observed depending on the miscible or immiscible nature of the components in the binary mixtures of molecules [40]. The changes in the phase behaviour during compression isotherm occurred mainly due to the different structure of the molecules. Some other factors, such as subphase pH, ratio of components in the mixture as well as also the temperature determine the state of separation of immiscible components [41]. The pressure- area isotherm (π- A) gives the important information about the thermodynamic nature of missing of the binary components, degree of miscibility of components and also the formation of separated microstructure in molecular level.

2. Complex Langmuir Monolayer

Now a days researchers are interested to study the different water soluble materials (Namely different biologically important fluorescent dyes, DNA, proteins and enzymes) using Langmuir Blodgett (LB) technique due to the vast technological applications of the ultra-thin films of this material. In this case a complex Langmuir monolayer is formed at the air-water interface due to the electrostatic interaction of the water-soluble materials from the water subphase with the oppositely charged preformed template Langmuir monolayer at the air-water interface [42].The nature of such types of complex Langmuir monolayer is different from the Gibbs monolayer. Here the changes in the complex Langmuir monolayeris observedby monitoring the changes in the surface pressure with time, keeping the barrier at a fixed position and continuous adsorption of the water-soluble materials to the preformed Langmuir monolayer changes the surface pressure with time.

Such type of interaction was observed when some water-soluble fluorescent dyes are come in contact with the preformed Langmuir monolayer of a lipid (DPPC), a complex Langmuir monolayer was formed at the air-water interface [43]. In this process first of all a preformed Langmuir monolayer of lipid (DPPC) was formed at the air-water interface keeping the surface pressure at 0.1mN/m. Then dilute aqueous solution of Rhodamine B was injected from the back side of the barrier so as not to disturb the preformed Langmuir monolayer as shown in figure 4.Water solubleRhB molecules crossed the barrier from inside the water subphase and reacted with DPPC molecules of the preformed DPPC monolayer and complex DPPC-RhB molecules were formed. Area per molecule of this complex monolayer was greater than the pure DPPC area per molecule. Due to the formation of more complex molecules at the interface with the passage of time surface pressure increases instead of keeping the barrier fixed at particular position. The graph shown in the figure 5 shows the progress of reaction and formation of stable complex monolayer at the air-water interface. The complex monolayer could be transferred onto any kind of substrate at a desired surface pressure to form mono- and multilayered Langmuir-Blodgett (LB) films.

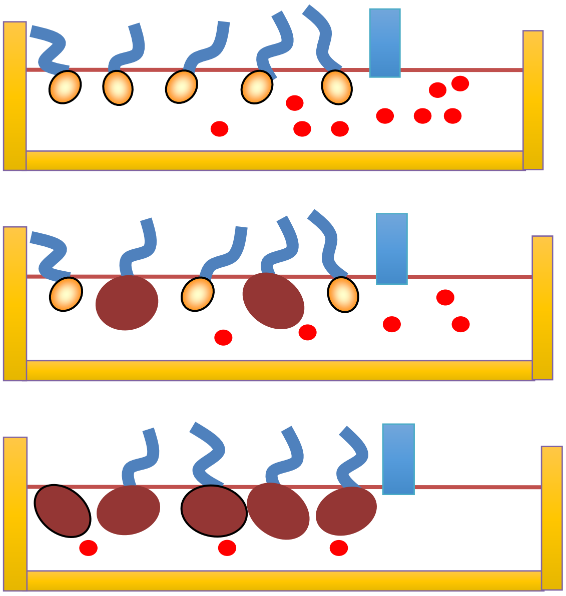


Figure 4: Schematic representation of theformation of a typical complex Langmuirmonolayer at the air-water interface of aLangmuir trough.

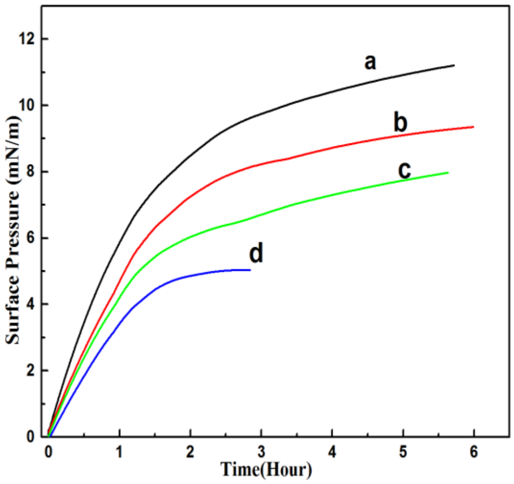


Figure 5: Surface pressure vs. time graph ofthe DPPC-RhB complex monolayer with variousamount of aqueous solution of RhB injected from back side of the barrier (a) 100 µL, (b) 75 µL, (c) 50 µL, (d) 25 µL.

3. Hybrid Langmuir Monolayer

Organic – inorganic hybrid films prepared by LB technique have been investigated in material science for their wide range of distinctive properties for innovative and technological applications. By controlling and optimizing various film formatting mechanisms, these hybrid materials can be used for various technological applicationssuch as sensors, electrode modifiers, non-linear optical devices and pyroelectric materials [44]. Generally hybrid Langmuir monolayer is formed at the air-water interface when some organic / inorganic nano particles (NPs) interact with any molecules in the subphase. One of the most promising and interesting inorganic nano particle which form hybrid Langmuir monolayer is nano-clay platelets. Clay minerals are naturally occurring nano particles and less toxic compared to other NPs. These sheet likeinorganic particles can incorporated into ultrathin hybrid Langmuir films [45]. These hybrid molecules show new physical properties which are not present in each of the separate components [46].

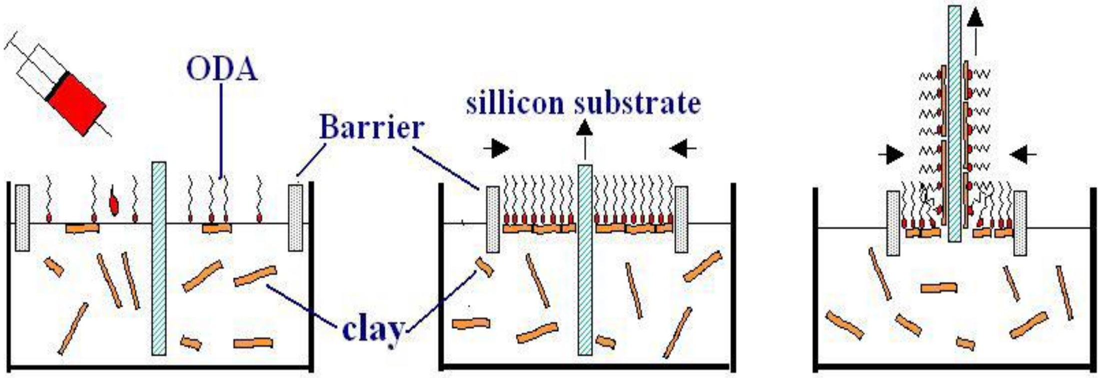


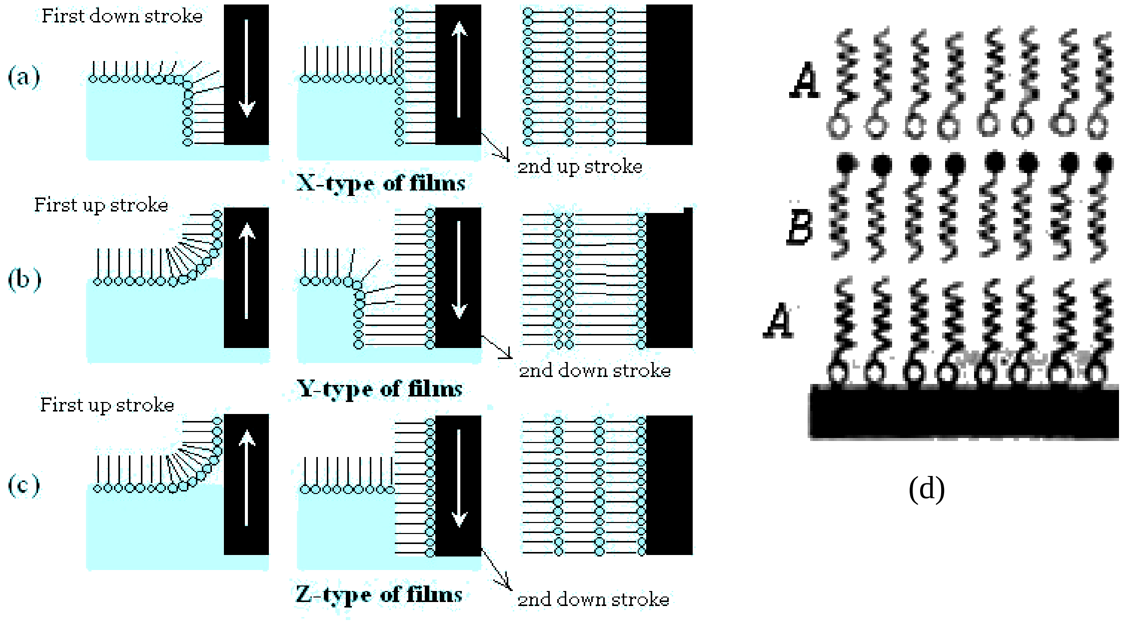
Figure 6: Schematic representation of the formation of organo-clay hybrid LB monolayer at the air-water interface

LB technique is mostly used for the preparation of organo-clay hybrid films. In this fabrication technique amphiphilic cation is spread on the surface of dilute anionic aqueous clay dispersion in Langmuir trough and the clay platelets get adsorbed onto the floating opposite charged amphiphilic monolayer at the air-water interface forming a floating hybrid Langmuir monolayer of clay-amphiphilic systems.During the adsorption process, electrostatic interactions play dominant role and clay platelets are adsorbed onto the floating monolayer [47]. The surface pressure–area per molecule isotherms confirm the formation of the hybrid monolayer at the air-water interface. The isotherm of the hybrid monolayer is shifted to larger area per molecule compared to the pure isotherm of the amphiphilic molecules and indicates the presence of the clay platelets in the hybrid monolayer. Figure 6 shows the schematic representation of the formation of organo-clay hybrid LB monolayer at the air-water interface. The hybrid organo-clay Langmuir monolayer can be transferred onto a suitable solid substrate to form mono and multilayered hybrid LB films. There are some other types of materials which can also be able to form stable hybrid LB monolayer such as transition metal complex [48], metal ions, enzymes [49], proteins [50, 51], graphite oxides [52] etc.

3. Langmuir-Blodgett technique: Film deposition onto solid substrates

The highly organized Langmuir monolayer at the air-water interface can be transferred onto a solid substrate to form Langmuir-Blodgett (LB) films Irving Langmuir and Katherin Blodgett first introduced the Langmuir-Blodgett technique for transferring the monolayer from air-water interface onto solid substrate. The surface pressure is kept constant during the film transfer and is properly chosen to be below the monolayer collapse pressure. In this case one monolayer as well several monolayers can be transferred onto solid substrate to form mono and multilayered films.

Three different types of film deposition techniques are available namely (a) X type, (b) Y type and (c) Z type. Substrates used for the film deposition techniques are hydrophilic or hydrophobic. The examples of hydrophilic substrates are glass, quartz glass, metal plates composed of oxides of chromium, aluminum or tin, silver and gold (conductive substrates) etc. On the other hand, mica, HOPG, silanized SiO2 etc. are the most common examples of hydrophobic substrates. Figure 7 (b) shows the most common form of LB film deposition.



(d)

Figure 7 (a) X-type deposition onto hydrophilic substrates; (b) Y- type deposition onto hydrophilicsubstrates; (c) Z- type deposition onto hydrophilic substrates (d) An alternate-layer Langmuir Blodgett film built up from monolayer of compound A and monolayer of compound B.

In case of hydrophilic substrate, the first monolayer is transferred on the substrate, during the upstroke through the monolayer. Therefore, before monolayer spreading, the substrate should be kept inside the subphase. By repeating the up-stroke and down-stroke through the monolayer a multilayered LB is formed onto the solid substrate. For hydrophobic substrate the monolayer is deposited on the first down-stroke through the interface. In such case, hydrophobic tail part of the molecule first interacts with the substrate and becomes hydrophilic. Then during down stroke, the second layer will be transferred as shown in figure 7 (b). This Y type deposition technique results in the stacking of head to head or tail to tail arrangement on the solid substrates and thus Y-type LB film is obtained. In X type deposition technique floating monolayer is transferred onto the substrate only during the down-stroke and in Z type only during up-stroke as shown in figure 7 (a) and 7 (c) respectively. In double trough LB instrument, alternate layer films can be produced by raising the substrate through a monolayer of one material (consisting of molecules of compound A, say) and then lowering the substrate through a monolayer of second substance (compound B) in the second trough. Thus, a multilayer structure consisting of ABABAB……. layer is produced as shown in figure 7 (d).

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WASTE WATER TREATMENT USING FENTON AND PHOTO-FENTON SYSTEM

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Abstract:

Earth is a blue planet, having plenty of water. In spite of this, access to clean and fresh water is challenging. Recently, due to population growth and increasing industrialization, due to the above facts wastewater treatment has got intense and undivided attention. Fenton/Fenton like system and photo-Fenton system is the sustainable technique for wastewater treatment. Recently some outstanding catalysts have been developed using nanotechnology. Nanotechnology plays apositive role for the advancement of heterogenous Fenton process. In this chapter a brief overview of the Fenton/Fenton like system and photo-Fenton process, mechanism of the Fenton/Fenton likes system and photo-Fenton process. In this work, latest case studies of wastewater treatment treatment using Fenton/Fenton like system and photo-Fenton process have been discussed.

Introduction:

Various wastewater treatment methods can be classified into three major categories, physical, chemical and biological methods. Physical methods including precipitation, coagulation, flocculation, adsorption, ultrafiltration, nanofiltration and reverse osmosisetc are the most important methods for wastewater treatment with some limitations like sludge formation, transfer of pollutant from one form to another. So, these methods are not very effective in today’s scenario. Mainly two types of biological methods are available aerobic and anaerobic treatment. These methods don’t applicable on the large amount pollutant. Other biological methods are very expensive and very difficult to operate. So, these biological methods also aren’t suitable for wastewater treatment. Various types of chemical methods are also available to treat the wastewater. Among these, advanced oxidation processes (AOPs) have received great attention in the field of wastewater treatment by environment scientists. AOPs mainly worked on the generation of •OH radicals. These •OH radicals works rapidly and non-selectively, which lead to degradation of most of the pollutants directly. Complete mineralization of the pollutants achieved in the process. Nowadays many works have been done on the wastewater treatment using various AOPs.

AOPs mainly divided into two categories-homogenous and heterogenousprocess. In homogenous process pollutant and catalyst are in same phase, where in heterogenous process pollutant and catalyst are in different phase. Generally, in homogenous system both pollutant and catalyst are in liquid phase. In heterogenous process pollutant are in liquid and catalyst are in solid phase. Fenton's process/ reaction is one of the most important AOP. It is discovered by H. J. H Fenton in 1984. Fenton and related reactions (Fenton like processes) consist of H_2O_2 with Iron ions. Combination of these two chemical forms the active oxygen species that oxidise different types of pollutants in the system. Nowadays various types of homogenous and heterogenous Fenton processes have been developed to treat wastewater treatment. Fenton system also worked in the presence of light or energy source. When Fenton process worked in the presence of any types of light or energy source it is known as photo-Fenton process. Presence of light source increases the efficiency of the Fenton process. The working process of Fenton system is represented in Fig.1.

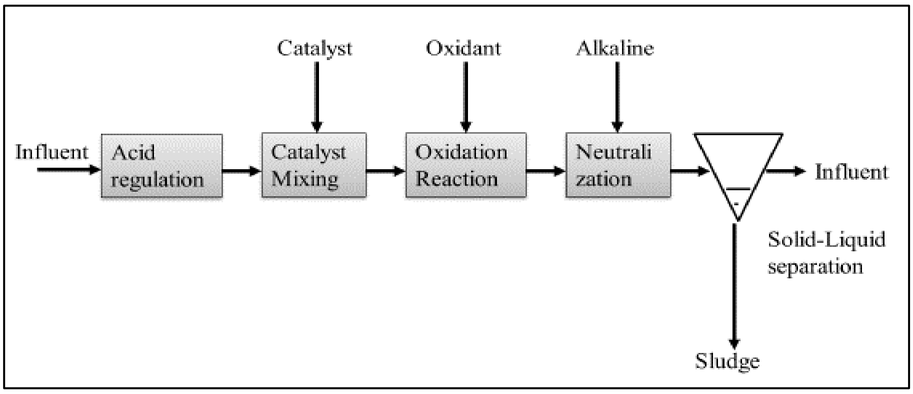

Figure 1: Schematic diagram of the Fenton process

In the present study a brief overview of Fenton/Fenton like system and photo-Fenton process, mechanism of the Fenton/Fenton like system and photo-Fenton process, and some recent case studies of wastewater treatment using Fenton/Fenton like system and photo-Fenton process have been discussed.

Mechanism of Fenton and photo-Fenton system:

Currently, Haber-Weiss mechanism and Bray-Gorin mechanism have been reported in the literature to explain the Fenton process. Bray-Gorin mechanism was proposed in 1932, which considered the high iron oxide intermediates (FeO^{2+}, FeO^{3+}) were produced in Fenton process. Haber-Weiss mechanism was reported in 1934, they reported that during Fenton process highly active oxide species (${}^{\bullet}OH$ radicals) are generated during Fenton process. Studies revealed that not only ${}^{\bullet}OH$ radicals but some other intermediates including ${}^{\bullet}OOH$ radicals, O_2^- etc also generates during Fenton process.

Bray-Gorin mechanism

$2Fe^{3+} + H_2O \longrightarrow Fe^{2+} + FeO^{2+} + 2H^+$ (1)

$Fe^{2+} + H_2O_2 \longrightarrow FeO^{2+} + H_2O$ (2)

$FeO^{2+} + H_2O_2 \longrightarrow Fe^{2+} + H_2O + O_2$ (3)

$Fe(OH)^{2+} \longrightarrow Fe^{2+} + FeO^{2+} + H_2O$ (4)

Haber-Weiss mechanism

$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$ (5)

$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + OH^-$ (6)

$RH + {}^{\bullet}OH \longrightarrow H_2O + R \longrightarrow$ further oxidation (7)

$Fe^{3+} + R^{\bullet} \longrightarrow Fe^{2+} + R^+$ (8)

$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + {}^{\bullet}OOH + OH^+$ (9)

${}^{\bullet}OH + H_2O_2 \longrightarrow {}^{\bullet}OOH + H_2O$ (10)

${}^{\bullet}OH + {}^{\bullet}OH \longrightarrow {}^{\bullet}OOH + OH^-$ (11)

Photo-Fenton mechanism:

$Fe(OH)^{2+} + hv \longrightarrow Fe^{2+} + {}^{\bullet}OH$ (12)

$H_2O_2 + hv \longrightarrow 2\,{}^{\bullet}OH$ (13)

Some important case studies in the field of wastewater treatment using Fenton/photo-Fenton system:

Ruppert *et al.* (1993) used 4-chlorophenol (4-CP) as the model pollutants in their Fenton and photo-Fentoninvestigation. They compared Fenton system with light having greater than 320 nm assisted photo-Fenton system. They reported that photo-Fenton system is more efficient than Fenton system under experimental conditions.

Spacek *et al.* (1995) used phenol, cyclohexanol (CyOH), and 4-nitroaniline (4-NA) and photo-Fenton reaction using UV-A light for the degradation study. They reported that all the three pollutants are easily degraded by the system. The following order of degradation of pollutants were obtained using the system Phenol > 4-NA >>CyOH.

Goi and Trapido (2002) used seven nitrophenols (2-nitrophenol, 4-nitrophenol, 2,5-dinitrophenol, 2,6-dinitrophenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 4-methyl-2,6-dinitrophenol) to know the efficiency of Fenton and phot-Fenton systems. They also studied hydrogen peroxide photolysis in the same system. They reported among all three methods photo-Fenton system is more efficient. Photo-Fenton system exhibited 85-90 % efficiency under experimental conditions.

Moraes *et al.* (2004) investigated mineralization of Saline Wastewater Contaminated with Hydrocarbons by the Photo-Fenton Process using UV light. They reported that complete mineralization has been achieved with in 4.5 h of reaction under experimental conditions.

Kavitha *et al.* (2004) used Fenton, solar-Fenton and UV-Fenton system for the degradation of phenol. They reported that among these three systems, UV-Fenton system is more efficient than Fenton and solar-Fenton system it exhibits 97 % efficiency under experimental conditions in 120 min. Fenton and solar-Fenton system exhibit 96 % and 41 % efficiency.

Gernjak *et al.* (2004) studied degradation of oil mill wastewater using solar photo-Fenton process at pilot plant. They reported that over 85% of COD and up to 100% of phenol index of oil mill wastewater were removed under experimental conditions.

Benitez *et al.* (2005) investigated comparison of Fenton and photo-Fenton system (UV light) for the degradation of Gallic acid (3,4,5-trihydroxybenzoic acid). They reported that UV light assisted photo-Fenton system is more efficient thanFenton system. Results indicate that Gallic acid (3,4,5-trihydroxybenzoic acid) is easily degraded in UV light assisted photo-Fentonsystem at neutral pH in 40 min. of reaction

Núñez *et al.* (2007) examined degradation of two reactive azo dyes, Procion Red H-E7B and Cibacron Red FN-R under Fenton's and photo-Fenton's systems. They used natural and artificial light photo-Fenton system. They reported that photo-Fenton system using natural sunlight is the most efficient system for the degradation of these two dyes under investigation.

Kasiri *et al.* (2008) used Fe-ZSM5 zeolite as the catalyst in heterogenous photo-Fenton system using UV-C light. They used C.I. Acid Blue 74 dye as the model pollutant in investigation. They reported that this heterogenous phot-Fenton system could easily degraded

C.I. Acid Blue 74 dye in 120 min under experimental conditions. Also, this heterogenous photo-Fenton system is more efficient and more powerful than homogenous photo-Fenton system.

Zapata *et al.* (2009) used commercial available pesticide formulation for the degradation study in solar photo-Fenton system. They used Vydate® (10% oxamyl), Metomur® (20% methomyl), Couraze® (20% imidacloprid), Ditimur-40® (40% dimethoate) and Scala® (40% pyrimethanil) as model pollutant. They reported that solar light assisted photo-Fenton system is very suitable method for the degradation of pollutant under investigation. Study revealed that solar photo-Fenton efficiency increases with temperature. The degradation efficiency is highest at 50^0C after this temperature, degradation efficiencyincreases with temperature.

García and Hodaifa (2017) investigated photo Fenton treatment of olive oil mill wastewater in presence of artificial UV lamp. In this study $FeCl_3$ used as catalyst and various concentration of H_2O_2 were used. They reported that acidic pH (3 pH) is favourable for the degradation of pollutants. More than 90 % of COD removal reported under experimental conditions.

Ebrahiem *et al.* (2017) used cosmetic waste water and photo-Fenton system for the degradation study in presence of UV lamp. Effect of various operationalparameter also investigated in the study. They reportedthat acidic pH (3 pH) is favourable for degradation under experimental studies. Process exhibited 90 % efficiency in 90 min. of reaction.

Jiang *et al.* (2019) modified a photo-Fenton system using CdS/rGO/Fe^{2+} catalyst for the degradation of phenol. They reported that most of the Fenton and photo-Fenton system worked at acidic pH but these new modified systems easily degrade phenol at neutral pH using visible light in 1 hr. This system opens new insights in photo-Fenton system.

Sun *et al.* (2020) used FeOCl based photo-Fenton system for the degradation study of Carbamazepine (CBZ) in the presence of UV light. They reported that UV/H_2O_2/FeOCl system degraded 92 % CBZ in 30 min. This new system exhibits higher photocatalytic activity than previously discussed Fenton/photo-Fenton system for the degradation of CBZ. In this study degradation pathway also analysed using LC − ESI − MS method.

Wang *et al.* (2020) used $Zn_{1-1.5x}Fe_xS/g\text{-}C_3N_4$ catalyst in visible light mediated photo-Fenton system for the degradation of p-nitrophenol. They reported that $Zn_{0.94}Fe_{0.04}S/g\text{-}C_3N_4$ exhibit higher photocatalytic activity under experimental conditions. This system degraded 96 % of p-nitrophenol in 60 min using simulated solar light.

Kordestani *et al.* (2020) used pharmaceutical wastewater containing meropenem and ceftriaxone antibiotics for the degradation study. In this study UV light assisted photo-Fenton system was used for pollution control. They reported that this system easily degraded waste water in 60 min under experimental conditions. 99 % of meropenem and 96.2% of ceftriaxone easily degraded using this system.

Conclusion:

This chapter gives an idea about how Fenton and Photo-fenton process is effectively used in wastewater treatment, the mechanism of Fenton and Photo-fenton process has been discussed and importance of highly active OH·Radical (acting as oxidant) and Fe (II) salt (acting as catalyst) is presented.The extensive study on Fenton and Photo-fenton processes has been done and it was found that under various experimental conditions Fenton and Photo-fenton systems are effective in treating a variety of polluted water from different sources like olive oil mills, pharmaceuticals, sewage etc. It has been observed that various newly synthesized photocatalysts($Zn_{0.94}Fe_{0.04}S/g\text{-}C_3N_4$, $CdS/rGO/Fe^{2+}$etc.) can perform brilliantly in waste water treatment under artificial light (UV/Visible) as well as natural light. Apart from this, in recent studies it has been observed that besides acidic pH, fenton and photo-fenton system has worked efficiently in neutral pH conditions as well.

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POLY(AZOMETHINE):SYNTHESIS, PROPERTIES AND APPLICATIONS

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Abstract:

The review deals with methods for the general preparation, properties and applications of polymeric azomethine.Material Science is the advance branch of science out of them polymer chemistry era is having multi-task applications. Poly(azomethine)s belong to a class of materials that are known for their excellent thermal stability, good mechanical strength, and environmental resistance and more particularly as promising materials with optoelectronic and photonic applications.Conjugated aromatic poly(azomethine)s (or polyimines) can also be used in several areas due to their versatile properties.

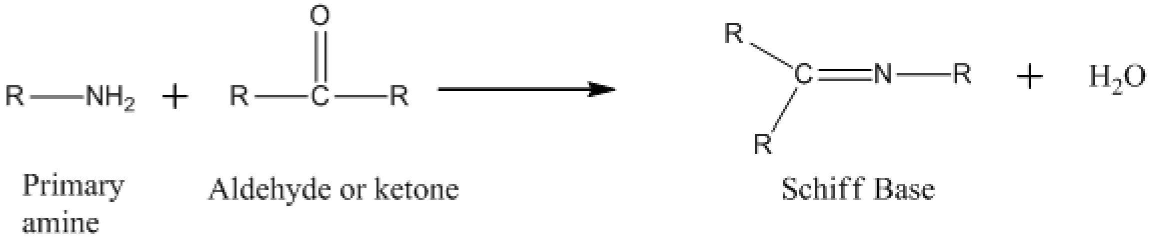
Keywords: Poly(azomethine), Material Science, Properties, Applications

Introduction:

Material science is advance branch of science, among this there is a group of alternately conjugated polymers which have exposed interesting electronic properties approaching them to some extent to inorganic semiconductors. Characteristic feature of conjugated polymers is alternation of conjugated polymers which distinguish them from other backbone [1]. Poly(azomethine) is an important class of the polymer world and makes human life easier by being used in textile, automobile, pharmacology, biomedical devices, surgical equipment, coating industry, structural engineering, electronic device applications etc. in daily life. Poly(azomethine)s in polyester and poly(azomethine) class have a considerably high thermal resistance, exhibit semi-crystalline behaviors in different mesophases and have a high optical transmittance. Aromatic poly(azomethines), known as the schiff bases, belong also to alternately conjugated polymers having azomethine linkage in the backbone, resembling vinylene one in which one CH methane group is replaced by nitro atom. Polymer belonging to this family has been for many years of interest due to their good thermal stability and interesting optoelectronic properties. There is poly(azomethine)s with alkoxy side chains that can be prepared by solvent-based poly(azomethine)s with alkoxy side chains that can be deposited by solvent based or spin-on techniques [2]. However, applicability of this method concerns soluble polymers only, and that their thin film can be deposited by solvent-based polymers only, and that is why thin film of insoluble poly(azomethine)s can be prepared by such methods as the thermal vacuum evaporation (TVE) or chemical vapor deposition (CVD) via polycondensation.Aromatic polymers containing both ester and azomethine units are the type of high-performance polymers with excellent thermal, physical and mechanical properties and are utilized in various fields such as electric, electronic, photonics and in industrial material field [3].

General Introduction of Schiff bases:

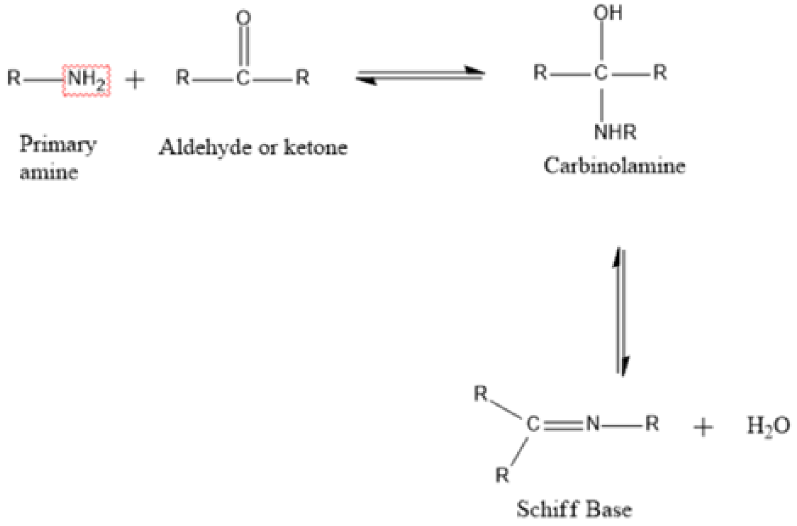
A Schiff base is a nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by C=N-R group. It is usually formed by condensation of an aldehyde or ketone with a primary amine according to the following scheme:



Scheme 1: General scheme of schiff base formation

Where R, may be an alkyl or an aryl group. Schiff bases that contain aryl substituents are substantially more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable [4]. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizablewhile those of aromatic aldehydes having effective conjugation are more stable.The formation of a schiff base from an aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis or upon heating [5].

Polymeric schiff bases have been the subject of numerous studies, after the pioneer investigations of D'Alelio's *et al.* at the end of the 1960s [5]. Poly schiff bases were synthesized by polycondensation of dialdehydes or diketones with aliphatic or aromatic diamine to give high molecular weight polymers. However, their rigidity causes poor solubility in organic solvents limited their practical applications in various fields [3]. One way to improve the solubility is to add flexible side chains onto poly(azomethine)s [4,5]. Schiff base polymers usually show base properties because of the C=N linkage in backbone. Interest has been focused on poly schiff bases because of their thermal stability, potential semiconducting or conducting properties when aromatic units are introduced in the main chain, and non-linear optical properties [6-8].



Scheme 2: Mechanism of schiff base formation

The co-ordination polymers derived from polymeric schiff bases have been extensively studied [9,10]. It is known that reaction of metal ions with organic ligands produces coordination systems having enhanced thermal stability and often improved chemical resistance [11-14]. Entezami*et al.* reported that the polymer derived from dihydrobenzofuro benzofuran-2,9-dicarbaldhyde-II with bis(cyanoacetate) monomer by Knoevnegel polycondensation in anhydrous THF has been having third-order non-linear optical. In this work, dihydrofuran derivatives as donor and bis(cyanoacetate) as acceptor parts were selected Poly(azomethine) or schiff-base polymers are interesting alternatives for to the luminescent polymer, poly(p-phenylenevinylene) (PPV), having CH=N linkages in the main chain that are comparable to C=C in PPV, and being capable of protonation and complexation with metal cations [15]. Aromatic poly(azomethine)s is of particular interest owing to their good thermal stability, mechanical strength, non-linear optical properties, semiconducting properties, environmental stability and fiber-forming properties. They may also be applicable in the field ofpolymer electronics, especially in view of the recent discovery that the photoluminescence of the conjugated polymers containing basic sites in the main chain could be modified by protonic (acid-base) doping [16]. Recent papers of Lehn *et al.* extend the poly(azomethine)s study to the design of constitutional dynamic polymers, which are opening new perspectives in materials science, being a very powerful alternative to nanofabrication and nanomanipulation for the development of nanotechnology [17].

Electrochemical and optoelectronic properties of poly(azomethine)s:

In the recent year's material scientist are busy to obtain functional azomethine polymers incorporating new properties such as luminescence and liquid crystallinity. The production of -CH=N- linkages does not require stringent reaction conditions; given the synthetic advantages of azomethines and their expected similar properties to their vinyl cousins, it is important to assess their suitability for replacing functional materials currently used in organic electronic devices. There are some reported data about luminescent poly(azomethine)s containing chromophoric units such as fluorene, triphenylamine, pyrene or thiophene side chains, but to the best of our knowledge [18-20].

Researchers are interested in investigating the effects of thiophene schiff-base polymers containing electron-withdrawing cyano groups in position 3 of the thiophene ring on the photophysical and electrochemical properties of the polymers [21]. Introduction of acceptor groups at the 3-position of the thiophene unit increases their oxidation potential. Roncali*et al* showed that the introduction of a cyano group at the vinylene linkagecould lead to a considerable reduction of the bandgap of the corresponding polymers [22]. Another important point is that the cyano groups induce a decrease in the HOMO level, and thus a stabilization of the neutral state of the polymers. In particular the modification of the electronic states, i.e. the bandgap and the positions of the HOMO and LUMO levels, enables useful control of the device engineering in photophysical applications such as photovoltaic diodes and electroluminescence [23]**.**

Application in medicine and pharmacy:

Imine complexes have a wide range of biological properties: antitumor, antiviral, antifungal, antibacterial [24]. They are also used in the treatment of diabetes and AIDS. As biological models, they help to understand the structure of biomolecules and the biological processes that take place in living organisms. They are involved in photosynthesis and the transport of oxygen in organisms. They are involved in the treatment of resistance to cancer drugs and are often tested as antimalarials. It could also be used for enzyme immobilization. [25, 26].

Biological activity:

Schiff bases are characterized by an imine group –N=CH-, which helps to clarify the mechanism of transamination and racemization reaction in biological system [27].It exhibits antibacterial and antifungal effect in their biological properties [28]. Metal-imine complexes have been widely investigated due to antitumor and herbicidal use. They can work as models for biologically important species.

Antibacterial properties:

Mortality increase caused by infectious diseases is directly related to the bacteria that have multiple resistances to antibiotics. The development of new antibacterial drugs enriched by innovatory and more effective mechanisms of action is clearly an urgent medical need [29].

Schiff bases are identified as promising antibacterial agents. For example, N-(Salicylidene)-2-hydroxyaniline is active against Mycobacterium tuberculosis.Schiff bases containing 2,4-dichloro-5-fluorophenyl moieties also take part in effective inhibition of bacterial growth. On the other hand, the compounds obtained from furylglyoxal and p-toluidene show antibacterial activity against: *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* and *Proteus vulgaris.* Isatin derived schiff bases present anti-HIV and antibacterial activity. Other schiff bases derivatives, which possess antibacterial activity are: benzimidazole, thiazole, pyridine, glucosamine, pyrazolone, hydrazide, thiazolidiones, indole, thiosemicarbazone, p-fluorobenzaldehyde [30].

Antifungal properties:

Fungal infections usually are not only limited to the contamination of surface tissues. Recently, there was a considerable increase in the incidence of systemic fungal infections, which are potentially lifethreatening. Exploration and development of more effective antifungal agents is necessity, and the individual schiff bases are considered to be promising antifungal medicines. Some of them, such as imine derivatives of quinazolinones possess antifungal properties against *Candida albicans, Trichophyton rubrum, T. mentagrophytes, Aspergillus niger* and *Microsporumgypseum*. Schiff bases and their metal complexes formed between furan or furylglycoxal with various amines exhibit antifungal activity against *Helminthosporium gramineum*-causing leaf stripe in barley, *Syncephalostrum racemosus*- contributing to fruit rot in tomato and *Colletotrichum capsici*-causing anthracnose in chillies [31].

Biocidal properties:

Schiff bases obtained by the synthesis of o-aminobenzoic acid and β-keto esters have found biocidal use against *S. epidermidis*, *E. coli*, *B. cinerea* and *A. niger*. By contrast, schiff bases of isatin derivatives are used in the destruction of protozoa and parasites.

Antiviral properties:

The use of vaccines may lead to the eradication of pathogens known viruses, such as smallpox, poliomyelitis (polio), whether rubella. Although there are many therapeutic ways to work against viral infections, currently available antiviral agents are not fully effective, which is likely to cause a high rate of mutation of viruses and the possibility of side effects. Salicylaldehyde schiff bases derived from 1-amino-3-hydroxyguanidine tosylate are good material for the design of new antiviral agents [32].

Antimalarial properties:

Malaria is a disease which when is neglected causes serious health problems. Human malaria is largely caused by four species of the genus Plasmodium (*P. falciparum, P. vivax, P. ovale and P. malaria*). The search for new drugs, vaccines and insecticides for the prevention or treatment of this disease is a priority. Schiff bases are interesting compounds, which could be part of antimalarial drugs. For example, the compound with such effect is Ancistrocladidine , which is a secondary metabolite produced by plants of the family Ancistrocladaceae and Dioncophyllaceae, and presenting an imine group in a molecular chain [32]. Cryptolepine, valid indolchinoline alkaloid, isolated from African plant *Cryptolepissanguinolenta*, also used in the treatment of malaria, is the product of multi-stage reaction, in which schiff base is involved.

Anticancer properties:

Some Schiff bases have a high antitumor activity. Imine derivatives of N-hydroxy-N'-aminoguanidine block ribonucleotide reductase in tumor cells, so that they are used in the treatment of leukemia.

Application in modern technologies:

Photoand thermochromic properties of schiff bases as well as their biological activity make them applicable in modern technology. Among others, they are used in optical computers, to measure and control the intensity of the radiation, in imaging systems, as well as in the molecular memory storage, as organic materialsin reversible optical memories and photodetectors in biological systems [32,33].

Due to their photochromic properties, Schiff compounds could act as photostabilizers, dyes for solar collectors, and solar filters. They are also used in optical sound recording technology [25]. Interesting are the properties associated with Schiff's rules: liquid crystal properties, chelation capacity, thermal stability, optical nonlinearity [30] and the ability to create the structure of a new type of molecular conductor using electrical properties, proton transfer [31]. Due to their thermal stability, Schiff bases can be used as phase stationary in gas chromatography. The optical nonlinearity of these compounds enables us to use them as electronic materials, optoelectronics (in optical switches), and photonic components [30]. Imine derivatives can be used to obtain conductive polymers. Various possible uses: as catalysts in photoelectrochemical processes, electrode materials and microelectronic devices, IC battery organs or electrochromic display devices (graphics output devices) [34]. Due to the presence of the imine group, the electron cloud of the aromatic ring and electronegative nitrogen, oxygen and sulfur atoms in the schiff bases molecules, these compounds effectively prevent corrosion of mild steel, copper, aluminium and zinc in acidic medium [30-35].

Table 3: Timeline of poly(azomethine) research [34-38]

Author	**Novelty**	**Results**	**Applications**
M. Palewicz *et al.*	Spectroscopic and photophysical properties of the poly(azomethine)s with triphenylamine moieties wereinvestigated	Current–voltage experiment confirmed the semiconducting propertiesof the polymer thin film and multiwall carbon nanotubes added to polymer caused the increase of conductivity.	Uses as active layers in electronic devices such as solar cells**.**
Hung-Ju Yen *et al.*	synthesized the azomethine–triphenylamine (AM–TPA)-based aromaticpoly(azomethine ether)s (PAMEs) from the new (AM–TPA)-based diol monomers**,**	All the obtained polymers revealed valuable electrochromic characteristics such as high contrast in visible region and unique blue/red electrochromic behavior.	Incorporation of azomethine groups into TPA-based polymers is a new approach for tuning the coloration changed.
Satoshi Tatsuura *et al.*	Fabricated polyazomethine conjugated polymer using 4-methoxy-o-phenylenediamine (MPDA LancasterSynthesis Ltd.) and o-phthalaldehyde	head-to-tail conjugated polymers would be promising for second order nonlinear optical (NLO) materials	Polyazomethine conjugated polymer film.
Michiel L. Petrus *et al.*	three new poly(azomethine)s with different substituents on the triphenylamine unit have been synthesized via a simple one-step polycondensation reaction	Because of the aromatic units and the absence of functional groups, the polymers showed good thermal stability but no glass transition (Tg).	Photovoltaic devices were fabricated.
Chenggang Wang *et al.*	A new derivative of conjugated aromatic poly(azomethine)containing the alkyl-substituted oligothiophene was prepared under ethanothermal reaction conditions.	The resulting polymer, PBTPI, has improved solubilityin organic solvents as imparted by the dibutyl-substitutedterthiophene linkages on the polymer backbone.	Applications in solid-state acid indicatorsand photonic materials.

Application in synthesis and chemical analysis:

Schiff bases are a group of organic intermediates, which are very often used in the synthesis and chemical analysis. They are exerted in the production of pharmaceutical and agrochemical industry. In the reaction with hydrogen cyanide schiff bases may form amino acid precursors (Strecker synthesis). Moreover, chiral schiff bases are used as initial substrates for the asymmetric synthesis of α-amino acids, and as catalysts in asymmetric synthesis. Furthermore, the imines obtained by the condensation reaction of arylamines and carbonyl compounds have determined a group of intermediates used in the preparation of important compounds [23].

Otherwise, schiff bases are precursors of reaction of polycyclic derivatives of quinoline and isoquinoline receiving by oxidative ring closure under the influence of ultraviolet light. They are also used for the preparation of acyclic and macrocyclic compounds, such as: cryptats, coronates and podates [35]. These compounds lead to the formation of Ruhemann's purple (reaction between an amino acid and ninhydrin), which allows to detect and assist in the identification of fingerprints [33].

Conclusion:

Poly(azomethine) materials is of considerable current interest in the last decades, but due to many different and distinct characteristics.Consequently, because of the high thermal stabilities of the poly(azomethine) can be promising candidates for aerospace applications, and they can be used to produce temperature-stable materials. Here in this chapter focus on preparation of azomethine and schiff base, properties and advance applications of poly(azomethine)s. This smart poly(azomethine)s is also having applications in medical fields such as anticancer drugs, antimicrobial, antimalarial, anti-inflammatory.

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STUDY OF ENTROPY AND THERMODYNAMICAL PROBABILITY ENSURE THE MAXIMUM VALUES IN THE EQUILIBRIUM STATE

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Abstract:

From a purely thermodynamical point of view, why does that entropy have to be a maximum at equilibrium? Say there is equilibrium, it is also true that even this stable equilibrium state would become. But then the system is no longer isolated, but there is no law that entropy increases for a non-isolated system. Thus in the equilibrium state both the entropy.

I guess my interest in the topic has changed, But at least I do see it's use in explaining how the entropy/energy evolves once you take the extensive parameters into your control and change the system.

Introduction:

Entropy is scientific concepts, as well as a computable physical property that is extreme generally associated with a state of disorder, randomness. Entropy is an extensive property because it be governed by on the mass of the working substance.

Boltzmann was ongoing from a very simple concept that the equilibrium state of the system in equilibrium state is maximum probability. But from the thermodynamically point of assessment the stability state of a system is maximum entropy. If the system is not equilibrium, then changes take place within the system until the equilibrium state or the state of maximum entropy is reached. Thus in the equilibrium state both the entropy and thermo dynamical probability have the maximum values which led to expect co-relation between them.

According to thermodynamics, entropy S of a system is related with temperature by the relation

$$dS = \frac{dQ}{T}$$

The above relation can be written as

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

$$\frac{1}{T} = k\beta = k\frac{\partial}{\partial E}\log W \text{ ………………………………(2)}$$

On using the above equations (1) and (2),We get

$$\frac{\partial S}{\partial E} = k\frac{\partial}{\partial E}\log W$$

On taking integration of the above equation

$$S=k \log W\text{……………..…..………………..(3)}$$

This is the required relation between entropy and probability and it is calledBoltzmann's statistical relation for entropy.

Again we can say asentropy and thermo dynamical probability have their maximum values i.e.

$$S=f(W)\text{……………………………….(4)}$$

Here S is the entropy and W is the thermodynamical probability of the state.

Method of Analysis:

To find out the nature of the function, let us consider two completely independent systems A and B having entropies S_1 and S_2 respectively. Since entropy is an extensive quantity, the entropy S of the two systems together must be equal to the sum of their separate entropies,i.e.

$$S=S_1 + S_2 \text{ ……………..……………..(5)}$$

If the probability of a is W_1 and that of B is W_2, then probability of finding both the systems at their respective given condition is

$$W= W_1 \times \frac{dy}{dx} \text{ ………………..………………(6)}$$

Thus we have

$$S= f(W)= f\ (W_1 W_2) \text{ …………….…………….(7)}$$

$$\text{Here,}S_1 = f(W_1)\text{………………..……………….(8)}$$

$$S_2 = f(W_2)\text{………………….……………..…(9)}$$

on substituting the value from equations(7),(8),(9) in equation(5),we get

$$f(W_1 W_2) = f(W_1) + f(W_2)\text{…………….…………….(10)}$$

Differentiating partially the above equation, with respect to W_1andW_2, we get

$$W_2 f'(W_1 W_2) = f'(W_1)\text{…………………………….(11)}$$

$$W_1 f'(W_1 W_2)= f'(W_2)\text{……………………………….(12)}$$

On using equations (11) and(12),we found

$$\frac{f'(W_1)}{f'(W_2)} = \frac{W_2}{W_1}$$

$$W_1 f'(W_1) = W_2 f'(W_2) = \ldots\ldots = \text{constant}$$

$$W_1 f'(W_1) = W_2 f'(W_2) = \ldots\ldots = k \ldots\ldots\ldots\ldots\ldots\ldots (13)$$

This gives

$$f'(W_1) = \frac{k}{W_1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

$f'(W_2) = \frac{k}{W_2}$……………….…………(15)

Onintegrating of the above equations (14) and (15), We get

$$f(W_1) = k \log W_1 + C_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

$$f(W_2) = k \log W_2 + C_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (17)$$

On using and solving equations (16) and (17), We can write a general equation

$f(W) = k \log W + C$ ……………………………(18)

With the help of equations(4) and (18), We can write

$$S = k \log W + C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (19)$$

This is the required relation between entropy and probability. Here k is universal constant and it is known as Boltzmann constant while the constant C is the integration constant, at absolute zero temperature S=0 and $W = 1$

$$C=0$$

On putting the value C=0,in equation(19),we get the relation between entropy and probability to be

$$S = k \log W \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (20)$$

The above equation states that the entropy of a system is proportional to the logarithm of probability of that system.The constant k plays a major role in statistical definition of entropy and it is used express Boltzmann factor.

The constant k looking in equation (20) can be well-known by considering the equivalent position in thermodynamics. Now we are considering the expansion for one mole of an ideal gas previously at pressure P_1 and volume V_1 into an evacuated chamber of volume V_2 and the final pressure is P_2 and the final volume is $V_1 + V_2$. Therefore the problem is to be found that isothermal change in the entropy of the ideal gas.

When the containers of volume V_1 and V_2 are connected to each other, the probability of finding one molecule in the first container of volume V_1 is $\frac{V_1}{V_1 + V_2}$.

As one mole of an ideal gas covers N molecules and the probability of combined event is equal to the product of the probabilities of separable and independent events, therefore, the probability of finding one mole of gas in the container of volume V_1

$$=\left(\frac{V_1}{V_1+V_2}\right)^N$$

The probability of finding one mole (= N molecules) of an ideal gas in the final volume$(V_1 + V_2)$ is

$$=\left(\frac{V_1+V_2}{V_1+V_2}\right)^N = (1)^N = 1$$

Hence from Boltzmann's relation, Since the universe, the irreversible processes are taking place continuously therefore the entropy of the universe goes on increasing and tends to maximum.

$$\Delta S = S_2 - S_1 = k\ log\ W_2 - k\ log\ W_1$$

$$\Delta S = \text{k log}\frac{W_2}{W_1} = \text{k log}\left(\frac{1}{\frac{V_1}{V_1+V_2}}\right)^N$$

$$\Delta S = \log\left(\frac{V_1+V_2}{V_1}\right)^{Nk} \text{…………………..(21)}$$

But the change in entropy the gas changes from one state to another state is given by

$$\Delta S = C_V \log\frac{T_2}{T_1} + \text{R log}\frac{V_1+V_2}{V_1}$$

As the change is isothermal, $T_1 = T_2$.

Therefore isothermal entropy is given by

$\Delta S = \text{R log}\frac{V_1+V_2}{V_1}$

$$\Delta S = \log\left(\frac{V_1+V_2}{V_1}\right)^R \text{……………..…………..(22)}$$

On using equation (21) and(22),we get

$$\log\left(\frac{V_1+V_2}{V_1}\right)^{Nk} = \log\left(\frac{V_1+V_2}{V_1}\right)^R$$

Nk =R or

$$\text{k}=\frac{R}{N} \text{ …………………………..…..(23)}$$

Where k is Boltzmann's constant, (the value of k = 1.380649×10^{-23} joule/kelvin)

Hence the constant k arising in relation (20) is analyzed as Boltzmann's constant.

It is a physical constant and it is obtained by taking a ratio of two constants namely gas constant and the Avogadro number.

Discussion:

(i) It is very difficult to form a clear idea of entropy because it cannot be felt temperature or pressure and it does not produce any effect which can be demonstrated. Entropy is a real physical quantity defined by the equation-

$dS=\frac{dQ}{T}$

The change in entropy is a perfect differential.

(ii) The second law of thermodynamics can be stated in terms of entropy of a system as

$dQ = T.dS$

(iii) When the substance absorbs heat, its entropy increase. Thus, increase in entropy implies a change to a less ordered state.

Conclusion:

It is clear that the equilibrium state both the entropy and thermodynamical probability has maximum value in equilibrium state. This is a very useful study for the principal of increase of entropy is intimately connected with the less order state. A high entropy system should be in great disordered. Thus, when the temperature of system is lowered, the amount of entropy and disorder in it decrease, with an increase in entropy, the thermal agitation and hence disorder of the molecules of substance increases. Thus the growth of entropy implies a transition from order to disorder. Thus the conclusion is that the entropy of a system is proportional to the logarithm of probability of that system.

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ROLE OF MATHEMATICAL MODEL – COVID 19

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Introduction:

COVID-19 was confirmed as a pandemic outbreak on January 22, 2020, by the World Health Organization. COVID-19 has impacted every segment of life like commercial establishment, education, economy, religion, transport, tourism, employment, entertainment, food security, sports, limiting human interaction, and above at all, testing our mental toughness. Therefore, researchers from several scientific areas have devoted to studying COVID-19. Epidemiology is the study of health and disease in human population. Mathematical epidemiology contributed to the understanding of the behavior of infectious diseases. Mathematical models are used in comparing, planning, implementing, evaluating and optimizing various detection, prevention and therapy control programs. So it is important for researchers, teachers, administrators and policy makers to understand and handle the critical situation.

Mathematical models of Covid 19:

Many scientists put their heads together in trying to find answers about the spread and infection of corona virus by examining virus samples. They use different tools to understand the procedure through which the disease transmits in a society and how to reduce or control it. The process of infectious diseases may be easily understood and described by using mathematical models. Mathematical model is a powerful tool that effectively helps in investigation of real world phenomenon and processes. Bernoulli was the first mathematician who gave idea about mathematical modeling of spread of an infectious disease during 1760. After that numerous researchers took interest in the said area. One can easily understand various physical and biological phenomenons and their mechanism through such models. This area has been very well extended from simple models to more complex and complicated models. We focus on varies mathematical models developed by many researchers in the literature.

SIR Model:

SIR model provide the foundation of mathematical modeling in epidemiology. The birth of these compartmental models dates back to 1927, with the seminal work of Kermack and McKendrick (1927). The simplest SIR model is the one without the so-called vital dynamics (which includes birth and death and some demographical data) and is described by

$$\frac{dS(t)}{dt} = -\beta S(t)I(t)$$

$$\frac{dI(t)}{dt} = -\beta S(t)I(t) - \gamma I(t)$$

$$\frac{dR(t)}{dt} = \gamma I(t)$$

$$\begin{cases} S(0) = S_0 > 0 \\ I(0) = I_0 > 0 \\ R(0) = R_0 = 0 \end{cases}$$

we can see that $\frac{d}{dt}$ [S(t)+I(t)+R(t)] = 0, therefore it is true that the population size is constant.

S(t) + I(t) + R(t) = N.

In classical SIR model β and γ represent transmission rate and recuperation rate respectively. It does not consider birth and death rate. So Juan B. Seoane-Sepúlveda *et al.* (2021) developed non-autonomous SIR type model with vital dynamics and non-constant population, calibrated according to exponentially decaying infection and death rates.

$$\begin{cases} S' = (\lambda - \mu)S + \lambda(I + R) - \beta SI \\ I' = \beta SI - \gamma I - \mu' I - \mu I \\ R' = \gamma I - \mu R \end{cases}$$

birth rate λ ; death rate due to death causes other than COVID-19 μ ; death rate due to COVID-19 μ'.

SIRD model:

Paul *et al.* (2020) employed the standard SIRD model where the population N is divided into sub-population of susceptible (S), infected (I), recovered (R) and dead (D) for all times *t*. Thus, N = S + I + R + D.

$$\frac{dS(t)}{dt} = -\frac{\beta S(t)I(t)}{N}$$

$$\frac{dI(t)}{dt} = -\frac{\beta S(t)I(t)}{N} - \gamma I(t) - \delta I(t)$$

$$\frac{dR(t)}{dt} = \gamma I(t)$$

$$\frac{dD(t)}{dt} = \delta I(t)$$

β, γ and δ are the parameters determining the characteristics of infection, recovery and deaths rate respectively.

One can realize that, with so many active infections, extensive mixing of the country wide population soon after the lockdown is over would cause a huge surge in the total number of infections which is nearly impossible to manage by any health care system. To estimate the asymptomatic population from the model, Paul *et al.* (2020) rewrite the equations as follows:

$$\frac{\mathrm{d}S(t)}{\mathrm{d}t} = \frac{-S\beta I_s + \beta' I_a}{N} \;;$$

$$\frac{\mathrm{d}I_a(t)}{\mathrm{d}t} = \frac{S(\beta I_s + \beta' I_a)}{N-(\alpha+v')I_a} \;;$$

$$\frac{\mathrm{d}I_s(t)}{\mathrm{d}t} = \alpha I_a - (v+\delta) I_s \;;$$

$$\frac{\mathrm{d}R(t)}{\mathrm{d}t} = v' I_a + v I_s \;;$$

$$\frac{\mathrm{d}\mathrm{D}(t)}{\mathrm{d}t} = \delta I_s$$

Here, the total infectious population is segregated into two compartments: (a) symptomatic I_s and (b) asymptomatic or mildly symptomatic I_a population. A susceptible person can be infected upon contact with a symptomatic or asymptomatic individual with rates β, β' respectively. The infected individual can remain asymptomatic or mildly symptomatic and transit into a symptomatic state with rate α . The asymptomatic and symptomatic persons can recover at rates v' and v respectively. For a symptomatic individual, death occurs with rate δ.

Munoz-Pacheco *et al.* (2021), developed a fractional- order SIRD model in the Caputo's sense as follows

$${}_{t_0}^{C}D_t^q S(t) = -rS(t)I(t),$$

$${}_{t_0}^{C}D_t^q I(t) = rS(t)I(t) - (a+d)I(t),$$

$${}_{t_0}^{C}D_t^q R(t) = aI(t),$$

$${}_{t_0}^{C}D_t^q D(t) = d\,I(t),$$

Where ${}_{t_0}^{C}D_t^q$ is the Caputo derivative given by

$$ {}_{t_0}^{C}D_t^q f\left(t\right) = \frac{1}{\Gamma\left(1-q\right)} \int_{t_0}^{t} \frac{f\left(\tau\right)}{\left(t-t_0\right)^q} d\,\tau, $$

being $0 < q \le 1$. When dealing with practical problems.

r, a, and *d* are infection, recovery and death rates, respectively.

SHIQ model:

Abdel-Haleem Abdel-Aty *et al.* (2021) expressed COVID 19 in the form of the following autonomous ordinary differential equations by considering, susceptible individuals *S*, healthy or resistant individuals *H*, infected and quarantine individuals *I* and *Q* respectively.

$$ \frac{\mathrm{d}S\left(t\right)}{\mathrm{dt}} = \lambda - \gamma S\left(t\right) I\left(t\right) - \left(d+\mu\right) S\left(t\right), $$

$$ \frac{\mathrm{d}H\left(t\right)}{\mathrm{d}t} = \alpha - \beta H\left(t\right) I\left(t\right) + \theta I\left(t\right) - \left(d+\mu\right) H\left(t\right), $$

$$ \frac{\mathrm{d}I\left(t\right)}{\mathrm{d}t} = \gamma S\left(t\right) I\left(t\right) + \beta H\left(t\right) I\left(t\right) + \delta Q\left(t\right) - \left(d+\mu+\eta+\theta\right) I\left(t\right), $$

$$ \frac{\mathrm{d}Q\left(t\right)}{\mathrm{d}t} = \eta I\left(t\right) - \left(d+\mu+\delta\right) Q\left(t\right). $$

SEIR model:

Hakimeh Mohammadi *et al.* (2020), considered the exposed population and developed the SEIR model as follows

$$ \begin{cases} \dfrac{\mathrm{d}S}{\mathrm{d}t} = \omega - \left(\beta_1 E + \beta_2 I\right) S - \mu S, \\ \dfrac{\mathrm{d}E}{\mathrm{d}t} = \left(\beta_1 E + \beta_2 I\right) S - \left(\lambda+\mu\right) E, \\ \dfrac{\mathrm{d}I}{\mathrm{d}t} = \lambda E - \left(\tau+\mu+\delta\right) I, \\ \dfrac{\mathrm{d}R}{\mathrm{d}t} = \tau I - \mu R, \end{cases} $$

where

$\omega = n \times N,$ N is the total number of individuals and n is the birth rate,

μ : the death rate of people,

β_1: the transmission rate of infection from E to S,

β_2: the transmission rate of infection from I to S,

λ : the transmission rate of people from E to I,

δ : the mortality rate due to the disease,

τ : the rate of recovery of infected people.

Hakimeh Mohammadi *et al.* (2020) moderate the system by substituting the time derivative with the Caputo fractional derivative as follows:

$$\begin{cases} \theta^{v-1C}D_t^v S(t) = \omega - (\beta_1 E(t) + \beta_2 I(t))S(t) - \mu S(t), \\ \theta^{v-1C}D_t^v E(t) = (\beta_1 E(t) + \beta_2 I(t))S(t) - (\lambda + \mu)E(t), \\ \theta^{v-1C}D_t^v I(t) = \lambda E(t) - (\tau + \mu + \delta)I(t), \\ \theta^{v-1C}D_t^v R(t) = \tau I(t) - \mu R(t), \end{cases}$$

where the initial conditions are $S(0) = S_0 > 0$, $E(0) = E_0 > 0$, $I(0) = I_0 > 0$, $R(0) = R_0 \geq 0$.

Table 1: Parameters and their description in the model

Parameters	**The Physical Interpretation**
λ	Recruitment rate susceptible
γ	Disease transmission rate
D	Natural death rate
α	Recruitment rate of healthy human
β	Transmission rate of healthy human
μ	Disease related death rate infected or suspected individuals
δ	Rate at which quarantine people get infection
θ	Cure rate of infected people in the quarantine class

SEIRD model:

Vipin Tiwari *et al.* (2020) use an improvised five compartment mathematical model, Susceptible (S)-Exposed (E)-Infected (I)-Recovered (R)-Death (D) (SEIRD) to investigate the progression of COVID-19 and predict the epidemic peak under the impact of lockdown in India.

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\beta I S$$

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \beta I S - \varepsilon E$$

$$\frac{\mathrm{d}I}{\mathrm{d}t} = \varepsilon E - \gamma I$$

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \gamma \left(1 - \delta\right) I$$

$$\frac{\mathrm{d}D}{\mathrm{d}t} = \delta \gamma I$$

Here β, ε, γ and δ are contact rate/transmission rate, incubation rate, recovery rate and death rate, respectively and known as model parameters.

SEIQR model:

Table 2: Parameters and description

Symbols	Description
S	Susceptible population
E	Exposed population
I	Infected population
Q	Isolated population
R	Recovered population
β	Rate at which susceptible population moves to infected and exposed class
π	Rate at which exposed population moves to infected one
γ	Presents the rate at which exposed people take onside as isolated
σ	Shows the rate at which infected people were added to isolated individual
θ	Rate at which isolate persons recovered
μ	Natural death rate plus disease-related death rate

Anwar zeb *et al.* (2020) developed SEIQR model to present the dynamical behavior of COVID-19 infection by incorporating isolation class

$$\frac{dS(t)}{dt} = A - \mu S(t) - \beta(N)S(t)(E(t) + I(t)),$$

$$\frac{dE(t)}{dt} = \beta(N)S(t)(E(t) + I(t)) - \pi E(t) - (\mu + \gamma)E(t),$$

$$\frac{dI(t)}{dt} = \pi E(t) - \sigma I(t) - \mu I(t),$$

$$\frac{dQ(t)}{dt} = \gamma E(t) + \sigma I(t) - \theta Q(t) - \mu Q(t),$$

$$\frac{dR(t)}{dt} = \theta Q(t) - \mu R(t).$$

SEQIR Model:

Pal *et al.* (2020) model structure of COVID-19 describes the dynamics of five sub-populations of Indians such as susceptible (S(t)), infected but not detected by testing population (E(t)), quarantined (Q(t)), confirmed infected population who are in under treatment in isolation word (I(t)), and who are lived in secured zone not affected by COVID-19 virus (R(t)).

Table 3: Parameters and their description in the model

Parameters	Meaning
Λ	The recruitment rate at which new individuals enter in the Indian population
α	The transmission rate from susceptible population to infected but not detected by testing population
β_1	The transmission coefficient from susceptible population to quarantine population
β_2	The transmission coefficient from infected but not detected by testing population to quarantine population
σ_1	The transmission rate from susceptible population to secured zone population
σ_2	The transmission coefficient form infected but not detected by testing population to secured zone population
σ_3	The transmission rate from quarantine population to secured one population
r_1	The transmission rate from infected but not detected by testing population to infected population for treatment
r_2	The transmission rate from quarantine population to infected population for treatment
d_2	Death rate of infected population due to Covid-19 infections
d_1	Natural death rate of all five sub-population

Assume the total population of India is N(t) and

$$N(t) = S(t) + E(t) + Q(t) + I(t) + R(t).$$

$$\frac{dS}{dt} = \Lambda - \alpha SE - \beta_1 S - \sigma_1 S - d_1 S$$
$$\frac{dE}{dt} = \alpha SE - r_1 E - \beta_2 E - d_1 E$$
$$\frac{dQ}{dt} = \beta_1 S + \beta_1 E - r_2 Q - \sigma_2 Q - d_1 Q$$
$$\frac{dI}{dt} = r_1 E + r_2 Q - \sigma_3 I - d_1 I - d_2 I$$
$$\frac{dR}{dt} = \sigma_1 S + \sigma_2 Q + \sigma_3 I - d_1 R$$

with initial densities:

$S(0) > 0, E(0) \geq 0, Q(0) \geq 0, I(0) \geq 0, R(0) > 0.$

SEQIJR model:

Zaibunnisa Memon *et al.* (2021) formulate a mathematical model of a nonlinear system of ordinary differential equations is given by

$$\frac{dS}{dt} = \prod + \gamma_2 (1-\theta) Q + \xi R - (\alpha I + \mu) S$$
$$\frac{dE}{dt} = \alpha IS - \left(\beta_1 + \beta_2 + \mu\right) E$$
$$\frac{dI}{dt} = \beta_1 E - \left(\gamma_1 + \delta_1 + \mu\right) I$$
$$\frac{dJ}{dt} = \gamma_1 I + \gamma_2 \theta Q - \left(\delta_2 + \mu\right) J$$
$$\frac{dR}{dt} = \delta_1 I + \delta_2 J - (\xi + \mu) R$$

to examine the dynamics of six classes: susceptible $S(t)$, exposed $E(t)$, quarantined $Q(t)$, infected $I(t)$, isolated $J(t)$ and recovered $R(t)$ subject to the non-negative initial conditions $S(0) \geq 0$, $E(0) \geq 0$, $Q(0) \geq 0$, $I(0) \geq 0$, $J(0) \geq 0$, $R(0) \geq 0$.

Impact of Mathematical model:

With the help of mathematical models, large number of infectious and other diseases has been studied. Using mathematical models, researchers first try to understand the dynamics of a disease, and afterwards they develop control and curing procedures for it. Scientists from the IITs of Kanpur and Hyderabad have applied the SUTRA Model to predict the Covid graph in India and COV-IND-19 Study group of University of Michigan researchers is analyzing epidemiologic data from India to make predictions and recommendations as it relates to the continued spread of COVID-19. A new mathematical simulation has concluded that the continued practice of mask wearing and social distancing during ongoing vaccinations could help to stem a potential surge in Covid-19 cases, particularly as more infectious variants emerge.

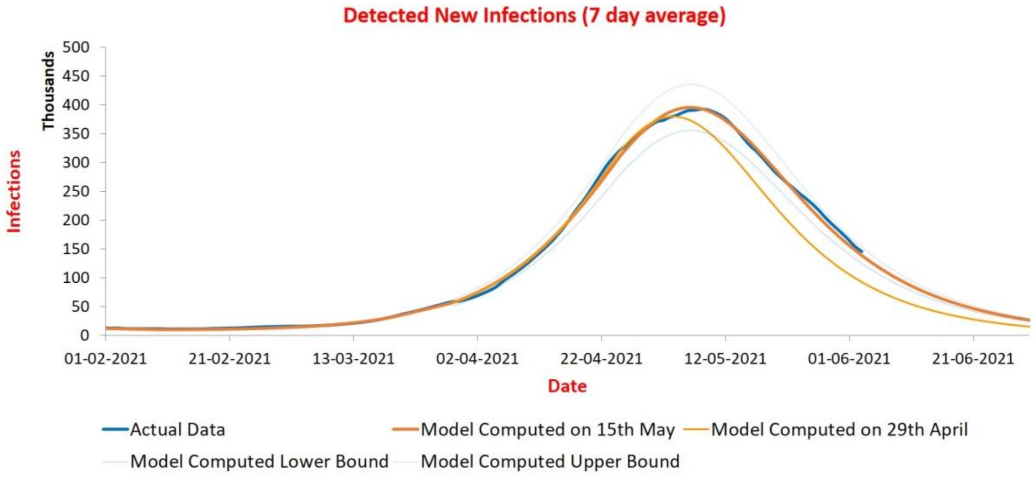

Figure 1: SUTRA Model prediction

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DIMENSIONS OF GREEN CHEMISTRY

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Introduction:

The idea of greening science created in the business and administrative networks as a characteristic development of contamination counteraction drives. In our endeavors to further develop crop assurance, business items and medications, we additionally made accidental damage our planet and people.

By the mid-twentieth century, a portion of the drawn out adverse consequences of these progressions couldn't be disregarded. Contamination stifled a large number of the world's streams and corrosive downpour crumbled woods wellbeing. There were quantifiable openings in the world's ozone. A few synthetic compounds in like manner use were associated with causing or straightforwardly connected to human malignant growth and other antagonistic human and ecological wellbeing results. Numerous administrations started to manage the age and removal of mechanical squanders and discharges. The United States shaped the Environmental Protection Agency (EPA) in 1970, which was accused of ensuring human and natural wellbeing through setting and upholding ecological guidelines.

Green science makes the EPA's command a stride further and makes another reality for science and designing by requesting that scientific experts and architects plan synthetic compounds, substance cycles and business items in a way that, at any rate, maintains a strategic distance from the production of toxics and waste.

Green Chemistry isn't governmental issues. Green Chemistry is certifiably not an advertising ploy. Green science isn't an unrealistic fantasy.

We can foster synthetic cycles and earth-accommodating items that will forestall contamination in any case. Through the act of green science, we can make options in contrast to dangerous substances. We can plan compound cycles that decrease squander and lessen request on reducing assets. We can utilize measures that utilization more modest measures of energy. We can do the entirety of this and still keep up with financial development and openings while giving reasonable items and administrations to a developing total populace.

Maintainable and green science in straightforward terms is only an alternate perspective about how science and substance designing should be possible. Throughout the long term various standards have been recommended that can be utilized when pondering the plan, improvement and execution of compound items and cycles. These standards empower researchers and specialists to ensure and profit the economy, individuals and the planet by discovering imaginative and inventive approaches to lessen squander, ration energy, and find trades for dangerous substances.

Note that the extent of these of green science and designing standards go past worries over dangers from synthetic poisonousness and incorporate energy protection, squander decrease, and life cycle contemplations like the utilization of more manageable or inexhaustible feedstocks and planning for end of life or the last mien of the item.

Green science can likewise be characterized using measurements. While a brought together arrangement of measurements has not been set up, numerous approaches to evaluate greener cycles and items have been proposed. These measurements incorporate ones for mass, energy, risky substance decrease or disposal, and life cycle natural effects.

Principles of Green Chemistry:

Green science is by and large dependent on the 12 standards proposed by Anastas and Warner. These days, these 12 standards of green science are viewed as the fundaments to add to practical turn of events. The standards include guidelines to carry out new synthetic items, new amalgamation, and new cycles.

1. The "preferred to forestall over to fix" guideline It is helpful to deduced forestall the age of waste rather than later on treating and tidying up squander.
2. The "iota economy" standard Synthetic creation courses must be arranged in a manner augmenting the consolidation of the multitude of mixtures utilized in the amalgamation into the ideal item.
3. The "less tricky substance unions" standard any place possible, such manufactured strategies must be yearned, which resort to and create mixtures of no or just immaterial poisonous quality to the climate and human wellbeing.
4. The "planning more secure synthetic substances" standard Chemicals ought to be created in a manner influencing their ideal usefulness, while, simultaneously, extensively diminishing their harmfulness.

5. The "more secure solvents and more secure helpers" rule Expenditure of assistant substances, like solvents, division specialists, and others, ought to be stayed away from at every possible opportunity; if unrealistic, innocuous helpers ought to be utilized.
6. The "plan for energy proficiency" guideline The ecological and financial effect of energy requests for substance cycles ought to be examined as far as followed by streamlining the necessary energy input. Any place practicable, synthetic blend ought to be done under gentle interaction conditions, subsequently, at surrounding temperature and pressing factor..
7. The "sustainable feedstocks" standard at whatever point doable in innovative and financial terms, engineered cycles should turn to such crude materials and feedstocks, which are inexhaustible as opposed to restricted.
8. The "subordinate decrease" standard repetitive derivatization, e.g., assurance/deprotection, the utilization of hindering gatherings, or transitory change of physical/compound cycles, requires extra reagents and regularly adds to extra waste age. Along these lines, at every possible opportunity, they ought to be stayed away from or decreased to a base.
9. The "catalysis" guideline by and large, reactant reagents are naturally better than stoichiometric reagents; these impetuses ought to be just about as particular as could be expected.
10. The "debasement" guideline Chemical items must be planned so that, toward the finish of their life expectancy, they don't avoid in the biosphere, yet break down into nontoxic corruption items.
11. The "continuous examination for contamination avoidance" rule Advanced insightful strategies must be created, which grant the constant, in-line measure checking and control a long time before dangerous substances are produced.
12. The "mishap counteraction by innately more secure magnetism" rule Compounds and the compound's recipe applied in a substance interaction ought to be picked in a manner limiting the danger of synthetic mishaps, incorporating the arrival of synthetics, explosions, or fire arrangement.

Application of green chemistry in solventless process:

A solventless cycle is a compound interaction that happens without a dissolvable. A dry media compound response or strong state substance response, every one of which might be alluded to as a solventless response, is a synthetic response that happens in a framework wherein there is no dissolvable.

There are two test conditions utilized to do the synthetic responses under dissolvable free conditions, for example, (a) response on strong help and (b) response with no dissolvable, strong help, or impetus . In the event of response on strong help, the reactants are at first adsorbed either on mineral help (alumina, silica dirts) or polymer support (polystyrene, polyethylene glycol) or by means of their answer in a suitable natural dissolvable of low bubbling. Then, at that point, the dissolvable is eliminated and the response is done in dry media between adsorbed reactants either by MW warming innovation or by pounding technique. At last, the items are gotten by elution utilizing diethyl ether or dichloromethane and sifted to take out the insoluble strong help. While the response with no dissolvable, strong help or impetus can be done between slick reactants in semi comparable sum with no adduct. On account of strong fluid combination, the response includes either solubilisation of the strong in the fluid stage or adsorption of fluid on the strong surface as an interfacial response. At the point when every one of the reactants are in strong state, then, at that point they require appropriate blending or homogeneity which can be accomplished by utilizing pounding innovation or MW warming strategies. Different responses like buildup, cycloaddition, modification responses, oxidation and decrease, and so forth are done dependent on this guideline.

Benefits of solventless process:

1. There is no response medium to gather, cleanse, and reuse, consequently eco-accommodating.
2. Item virtue is high, so stays away from broad purging utilizing chromatography, just recrystallization is needed now and again.
3. Responses are effortless, regioselective.
4. High return and less an ideal opportunity for the fulfillment of response. 544 Green Approaches in Medicinal Chemistry for Sustainable Drug Design
5. Cycle is financially savvy.
6. Straightforward workup strategy and no requirement for particular equipment's.
7. Utilitarian gathering insurance deprotection can be stayed away from.
8. Low energy utilization
9. Dissolvable free responses are monetary on the grounds that natural solvents are costly.

10. Dissolvable free responses are less or no risky except for if there should be an occurrence of responses under solvents, solvents are unstable, combustible, poisonous, and cancer-causing.
11. More productive with greater selectivity when contrasted with responses did in solvents.

Limitations of of solventless process:

1. Homogenous reactants should blend to a response framework.
2. Solvents are needed during workup (e.g., extraction).
3. Unacceptable for dissolvable helped compound responses.
4. High consistency in response framework.

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MICRONUTRIENT STATUS AND PHYSICO-CHEMICAL PROPERTIES STUDY OF SOILS OF CHAKUR TASHIL AREA OF LATUR DISTRICT

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Abstract:

The natural environment is clean, but due to multifarious activities of man, it gets polluted resulting in what is called environmental pollution. In the present study it was preferred to investigate the soil samples for its physico-chemical analysis of some parameters and micronutrient status of DTPA-Fe, Cu, Mn and Zn in soils of Chakur tahsils of latur district. Fifteen representative samples were collected and analyzed for soil properties and fertility status. The results obtained that the study area soils are neutral to alkaline in soil reaction, electrical conductivity in safe range, low to high in organic carbon content and non-calcareous to calcareous in nature. Considering soil nutrient index values these soils are deficient in DTPA- Zn while Sufficient in DTPA-Fe, Cu and Mn.

Keywords: Micronutrient. Physico-chemical, soil analysis, Nutrient Index

Introduction:

The soil is a complex organization being made up of some six constituents' namely inorganic matter, organic matter, soil organisms, soil moisture, soil solution and soil air. Roughly, the soil contains 50-60% mineral matter, 25-35% water, 15-25% air and little percentage of organic matter (Chatwal *et al.*, 2005). The micronutrient is essential for the proper biochemical transformations within the plant body, so as to yield the desired end products, Zn is essential for protein and auxin production, Cu is a constituent of cytochrome oxidase, Fe helps in photosynthesis while Mn is essential for photosynthesis, carbon assimilation and nitrogen metabolism. Soil fertility is one of the important factors controlling yield of the crops soil characterization in relation to evaluation of fertility status of the soil of an area or region is an important aspects in context of sustainable agricultural production because of imbalanced and inadequate fertilizer use couples with low efficiency of other inputs, the production efficiency of chemical fertilizer nutrients has declined tremendously under intensive agriculture in recent years (Yadav and Meena, 2009). Due to these in view and also lack of information on micronutrients status to identify the emerging micronutrient deficiency or toxicity in the soils, therefore Fifteen representative samples were collected to investigate the soil samples for its physico-chemical analysis of some parameters and micronutrient status of DTPA-Fe, Cu, Mn and Zn in soils of Chakur tahsils of latur district.

Material and Methods:

Chakur is situated in Latur, Maharashtra, India, its geographical coordinates are 18° 30' 0" North, 76° 53' 0" East. its original name (with diacritics) is Chākūr. The Latur District is in the south-eastern part of the Maharashtra state. Latur town is situated on the 18.7° latitude and 73.25° longitude. The district is situated on the Maharashtra Karnataka boundary. The entire district of Latur is situated on the Balaghat plateau, 540 to 638 mtrs from the mean sea level. Total fifteen representative soil samples were collected in the depth of 0-20 cm from the surface of soil from different villages in the Chakur Tahsil area in the year 2018. The soil samples were preserved in polythene bags for further analysis. The chemicals and reagents used for analysis were of A.R. grade from S.D Fine and Merck. pH values were determined using Equiptronics, pH meter as described by Jackson (1967). For this 20 g soil sample was mixed with 40 ml distilled water in 1: 2 ratio. The suspension was stirred intermittently with glass rod for 30 minutes and left for one hour. The combine electrode was inserted into supernatant and pH was recorded. pH value as a measure of the hydrogen ion activity of the soil water system and expresses the acidity and alkalinity of the soil. It is a very important property of soil as it determines the availability of nutrients, microbial activity and physical condition of soil. Electrical conductivity (EC) expresses ion contents of solution which determine the current carrying capacity thus giving a clear idea of the soluble salts present in the soil. The electrical conductivity of a soil samples was determined on an Equiptronics digital electrical conductivity bridge for which 20g soil was added in 40ml distilled water. The suspension was stirred intermittently for half an hour and kept it for 30 minutes without any disturbances for complete dissolution of soluble salts.

The soil was allowed to settle down and then conductivity cell was inserted in solution to take the reading to record the EC values. Organic matter is useful in supplying nutrients and water to the plants and also provides good physical conditions to the plants. The quantity of organic carbon in the soil was estimated by using modified Walkey - black method (Walkey and black, 1934) as described by Jackson (1967). 1g finely ground dry soil sample was passed through 0.5mm sieve without loss and was taken into 500ml conical flask. To this 10ml of 1N potassium dichromate and 20 ml con. H_2SO_4 were added and the contents were shaken for a minute and allowed to set aside for exactly for 30 minutes and then 200ml distilled water, 10ml phosphoric acid and 1ml diphenylamine indicator were added. The solution was titrated against standard ferrous ammonium sulphate till colour changes from blue violet to green. The blank titration was also carried without soil. Micronutrients like Cu, Zn, Fe, Mn is estimated by using Atomic Absorption Spectrophotometer employing standard methods (Trivedy and Goel, 1984). Micronutrients include iron, manganese, zinc, copper, boron, chlorine and molybdenum. The term refers to plant's needs, not to their abundance in soil. They are required in very small amounts but are essential to plant health in that most are required to speed up plant's metabolisms. They are generally available in the mineral component of the soil and the method commonly used for determination of available micronutrients in soil samples is by Lindsay and Norvell (1978) This method consists of use of DTPA (Diethylenetriaminepentaacetic acid) which has been widely accepted for the simultaneous extraction of micronutrients like Zn, Cu, Fe Mn in neutral and alkaline soils. The soil nutrient index was calculated according to the procedure given by Ramamoorthy and Bajaj (1969)

Result and Discussion:

Micronutrient status and values of physico-chemical parameters of soil samples of Chakur tahsil area of Latur district are presented in table 1. The color of soil sample was observed visually and it was found to be black for all the samples. The pH of soil ranging from 7.00 to 8.51 with an average value of 7.56. The values of pH showed that they lie in the alkaline side of the pH scale. This may be because of formation these soils from basaltic parent material rich in basic cations as reported by Mali and Raut (2001). Similar results were reported by Ram *et al.* (1999). The pH range of 6 to 8 is useful for the growth of plants. Electric conductivity of soil ranging from 0.15 to 0.48 dsm^{-1} with average value of 0.30 dsm^{-1}. The value of conductivity is the measure of ions present in the sample. The conductivity values can vary with the chemical properties of soil, if the soil is contaminated by chemicals or if it is saline, the depth of soil sample.

Table 1: Physico-chemical parameters and Micronutrient status of soil samples of Chakur tahsil area of Latur district

Sample No	pH	EC (dSm^{-1})	OC ($g\ kg^{-1}$)	$CaCO_3$ ($g\ kg^{-1}$)	Fe ($mg\ kg^{-1}$)	Mn ($mg\ kg^{-1}$)	Cu ($mg\ kg^{-1}$)	Zn ($mg\ kg^{-1}$)
1	7.05	0.30	7.0	50.9	8.69	7.48	1.40	0.78
2	7.5	0.23	3.5	60.1	7.78	8.29	2.10	0.29
3	7.04	0.19	6.5	54.6	7.58	8.60	2.21	0.37
4	7.66	0.36	3.9	52.9	10.22	6.40	1.47	0.33
5	7.97	0.40	5.5	60.4	9.46	11.9	2.17	0.40
6	7.2	0.15	6.7	53.2	7.61	8.65	2.36	0.38
7	7.12	0.20	5.8	48.3	7.58	8.54	2.29	0.32
8	7.92	0.48	5.4	59.8	9.00	12.5	2.01	0.39
9	7.42	0.42	7.7	67.5	5.60	12.2	1.98	0.48
10	7.99	0.45	5.1	66.5	7.00	9.80	1.52	0.41
11	7	0.21	5.9	59.4	7.50	10.9	2.50	0.30
12	7.85	0.29	3.7	58.2	7.75	8.22	2.02	0.31
13	7.55	0.16	4.9	60.2	6.35	8,75	1.25	0.45
14	8.51	0.45	5.3	60.1	10.0	12.08	2.00	0.35
15	7.66	0.27	4.7	53.7	7.38	10.66	1.60	0.40
Total Average	**7.56**	**0.30**	**5.44**	**57.7**	**7.9**	**9.66**	**1.92**	**0.39**

The organic carbon content was ranging from 3.5 to 7.7 g kg^{-1} with an average value of 5.44 g kg^{-1}. The high content of organic carbon might be due to addition of organic matter through either artificially or naturally and its subsequent decomposition. These results were in confirmatory with results reported by Waikar *et al.* (2004). The free $CaCO_3$ content was ranging from 48.3 to 67.5 g kg-1 with a average value of 57.7 g kg-1. These soils are indicating non-calcareous to highly calcareous nature. Fe is essential for chlorophyll and protein formation, photosynthesis, electron transfer oxidation and reduction of nitrates and sulphates and other enzyme activities. Fe is one of the most common nutrients for plant growth and development because it exists in low-soluble form that is hardly available for plants. In the soils under study the concentrations of DTPA- Fe ranging from 5.6 mg kg^{-1} to 10.52 mg kg^{-1} with an average value 7.9 $mgkg^{-1}$. This high DTPA- Fe content in soil may be due to presence of minerals like Feldspar, Magnetite, Hematite and Limonite which together constitute bulk of trap rock in these soils (Vijaya Kumar *et al.,* 2013). DTPA-Mn has oxidation influenced by both chemical and microbiological factors. Its activities have many enzymes reaction involved in the metabolism of organic acids Mn function along with Fe (Lindsay and Norvell, 1978) in formation of chlorophyll. Table 1 shows the range of the Mn content in the soils from the area from 6.40 mg kg^{-1} to 12.5 mg kg^{-1} with an average value 9.66 $mgkg^{-1}$. The relative high content of Mn in these soils could be due to the soils derived from basaltic parent material which contained higher ferromagnessiume minerals. The DTPA-Cu is an essential micronutrient for normal plant growth. As DTPA-Cu is strongly bound to soils it is very immobile and hence the plant roots are frequently higher in Cu concentration than other plant tissues. In the soils under study the concentrations of DTPA-Cu range from 1.40 mg kg^{-1} to 1.40 mg kg^{-1} with an average value 1.92 $mgkg^{-1}$ The higher amount of DTPA-Cu in surface layer might be due to higher biological activities and chelating effect (Kadao *et al.,* 2002; Jibhakate *et al.,* 2009). The DTPA-Zn content in the soils ranging from 0.30 to 0.78 mg kg^{-1} with an average value of 0.39 mg kg^{-1}. This low content of DTPA-Zn in these soils might be due to fact that under alkaline conditions, the zinc cations are changed largely to their oxides or hydroxides and thereby lower the availability of zinc. The similar results were also reported by Meena *et al.* (2006)

Soil Nutrient Index Value:

As per the NIV developed by the Ramamoorthy and Bajaj (1969) the nutrient index value for soils of Chakur tahsils of Latur district are deficient in DTPA- Zn while Sufficient in DTPA-Fe, Cu and Mn

Conclusion:

The Conclusion can be drawn that the soils of Chakur tahsils of Latur district are neutral to alkaline in soil reaction, safe in electrical conductivity, low to high in organic carbon content and non-calcareous to calcareous in nature. According to the concept of soil nutrient index soils of Chakur tahsils of Latur district are deficient in DTPA- Zn while Sufficient in DTPA-Fe, Cu and Mn content.

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A REVIEW ON GREEN SYNTHESIS OF NANOPARTICLES USING PLANT EXTRACTS

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Abstract:

Green chemistry aims to create chemical products and processes that reduce the generation of harmful substances. In recent years, natural products, particularly plant secondary metabolites, have been widely studied for their potential in synthesizing silver nanoparticles. Green synthesis of nanoparticles (NPs) using plant extracts is an eco-friendly alternative to conventional methods, leveraging plant bioactive compounds as reducing and capping agents. This approach offers advantages such as non-toxicity, sustainability, and the production of stable, biocompatible NPs with enhanced properties. Various metal and metal oxide NPs, including silver, gold, and zinc oxide, have been successfully synthesized. The green method reduces environmental impact and has broad applications in medicine, catalysis, and environmental remediation. This review examines the principles, benefits, and challenges of plant-mediated NP synthesis.

Keywords: Green Synthesis, Biological Synthesis Nanoparticle, Phytochemicals

Introduction:

The rapid advancement of nanotechnology has enabled the development of materials with novel properties and applications [1,2,3]. The nanoparticles exhibit notable characteristics that diverge from those of the bulk material, attributed to the enhanced surface-to-volume ratio. Nano-sized materials have a wide range of applications across various fields [4,5,6,7]. The production of nanoscale materials is a crucial chemical activity. At present, both chemical and physical procedures are employed for this purpose; nevertheless, these techniques may be suboptimal due to their elevated costs and probable environmental contamination. Consequently, there is a necessity to create environmentally sustainable alternatives (green synthesis) for the entire production process, which has attracted worldwide study attention. Conventional synthesis procedures, whether physical or chemical, generally take place under high conditions. Conversely, biological methods are typically conducted at ambient temperature and pressure, indicating simplicity, energy efficiency, and reduced toxicity or harm to humans and the environment [8]. An essential chemical process is the synthesis of materials on the nanoscale. Presently, physical and chemical procedures are used for this; nevertheless, these methods might not be ideal because of their high prices and the likelihood of environmental pollution. (fig. 1) The need to develop eco-friendly substitutes (green synthesis) for the full manufacturing process has piqued the interest of researchers all around the globe. Physical and chemical synthesis methods typically operate at elevated temperatures

Green methods, which are cheaper, easier, and safer than physical and chemical methods, are a promising alternative. Among the various methods of synthesizing nanoparticles, green synthesis using plant extracts has emerged as a promising alternative to conventional chemical methods. Traditional synthesis often involves toxic chemicals, high energy consumption, and generates hazardous waste, raising significant environmental concerns. In contrast, plant-mediated synthesis offers a sustainable, eco-friendly approach that utilizes the natural reducing and stabilizing properties of phytochemicals found in plants.

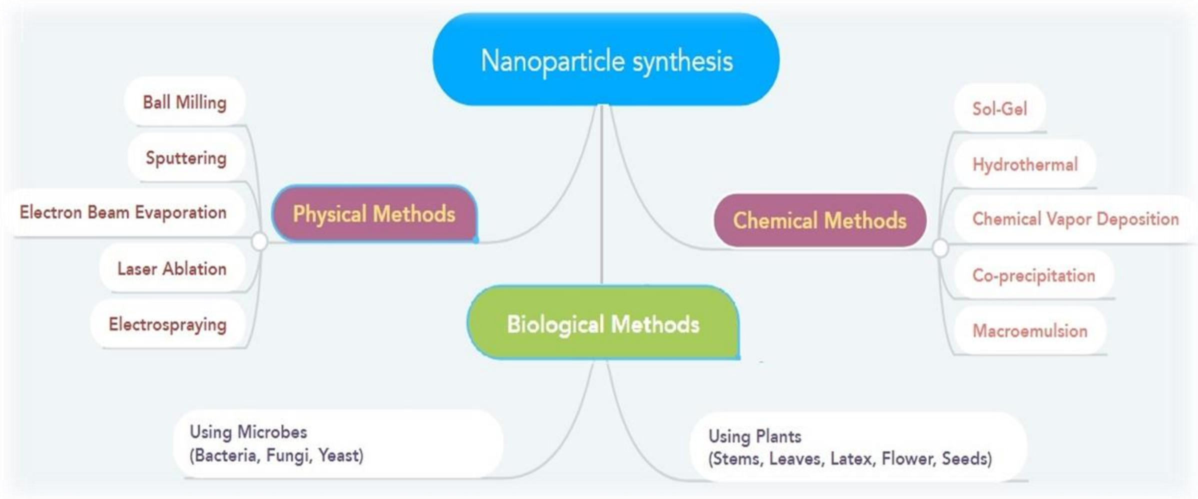

Figure 1: Synthesis of nanoparticles through various methods

Green nanomaterials have many uses, including contaminant remediation, antifungal, antibacterial, biomedical, and photocatalytic activity [9, 10] Figure 2 shows many benefits of green synthesis.

Figure 2: Advantages of eco-friendly nanoparticle synthesis.

Plants are frequently utilized in nanomaterial synthesis because of the reductive properties of their phytochemicals. Plant-assisted synthesis is preferred for its stability, speed, and scalability, with leaves being the most widely used due to their high metabolite content. While the selection of specific plants is often based on availability and traditional uses, those rich in compounds like polyphenols, alkaloids, and flavonoids enhance nanoparticle formation. These compounds act as reducing agents, enabling the transformation of metal ions into nanoparticles. Synthesis of nanoparticle using phytochemicals is a safe, cost-effective method that ensures stabilization, size control, and prevents agglomeration. The summary of Au, Ag, Pd and Cu nanoparticles is reported in table 1. Phytochemicals function as reducing and capping agents in this process. Recently, Iridoid glycosides have been explored for synthesizing metal oxide nanoparticles [11–18].

Figure 3 represents the steps involve in preparation of plant extracts and the synthesis of nanoparticles.

Preparation of Plant Extract: Fresh or dried plant materials are extracted with solvents like water, ethanol, or methanol to yield a concentrated phytochemical-rich extract.

1. **Reduction of Metal Ions:** The plant extract is combined with a metal salt solution (e.g., $AgNO_3$, $AuCl_3$) under controlled conditions (pH, temperature, and time) to reduce metal ions into NPs.

2. **Stabilization:** Phytochemicals in the extract stabilize nanoparticles by preventing. Agglomeration

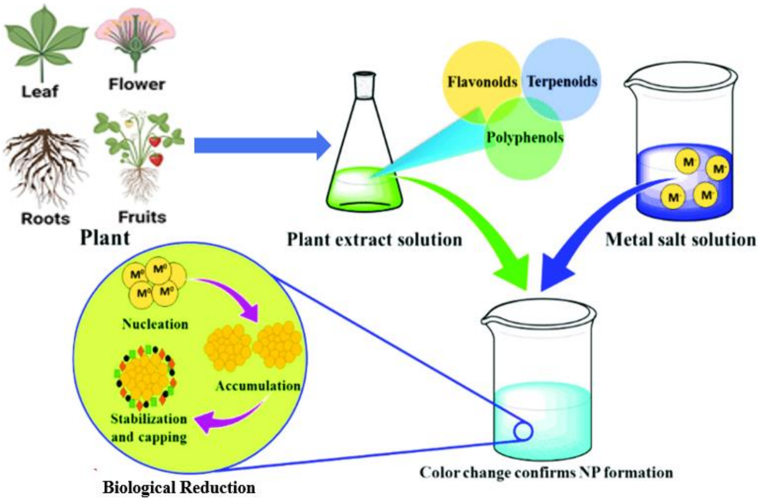

Figure 3: Plant-mediated biosynthesis of nanoparticles.

Mechanisms of Synthesis

The mechanisms underlying the green synthesis of nanoparticles involve complex interactions between metal ions and phytochemicals (fig. 4). Key processes include:

- **Reduction:** Phytochemicals donate electrons to metal ions, reducing them to their elemental form and facilitating nanoparticle formation.
- **Capping and Stabilization:** The phytochemicals adsorb onto the surface of the nanoparticles, providing stability and preventing aggregation.
- **Size and Shape Control:** The specific phytochemicals present, along with reaction conditions, influence the size, shape, and morphology of the nanoparticles.

Proteins and enzymes reduce metal ions to nanoparticles through strong reducing activity, with amino acids influencing nanoparticle size, shape, and yield. Flavonoids chelate and reduce metal ions, aiding in nanoparticle formation and aggregation. Saccharides like glucose reduce metal ions and promote synthesis by oxidizing to carboxyl groups. Polyphenols act as ligands, forming stable metal ion complexes that decompose at high temperatures to release nanoparticles. Molecules with hydroxyl groups, particularly in ortho and para positions, form complexes with metal ions, stabilizing nanoparticles more effectively. [19-21].

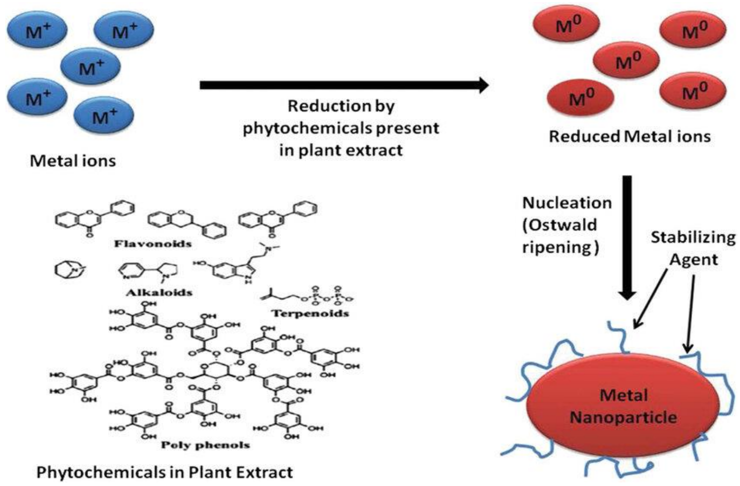

Figure 4: Schematic representation of reduction of metal by phytochemicals present in the plant extract

Table 1: Summary of plant derived metallic nanoparticles

Metal	***Plant Material***	**Size and shape**	**Reference**
Gold (Au)	*Lantana camara flower*	4-12 nm, spherical	[22]
	Leaf of Cannbis sativa	10-35 nm	*[23]*
	Leaves of P. benghalensis	10-50 nm	[24]
	Salacia chinensis	1.5 ± 0.8 nm distorted spherical	[25]
	Justicia glauca	32.5 ± 0.25 nm	[26]
	Stevia rebaudiana	5-20 nm	[27]
Silver (Ag)	*Banana (Musa paradisiaca) peels*	23.7 nm	[28]
	Alysicarpus monilifer leaf	5-45 nm	[29]
	Acacia senegal	<10 nm, spherical	[30]
	Curcuma aromatica	10-30 nm,	[31]
	Mangifera indica	32 nm	[32]
	Azadirachta indica	34 nm	[33]
	Ficus carica	54-89 nm	[34]
Palladium (Pd)	*Black tea leaves*	5-8 nm, spherical	[35]
	Rosa canina fruit extract	10 ± 33 nm spherical	[36]
	Citrus medica Linn juice juice	10-60 nm	[37]
Copper (Cu)	*Cardiospermum halicacabum*	30-40 nm	[38]
	Plectranthus amboinicus	16-25 nm, crystalline	[39]
	Azadirachta indica	48 nm, cubic	[40]

Applications of Plant-Mediated Nanoparticles

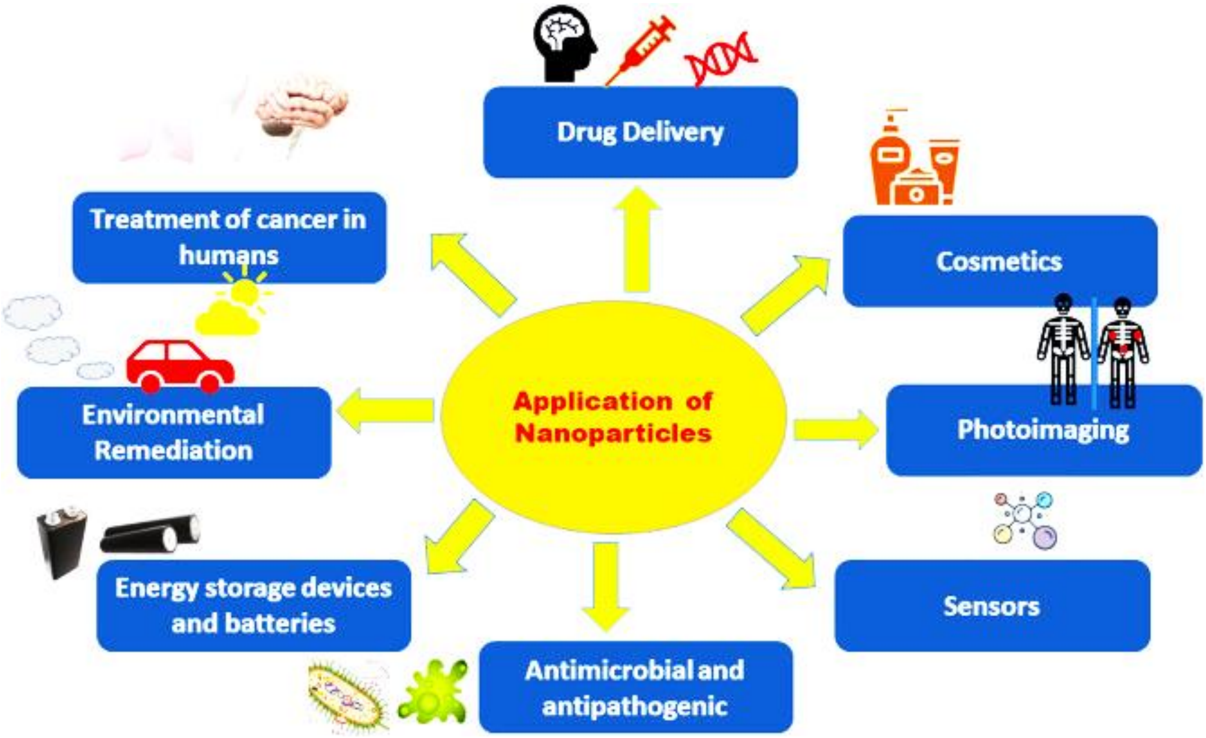

Figure 5: Application of nanoparticles

Nanoparticles are in high commercial demand due to their diverse applications across industries, electronics, environmental sectors, energy, and especially in biomedicine field. This field has done a lot of research on NPs, like the most well-known Ag NPs, because of their enormous interest in biological applications. NPs, including Ag and AuNPs, have attracted a lot of attention in this field due to their potential biological usesPlant-derived green nanoparticles are less likely to induce severe side effects in humans compared to chemically synthesized nanoparticles and offer a broad spectrum of applications (Table 1).The unique properties of nanoparticles synthesized using plant extracts have led to their application in various fields :

- **Biomedical Applications:** Silver nanoparticles synthesized from plant extracts exhibit potent antimicrobial activity, making them valuable in medical applications such as wound dressings and drug delivery systems.
- **Catalysis:** Plant-mediated nanoparticles have shown high catalytic activity in various chemical reactions, contributing to more sustainable and efficient processes.
- **Environmental Remediation:** Nanoparticles synthesized from plant extracts can be used for the removal of pollutants from water and soil, offering eco-friendly solutions for environmental cleanup.

- **Agriculture:** Plant-derived nanoparticles can enhance crop yield, protect against pathogens, and improve nutrient uptake, promoting sustainable agricultural practices.

Nanomedicine plays a crucial role in human health protection through various mechanisms, including antimicrobial, antiparasitic, antiproliferative, pro-apoptotic, and oxidative activities, as well as anti-inflammatory effects. [41- 46]. Precision farming with controlled release of agrochemicals, target-specific delivery of biomolecules, more effective nutrients absorption, detection and control of plant diseases, etc.) is agriculture [47-48]. Applied to bioengineering (photocatalysts, biosensors, biocatalysts, etc.) and food science and technology (methods for processing, storing, and packaging) [49] Sunscreen is a component of many cosmetic products, including nanoemulsions, anti-aging creams, hair growth serums, and delivery systems for bioactive compounds [50].

Challenges and Future Directions

Despite the promising potential of plant-mediated synthesis, several challenges remain:

- **Scale-Up:** Transitioning from laboratory-scale synthesis to industrial production requires optimization of processes to ensure reproducibility and cost-effectiveness.
- **Standardization:** Establishing standardized protocols for plant extract preparation and nanoparticle synthesis is crucial for consistent quality and reproducibility.
- **Characterization:** Advanced characterization techniques are needed to accurately analyze the size, shape, and properties of plant-mediated nanoparticles.

Conclusion:

The green synthesis of nanoparticles using plant extracts represents a significant advancement in sustainable nanotechnology. By harnessing the natural properties of plants, this approach offers an eco-friendly alternative to traditional chemical methods, promoting environmental responsibility and reducing reliance on toxic substances. Continued research and development in this field will be essential to overcome existing challenges and unlock the full potential of plant-mediated synthesis, paving the way for innovative applications in various industries.

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