# Education in Chemical Science and Technology

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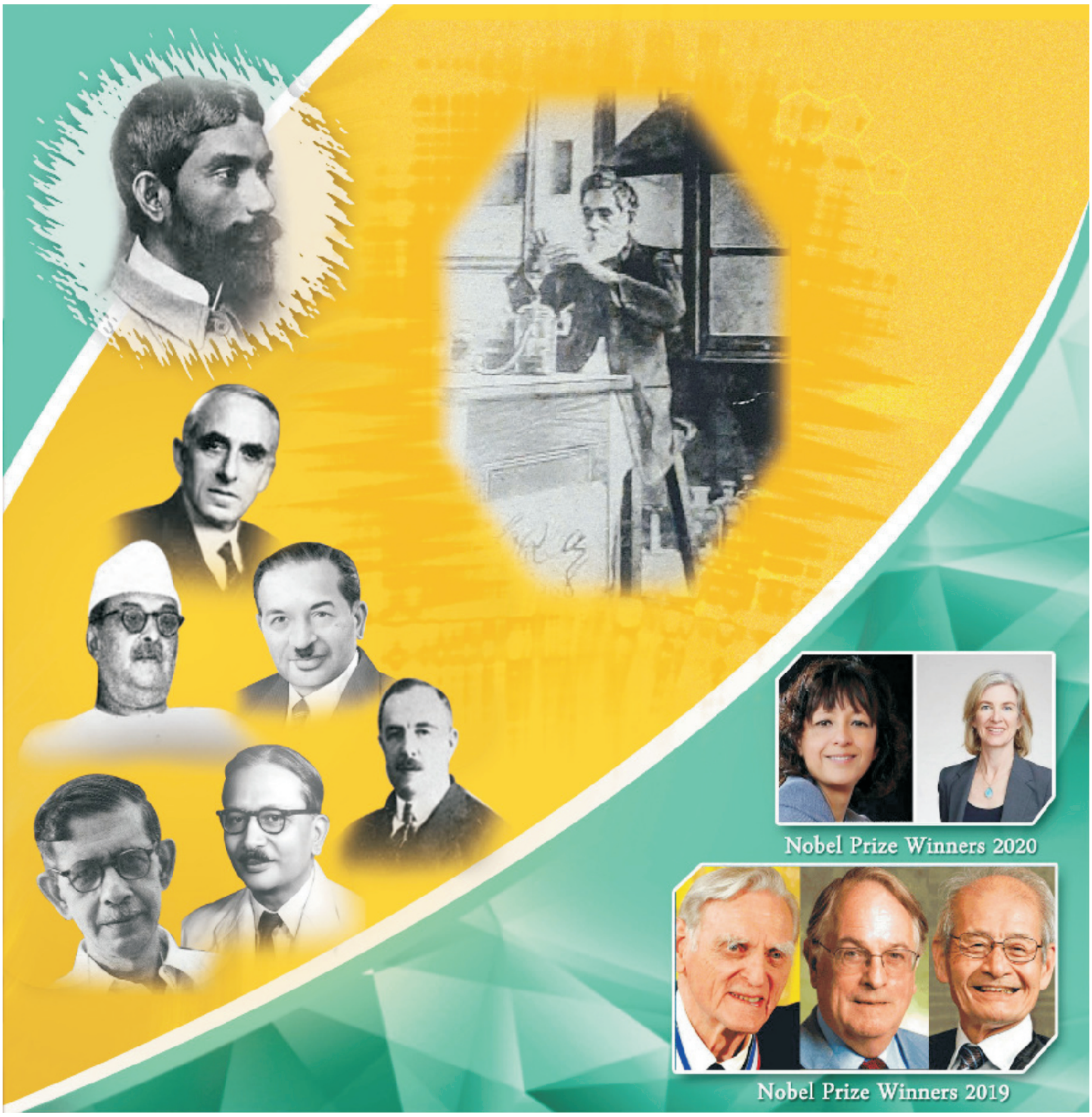

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# Education in Chemical Science and Technology

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# PREFACE

The 7th issue of this book series of "**Education in Chemical Science and Technology**" is shaped with eight articles in the different domain which will be valuable literature for the students those who are willing to adopt Chemistry as a part of their career.

In the first article, Prof. D. V. Prabhu from Wilson College, Mumbai & General Secretary, Association of Chemistry Teachers explained the role of catalysts in green chemistry in his unique style of easiest explanation. He enlightened the role of catalysis towards better atom economy, minimum waste production, eco-friendly products and emissions, and reusability of catalyst materials.

Prof. Chittaranjan Sinha from Jadavpur University, Kolkata and Honorary Secretary, Indian Chemical Society who is popular as 'CRS Sir' among inorganic chemistry students, explained beautifully a very modern topic MOF (Metal-organic framework), and the chemistry behind it, in the second article. The uniqueness of this topic is the structural correlation between house frame and MOF frame which will be an easier tool to understand the topic.

In the third article, Prof. Sagar Pal, an Organic Chemist from IIT (ISM) Dhanbad has explained the formation of polysaccharide-based hydrogels in controlled drug delivery applications.

Prof. Pijush Khatua *et al.* from Haldia Institute of Technology, Haldia explained the role of polymers, resins, adhesive towards the formation of composite material in the fourth article of this book. He also emphasized "Why fiber-reinforced composites are impotent for surviving in the future?", which will promote higher learners to find their projects in this beautiful field.

In the fifth article, Dr. Tarun Kumar Barik *et al*. from IIT-Kharagpur explained the deeper understanding of Foam-Raman spectroscopic characterization and its applications in different fields.

Dr. Partha Pratim Bag from SRM University, Sikkim explored the correlation between the engineering techniques and the chemistry behind the crystal structure of the molecule in the sixth article.

In the seventh article, Prof. Radha Das *et al*. from Haldia Institute of Technology, Haldia reported an original project outcome on the adsorption performance of Indian neem leaf powder for the removal of cationic Methylene Blue dye from effluents of the dye industry, its kinetics, and reaction isotherm.

And at the end, Dr. Madhurima Jana *et al.*, NIT-Rourkela explained how alcohol as a co-solvent plays an important role in the structure and stability of proteins.

We appreciate the academic contribution of all the authors who kindly responded to our invitation and contributed their articles. We are also thankful to all the council members and advisors of Indian Chemical Society for their valuable suggestions to bring this issue towards our readers.

Last but not least, the help of the Office Staff of the Society and Staff of the Press are thankfully acknowledged for their kind help in every aspect of this publication.

Inspite of our best efforts some unintended eorrors might have gatecrashed in for which we express our sincere apology.

We believe that the present issue would be warmly accepted by our readers. We shal be highly obliged to accept any suggestions and critisim from the readers for future improvement.

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# Education in Chemical Science and Technology

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NOTE : As asterisk in the heading of each paper indicates the author for correspondence.

**Edu. Chem. Sci. Tech.,**
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# Importance of catalysis in Green Chemistry

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Green Chemistry aims at the design of products that minimize the use and generation of harmful substances which harm the environment. Green Chemistry is based on the 12 Principles of Green Chemistry enunciated by Paul Anastas and John Werner in the '90s, which provide a blueprint for sustainable development. Among these, the use of catalysts to improve atom economy and yield of reactions is most important. Catalysts are the pillars of Green Chemistry and worldwide, there is a constant search for novel catalysts. Atom economy of a chemical reaction is a theoretical measure of the amount of starting material that has got converted into the desired useful product and is a reliable metric of the greenness of a reaction.

% Atom economy = [Mass of desired product]/[Total mass of all products]×100

Thus, 100% atom economy means 0% waste.

Green catalysts are preferred because of their distinct advantages:

(I) better atom economy,
(II) minimum waste production,
(III) eco-friendly products and emissions,
(IV) reusability.

Some examples of Green catalysts which are widely used are biocatalysts which include enzyme catalysts, phase transfer catalysts, and nano catalysts.

Keywords: Green Chemistry, sustainable development, Green catalysts, atom economy, reaction yield, bio-catalysts, enzyme catalysts, phase transfer catalysts, nano catalysts.

## Introduction

In the last few years, there has been a constant and vigorous debate between the Development and Conservation of the environment. Man has been using natural resources at an alarming rate leaving behind toxic byproducts which are hazardous to the environment. Today, there is a general acceptance that there should be a balance between development and conservation. The 12 Principles of Green Chemistry[1–5] provide a basis to maintain this balance which is crucial for the conservation of the environment.

Sustainable Chemistry is a scientific concept that aims at improving the efficiency with which natural resources are used to meet the needs for chemical products. Thus, Green Chemistry is a tool to build a sustainable society. Sustainable development uses technology that requires fewer resources and produces minimum waste thereby reducing the damage to the environment by manmade materials and the processes used to produce them. It is based on the 3R's principle – Reduce, Reuse, and Recycle. Green Chemistry provides feasible alternatives to prevent further damage to the environment and promotes sustainability through the design of eco-friendly products by substitution of hazardous reagents[6].

## Some basic concepts of catalysis

A catalyst is a substance that accelerates the rate of a reaction but remains chemically unchanged at the end of the reaction i.e. its chemical composition and amount remain unchanged. Catalysts are very specific in their action and a particular catalyst is effective for only one reaction and ineffective for other reactions. A catalyst takes an active part in the reaction but does not appear in the end product of the reaction.

A catalyst lowers the minimum energy required for the reaction to take place and hence increases the rate of reaction. This energy threshold called Energy of Activation (E) is related to the absolute temperature T by the Arrhenius equation, $k=A\ e^{-E/RT}$ where k is rate constant, R is the gas constant and A is a constant. The temperature has the most profound effect on the rate of reaction.

E and E′ are the energies of activation of the uncatalyzed and catalyzed reactions respectively. Since $E' < E$, the rate of the catalyzed reaction $k' >$ rate of uncatalyzed reaction k.

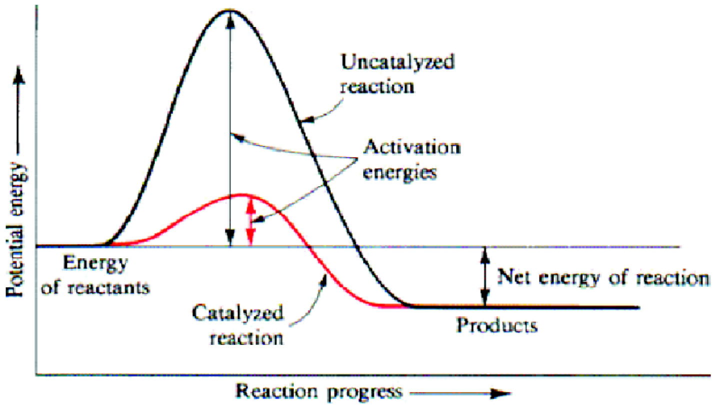


**Fig. 1.** Effect of catalyst on the rate of reaction.

### Mechanism of catalysis

The catalyst forms an unstable short-lived intermediate with the reactant. The intermediate then decomposes to give the product and the catalyst comes out unchanged.

Reactant + Catalyst → Intermediate

Intermediate → Product + Catalyst

Example: Friedel Craft's reaction using anhydrous $AlCl_3$ as catalyst

$CH_3COCl$ + an. $AlCl_3$ → $[CH_3COCl.AlCl_3]$

Acetyl chloride Intermediate

$[CH_3COCl.AlCl_3] + C_6H_6 \rightarrow CH_3COC_6H_5 + HCl + AlCl_3$

Acetophenone

$CH_3COCl + C_6H_6 \longrightarrow CH_3COC_6H_5 + HCl$

### Classification of catalysts

Catalysts are broadly classified as (i) homogeneous catalysts and (ii) heterogeneous catalysts. In homogeneous catalysis, the catalyst is in the same physical state (phase) as the reactants and products. These are reactions occurring in the gaseous phase or solution.

e.g. Inversion of sucrose using HCl catalyst takes place in solution.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+ \text{ catalyst}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The reactant and products are optically active. During the reaction, the angle of rotation of polarized light changes from right to left hence inversion. The rate of inversion is monitored in a polarimeter. Acid, base, and enzyme-catalyzed reactions belong to the homogeneous catalysis category. Homogeneous is more effective than heterogeneous catalysts but they cannot be isolated from the reaction system and hence are not reusable. In heterogeneous catalysis, the catalyst is in a different physical state than the reactants and products. Usually, the heterogeneous catalyst is solid in finely divided conditions.

Examples:

(1) $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

$2SO_3 + 2H_2O \rightarrow 2H_2SO_4$

The consumption of sulphuric acid is a barometer of a country’s economic progress and development.

(2) Haber’s ammonia process, $N_2 + 3H_2 \xrightarrow{Fe(Mo)} 2NH_3$

Ammonia is used for the preparation of nitrogenous fertilizers hence this reaction is very important in agriculture to increase food production.

(3) Hydrogenation of ethylene to ethane using Raney nickel catalyst

$$CH_2{=}CH_2 + H_2 \xrightarrow{\text{Raney Ni}} CH_3CH_3$$

Heterogeneous catalysts are less effective but preferred because they are easy to isolate and can be reused. Most industrial processes use solid catalysts.

### Role of catalysts in Green Chemistry

#### (1) Improvement in atom economy:

A catalyst should improve the atom economy of a reaction. Atom economy of a reaction is a theoretical measure of the amount of starting material that ends up as the desired final product. Atom economy is the most widely used metrics to measure the greenness of a reaction.

% Atom economy = [Mass of desired product]/[Total mass of all products]×100

Thus, the greater the % atom economy, the greener (efficient) is the reaction. i.e. 100% atom economy means 0% waste. Atom economy can be maximized by designing the synthesis so that the final desired product contains the maximum proportion of the starting material and few or no atoms are wasted. This can be achieved by the use of a suitable catalyst.

**Illustration 1:** The atom economy of the extraction of iron from its ore using carbon can be calculated as follows:

$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$

Mass of reactants = 2[2×55.84 + 3×16] + 2[12] = 355.36 amu

Mass of products = 4[55.84] + 3[44] = 355.36 amu

The desired product is Fe.

% Atom economy = [Mass of desired product]/[Total mass of all products]×100

= [4(55.84)/355.36]×100 = 62.85%

**Illustration 2:** Aniline can be prepared by old and new methods:

The old method used $FeCl_3$.HCl as the catalyst

$4C_6H_5NO_2 + Fe + 4H_2O \rightarrow 4C_6H_5NH_2 + 4Fe_2O_3$

Nitrobenzene Aniline

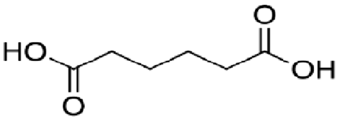
% Atom economy = 35%

The new method uses a Nickel catalyst at 300°C and 5 psi pressure.

$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$

% Atom economy = 72%

**Illustration 3:** Adipic acid is a very important starting material for the manufacture of Nylon 6:



Adipic acid

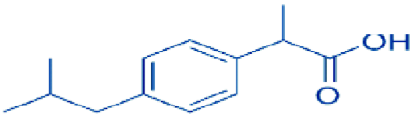
The conventional method uses carcinogenic benzene as the starting material, $Ni/Al_2O_3$ as the catalyst, and nitric acid as the oxidizing agent. Nitric acid produces nitrous oxide $N_2O$ which contributes to the greenhouse effect and destruction of ozone in the stratosphere. The reaction takes place in 3 steps and has an atom economy of 55.7%.

In the new method (greener method), the starting material is Cyclohexene, $Na_2WO_4$ is the catalyst, and 30% $H_2O_2$ is the oxidizing agent. This one-step synthesis proceeds in an aqueous medium at a lower temperature and has an atom economy of 67%. Both the reactant and product are environmentally benign.

**(2) Optimization of reaction yield:**

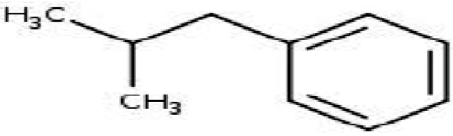
A catalyst should improve the yield of a reaction.

**Illustration 4:** Ibuprofen is an analgesic drug just like Aspirin (Acetyl salicylic acid):



Ibuprofen

2-Methylpropyl benzene is the starting material for both the conventional and new methods of synthesis.



2-Methylpropylbenzene

The original synthesis required 6 steps and resulted in the production of secondary by-products which were a waste. The catalyst anhydrous $AlCl_3$ was not efficient as it got hydrated and was rendered ineffective. The yield was 40%. The new method uses Raney nickel as the catalyst which can be recycled and reused. The yield is 77%.

**Illustration 5:** Nickel catalyst increases the yield of hydrogenation of propene to almost 100%:

$CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3$

Propene Propane

### Aims of Green Chemistry

(1) Prevention of waste and pollution by maximizing atom economy and avoiding chemical derivatization.

(2) Saving of energy by use of suitable catalysts and renewable feedstock which is readily available, carrying out reactions at ambient temperature and use of microwave radiation and ultra sound energy as substitutes for conventional heating.

(3) Ensuring safety at the workplace by using environmentally friendly solvents like water and substances with minimum potential of chemical accidents and use of protective laboratory gear.

One of the 12 principles of Green Chemistry is to use catalysts in preference to stoichiometric reagents. Stoichiometric reagents are usually used in excess leading to wastage of the reagent and can carry out a reaction only once. On the other hand, catalysts are effective in small amounts and can carry out a reaction many times, and are thus cost-effective.

### Green catalysts

Over the last few years, a new breed of novel catalysts called Green catalysts has been developed.

Green catalysts are eco-friendly as:

(1) they minimize waste production and hence pollution,

(2) they improve atom economy so that the maximum amount of reactant is converted into the desired product,

(3) products/emissions of catalyzed reactions do not harm the environment e.g. toxic fumes of greenhouse gases are not emitted,

(4) they can be recovered and reused.

Biocatalysts which are biological materials like enzymes are good examples of

Green catalysts. Enzymes are complex proteins composed of the 20 naturally found amino acids, produced by living cells. Enzymes catalyze several biochemical reactions and are very specific in their action e.g. Urease catalyzes the hydrolysis of urea and no other reaction.

$$CO(NH_2)_2 + 2H_2O \rightarrow CO_2 + 2NH_3$$

Enzymes are named after their functions like oxidoreductases, transferases, hydrolases, and isomerases. The catalytic activity of these homogeneous catalysts depends on temperature and pH. They are effective at room temperature and get desensitized at around 50°C.

Enzymes are used as catalysts in medicine for the following reasons:

(I) High stereoselectivity resulting in the formation of only one isomer-this decreases the cost of the medicine and the problem of disposal of the unwanted isomer. Chirality is a most critical criterion for the pharmacological effect of medicines e.g. the Thalidomide tragedy in the UK was due to a racemic mixture of the isomers of the drug.

(II) Enzymes find specific applications in medicine, pharmacology, food, and textile industries. The human body runs on enzyme catalysis. Proteins are enzyme catalysts that perform many functions in the body including generating signals for the movement of limbs and helping to digest food.

### Nano catalysts

Nano catalysts in powdered form have a large surface to volume ratio and are excellent catalysts[7] e.g. silica and platinum nano particles. Titania ($TiO_2$) based nano particles are used as green photo catalysts which have applications in the utilization of solar energy, waste, and pollution treatment. Titania can catalyze the oxidation of organic carbonaceous substances to $CO_2$ in the presence of oxygen and water and may find use in the biodegradation of effluents like dairy and domestic wastes in the presence of organisms like *E. coli* [8].

Nano crystalline alkaline earth oxides are good adsorbents for toxic gases like $SO_2$, $NO_2$, and HCl. Nano crystalline MgO particles are effective catalysts for dehydrogenation reactions

### Phase transfer catalysts (PTC)

Phase transfer catalysts have important applications in various organic reactions[4,9,10]. Organic compounds are soluble in organic solvents but reagents like KCN, NaCN, NaCl, NaOH, etc. are not soluble in organic solvents. A phase transfer catalyst can transfer the active reagent from the aqueous phase to the organic phase so that it can take part in the reaction. Commonly used PTCs are quaternary ammonium salts (QAS) and crown ethers.

$$\underset{\text{Benzyl chloride}}{C_6H_5.CH_2Cl} + \text{aq. KCN} \xrightarrow{\text{QAS}} \underset{\text{Benzyl cyanide}}{C_6H_5.CH_2CN}$$

(fast reaction with 90% yield)

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow{\text{KMnO}_4\text{ + Crown ether}} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

The crown ether complexes with the $K^+$ ion of $KMnO_4$ and $MnO^-$ remain outside the crown ether. Thus, $KMnO_4$ is transported into the organic phase where toluene is present. PTCs are widely used in the green synthesis of pharmaceuticals and agrochemicals like herbicides and insecticides.

### Conclusions

Green Chemistry focuses on the design of products that minimizes the use and generation of hazardous starting materials. The use of green catalysts improves atom economy and efficiency of reactions. Green Chemistry should be incorporated in a big way in the curriculum to understand the principles of Green Chemistry based on the 3R's – Reduce, Reuse and Recycle and to learn to modify the existing processes to make them environmentally friendly.

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**Dr. D. V. Prabhu**

Dr. D. V. Prabhu is Former Head and Adjunct Professor of Chemistry, Wilson College, Mumbai and former Dean of Faculty of Science, University of Mumbai. His research interests are Reaction Kinetics, Catalysis and Environmental Chemistry. He has published 60 papers in peer-reviewed journals and presented 92 papers in national and international conferences in India and abroad. He is the author of 6 ISBN books in Physical and Analytical Chemistry. Dr. Prabhu has been a member of the DAE appointed National Steering Committee for organizing Science Olympiads in India and has served as Head Mentor and Delegation Leader of the Indian delegations to four International Chemistry and Junior Science Olympiads. He is the Editor in Chief of GP Globalize Research Journal of Chemistry which is abstracted in Chemical Abstracts, CAS, USA. He served as the President of ICS (Mumbai Branch) during 2000-2002. Dr. Prabhu was elected Fellow of the Royal Society of Chemistry (FRSC) in 2019.

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# Framework Chemistry renovating our insight into the Chemical Sciences

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## Introduction

A 'frame' is a structure (rigid or flexible) in a definite pattern that surrounds something such as a picture, door, plot etc., and 'Framework' is an important supporting structure of a building, vehicle, or geometrical object. In Chemistry 'Framework' refers to the solid-state structure of the molecules/materials, surface morphology, and different synonymous terminology is used such as Covalent organic frameworks (COFs), Coordination Polymers, Coordination Network, Coordination Framework, Metal-Organic Framework (MOF), Metal-organic coordination networks (MOCNs)[1–5]. MOFs are the coordination polymer with sizeable porosity and crystalline geometry and dimensionality. These polymeric coordination networks significantly extended along with one (1D)-, two (2D)- and three (3D)-dimensioning by the repeating unit of coordination sphere (Fig. 1). The components under certain experimental conditions (heat, light, pressure, solvent, catalyst) are orderly organized to generate oriented. In this contrast, coordination compounds are aggregated via coordinate bonds, and weak chemical bonds (secondary forces) in the infinite array lead to fabricating coordination polymers.

A coordination polymer is an inorganic or organometallic polymer structure containing metal ions linked by organic bridging ligands with repeating coordination entities extending in 1, 2, or 3 dimensions.[1]solids.

Organic polymers (Fig. 3) are typically macromolecules with high molecular weight and are associated with the repeating unit of monomer or oligomers through covalent bonds. Moreover, secondary forces like hydrogen bonds or van der Waals contacts are associated to exhibit the structural directionality in the coordination polymer which is much weaker than the coordinate bonds.

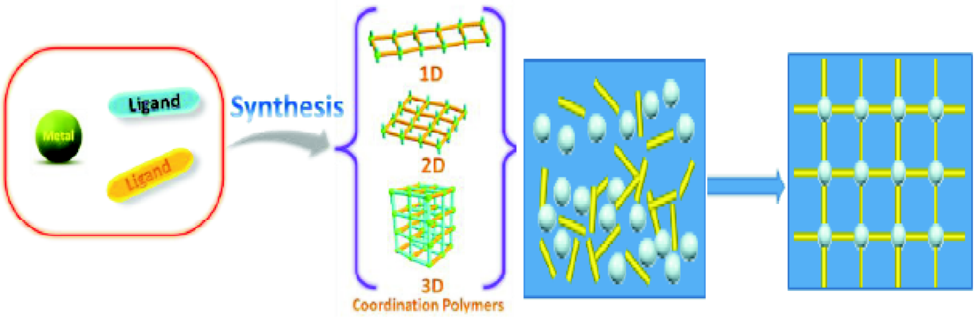


**Fig. 1.** Schematic representation of synthetic approach of 1D, 2D, and 3D coordination polymers from the starting framework synthons (materials) and (b) randomly moving components of reactants to ordered complex form.

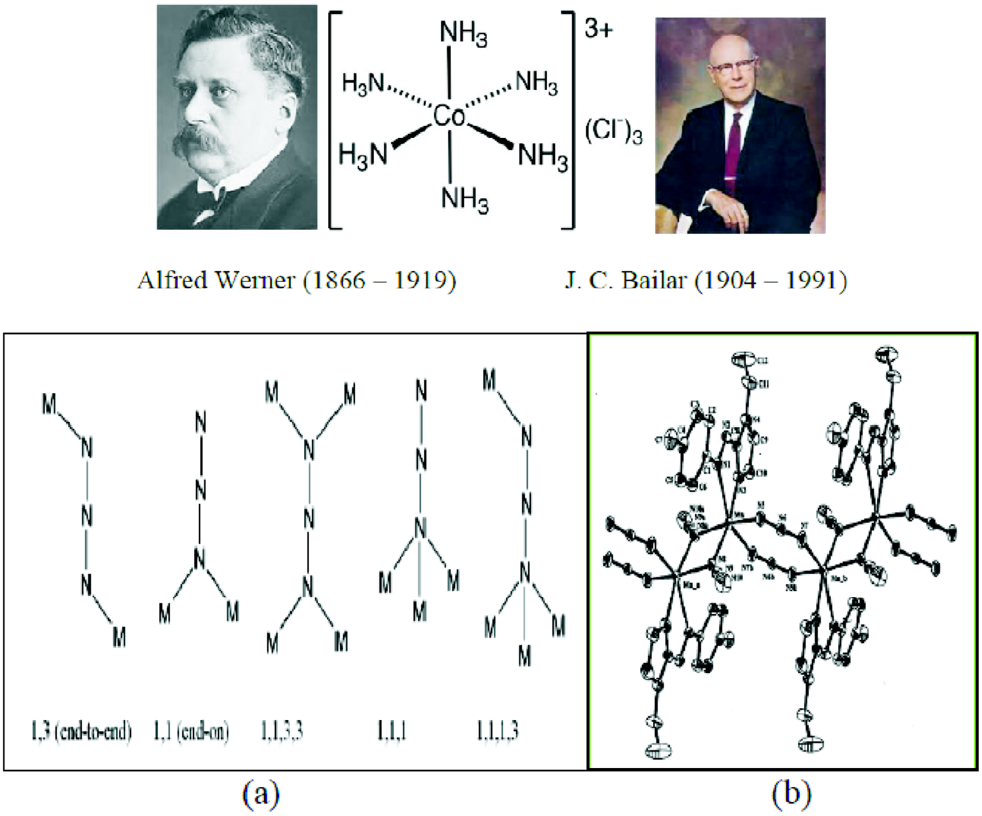


**Fig. 2.** (a) Initiator of Coordination Theory, Alfred Werner, naming 'Coordination Polymer' by J. C. Bailar and (b) a Coordination polymer constituted by repeating of $\mu_{1,1}$ and $\mu_{1,3}$-$N_3^-$ coordination about Mn(II).

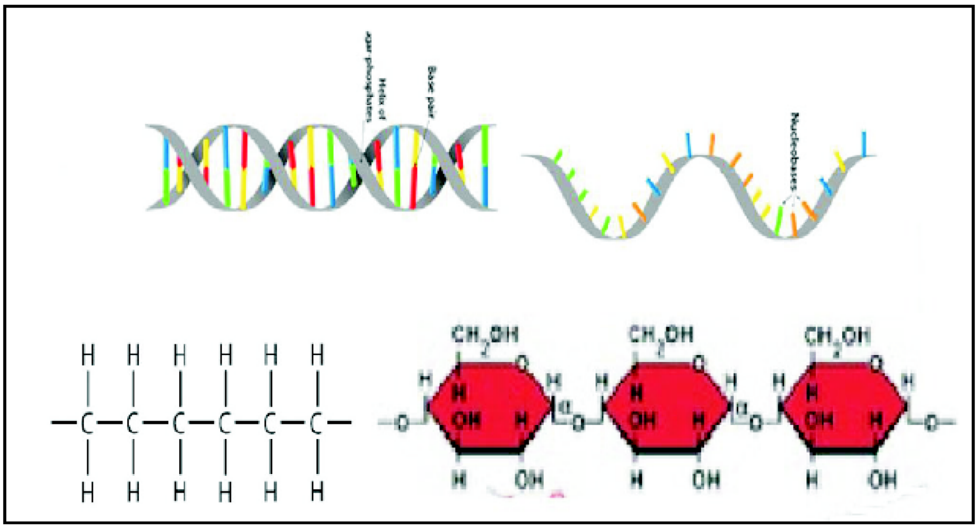


**Fig. 3.** Examples of Organic Polymers – Polythene, Starch, DNA, RNA etc.

Since 1913, the Nobel Prize in Chemistry was awarded to Alfred Warner (Fig. 2) for the establishment of the coordination compounds in the field of inorganic chemistry. The earlier investigation and development in the new field has been explored gradually. Consequently, this area has been broadening to establish the structure-property-application relationship. But in late 1964, the term “Coordination polymer” was first introduced by J. C. Bailar, subsequently; he originates the relations between organic polymers and inorganic coordination polymeric species[6].

## Structural diversity

Transition-metal ions and their clusters have been largely exploiting to set up the structural diversity in the coordination polymers of preferably the geometry around the central metal such as linear, T- or Y-shaped, tetrahedral, square-planar, square-pyramidal, trigonal-bipyramidal, octahedral, trigonal-prismatic, pentagonal-bipyramidal, and the corresponding distorted forms are summarized in Fig. 4. The metal-organic polymers have earned a lot of possibilities to gain a large number of structural arrangements with variable designs and topologies through modifying the metallic connectors and by changing the size or

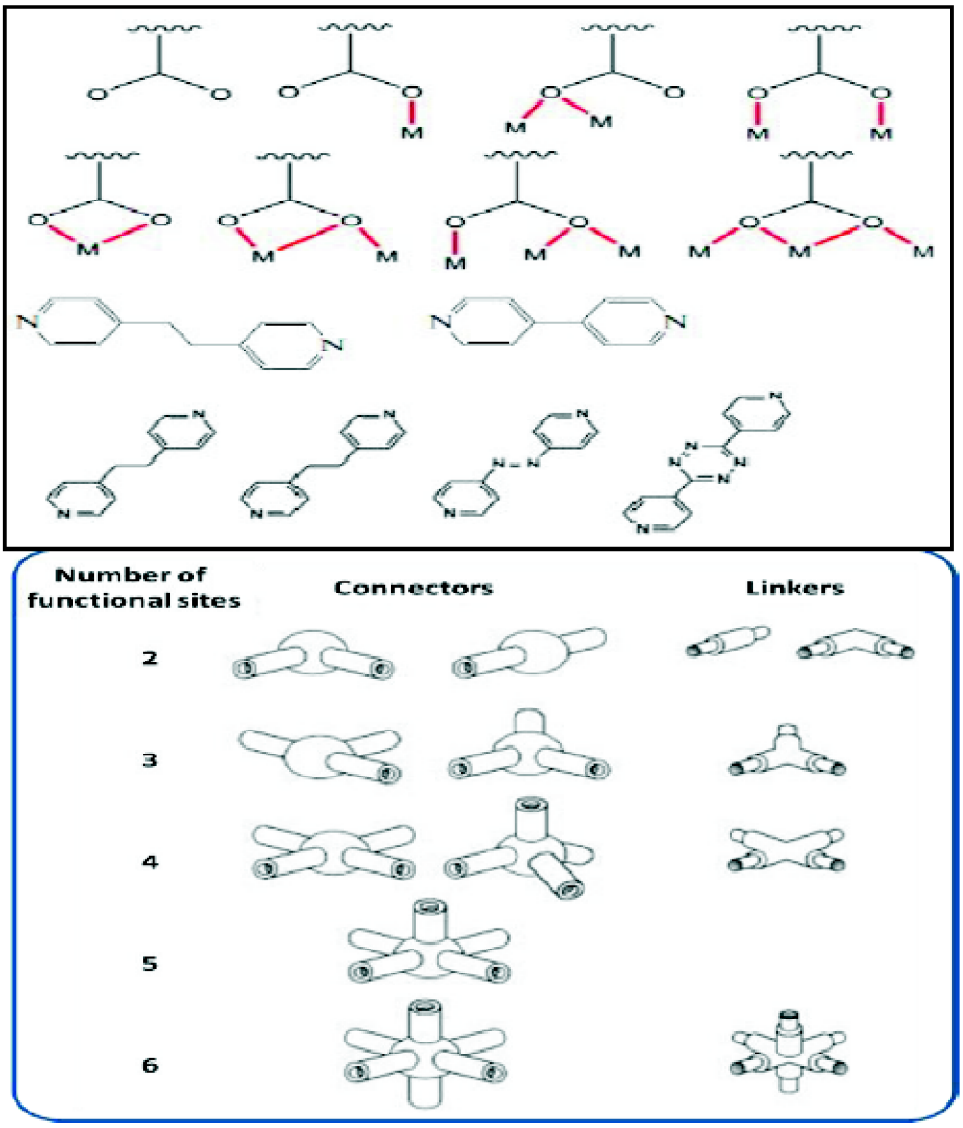


**Fig. 4.** Carboxylate and pyridyl linkers and schematic representation of metal nodes as secondary building blocks (SBUs) in CPs.

functionalizing the organic linkers. Thus, carboxylate linkers and their derivatives became popularized in the field of coordination chemistry. Moreover, poly-carboxylates are widely utilized due to their versatile binding modes towards the metal ions and the binding strength boosts their thermal and chemical stability compound depends upon the reaction conditions.

In general, supramolecular chemistry is an interface where supramolecular building blocks are held by a large number of supramolecular interactions or, non-covalent interactions. The term '*supramolecular interaction*' (Fig. 5) covers a substantial range of attractive and repulsive forces. These types of interactions stabilize many important systems like organic molecules, biological macromolecules, and the structural motif of the coordination polymers. From the crystal engineering point of view, non-covalent interactive forces lead an important role in the design and synthesis of molecular crystals and also conserving the three-dimensional structure. The dynamic nature of such non-covalent forces signifi-

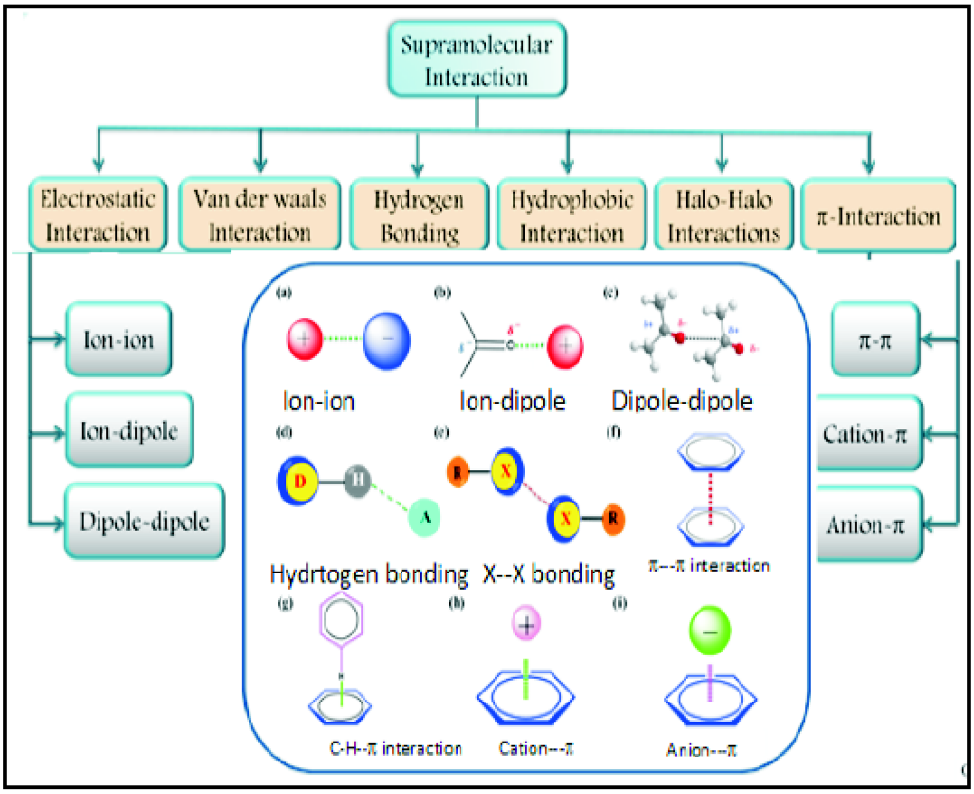
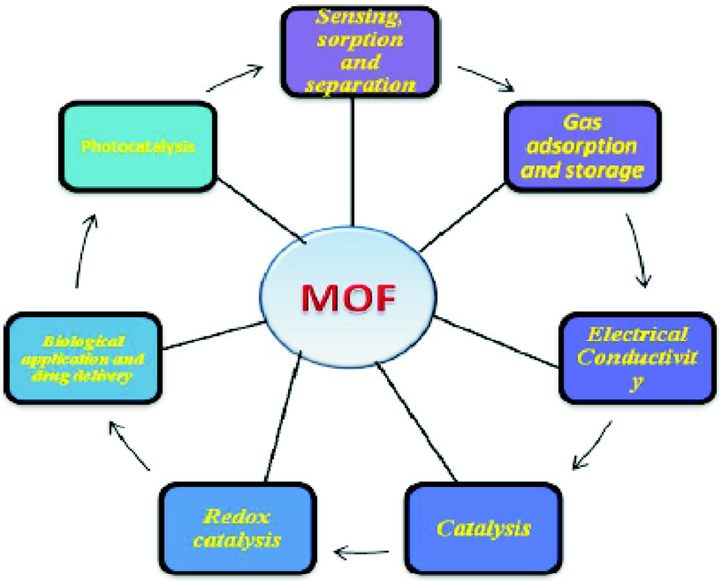


**Fig. 5.** Types of supramolecular interactions.

cantly implicated in many interdisciplinary subjects like chemistry, biology, physics, and engineering.

The structure, physical and chemical properties of coordination polymers are easily tunable by judicious choice of metal ions or metal clusters and suitable organic linkers. This unique capacity has led to designing various coordination



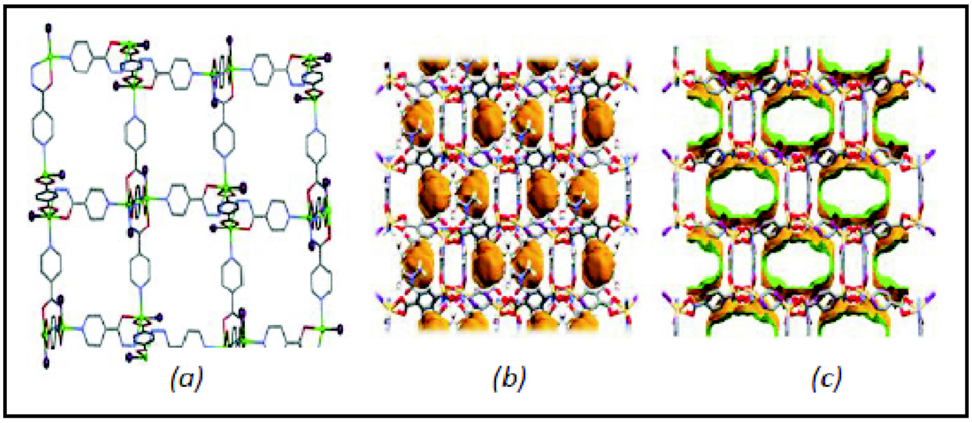

(a) (b) (c)

**Fig. 6.** (a) The single 2D layer of Cd(II)-isoniazid; (b) the channel arrangements of voids surfaces along the c-axis with solvent molecule and (c) without solvent molecule.

polymers and the control over the structural geometry has earned a new field of research in material science. Yaghi and co-workers have developed the term 'reticular chemistry'[7] for understanding molecular chemistry and its accuracy in making and breaking bonds of a solid-state framework structure. This field has advanced by synthesizing several robust and highly porous coordination polymers of polycarboxylic acids for potential application in gas storage and separation[7,8]. Besides these robust molecular frameworks, Kitagawa and co-workers, get familiarized in synthesizing several functional coordination networks[9] to introduce surface porosity and flexibility in the materials.

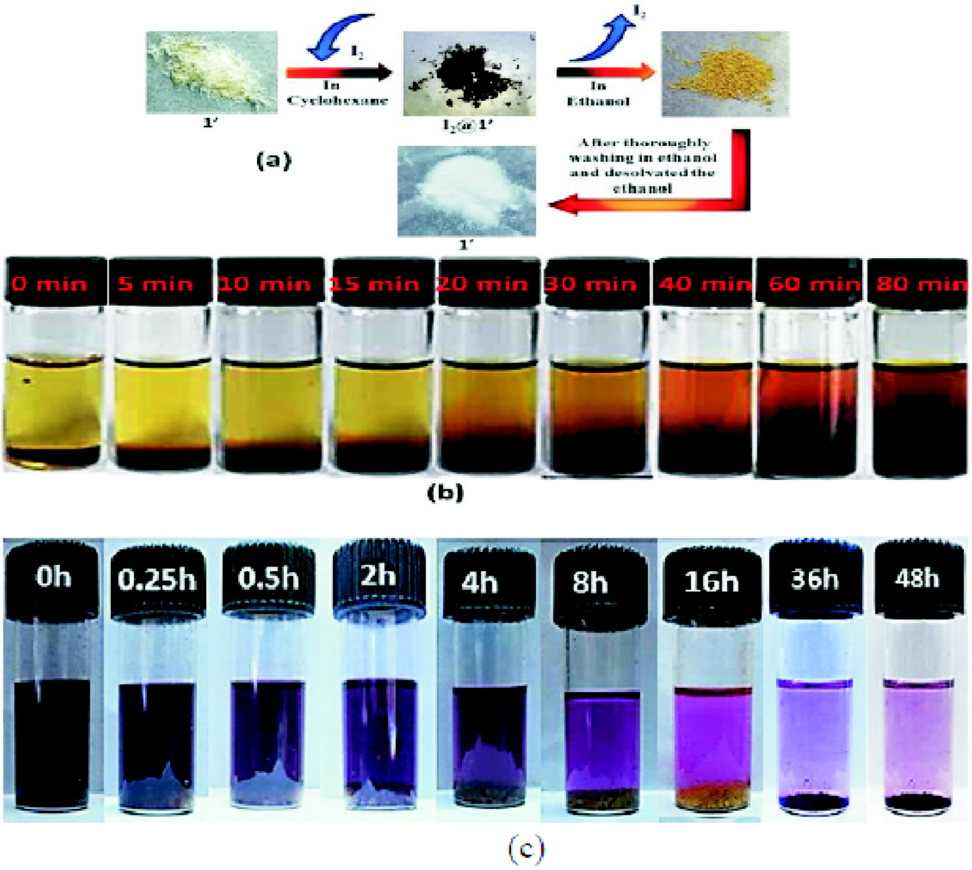


**Fig. 7.** (a) Porous cavity in Cd-isoniazid adsorbs $I_2$ and turned to brown-black and washing with ethanol removes and turned to pale-yellow to colourless; (b) $I_2$ release to EtOH solution and (c) $I_2$ uptake from cyclohexane solution.

## Applications of Metal-Organic Frameworks

The metal-organic coordination polymers have been explored in various fields (Fig. 5) of applications – such as gas storage, separation of gases and industrially important liquids, carbon capture and conversion, electrical conductivity, drug delivery, heterogeneous catalysis, redox catalyzes, photocatalysis, sensing, etc.[3–9].

Cd-based Porous Coordination Polymer (PCP) $\{[Cd_2I_2(BDC)_2(INH)_2]\cdot(2DMF)(H_2O)\}_n$, (**1**), has been synthesized from the layering of methanol solution of isoniazid (INH) to DMF-water solution of $CdI_2$ followed by ethanol solution of terephthalic acid ($H_2BDC$) and neutralized with $Et_3N$. Honeycomb (hcb)-type two-dimensional 2D polymeric sheets are polycatenated by π-π stacking and hydrogen bond interaction (Fig. 6). Upon thermal treatment, Complex **1** has been transformed to a robust solvent-free activated state, $[Cd_2I_2(BDC)_2(INH)_2]n$, **1′**, and nitrogen adsorption-desorption analysis has displayed mesoporous channel (~14.7 nm) with a very high specific BET surface area. The compound **1′** is used to sorb iodine. The ease of reversible iodine sorption and desorption with the change from nonpolar to polar solvent has paramount importance for the application of this PCP (Fig. 7)[10].

## Conclusion

The chemistry inside MOFs may be monitored by functionalizing organic units and is known as the post-synthetic modification or by “defect engineering” (which is the removal of some linkers) to generate chemically/physically active pores. Many material properties will depend on imperfections, engineered or not, adding amorphous, or partially amorphous, materials as a flavor to the materials. Metal-Organic Frameworks, or MOFs, have appeared as an extensive class of crystalline materials with ultrahigh porosity (up to 90% free volume) and massive internal surface areas, extending beyond 6000 $m^2/g$. These properties, together with the extraordinary degree of variability for both the organic and inorganic components of their structures, make MOFs of interest for prospective applications in clean energy, most significantly as storage media for green energy gases such as hydrogen and methane, and as high-capacity adsorbents to meet various separation needs.

Additional applications in membranes, thin-film devices, catalysis, and bio-

**Fig. 8.** The structural correlation between house frame and MOF frame.

medical imaging are increasingly gaining importance. On a fundamental level, MOFs epitomize the beauty of chemical structures and the power of combining organic and inorganic chemistry, two disciplines often regarded as disparate. Since the 1990s, this area of chemistry has experienced almost unparalleled growth, as evidenced by not only the sheer number of research papers published but also the ever-expanding scope of the research. One of the hallmarks of MOFs is their topologically diverse and aesthetically pleasing structures, many of which are derived from minerals in nature. O'Keeffe and Yaghi demonstrate such an approach by deconstructing crystal structures of MOFs into their underlying topological nets, thereby laying a foundation for the subsequent description and design of other MOF structures. The frame of a building may be correlated with the framework structure of MOF (Fig. 8).

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**Prof. Chittaranjan Sinha**

Dr. C. Sinha, Professor and Former Head, Department of Chemistry, Jadavpur University, Kolkata started research in Burdwan University on metal assisted C-H activation, coupling (C-N, C-O) reactions; coordination chemistry of arylazoimidazoles, arylazopyrimidines with chemical, electrochemical reactivities. Azoimidazole appended polymers are designed for heavy metal purification, separation. Photochromism of arylazoimidazoles and their metal complexes were explored when he joined Jadavpur University. Photoluminescent molecules are used for sensing of ions and molecules at trace level (nM). Functionalisation of sulfonamide antibiotics and their metal complexes are characterized and biomedical applications are studied. His group is engaged on the design of Coordination polymers/MOFs and their applications in gas absorption, photoconductivity, ion sensing, catalytic reactions, C-C coupling reactions, magnetic measurements etc. So far, he has published 350+ research articles; 46 students awarded Ph.D. degree; Scopus h-index is 42 and citations >6000. Dr. C. Sinha included in the Stanford University's list of the top 2% scientists in the world out of 1494 scientists from India.

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# Polysaccharide based hydrogels in controlled drug delivery applications

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In recent years, polymeric hydrogels received noteworthy attention in the field of biomedical applications[1,2]. The term 'hydrogel' was first reported in 1894 as a colloidal gel of inorganic salts[3]. For the first time, crosslinked polymeric hydrogel derived from poly(vinyl alcohol) was reported[4]. Later in 1960, Wichterle and Lim were introduced as poly(hydroxyethyl methacrylate) based hydrogel that was used in contact lens application (Fig. 1)[5].

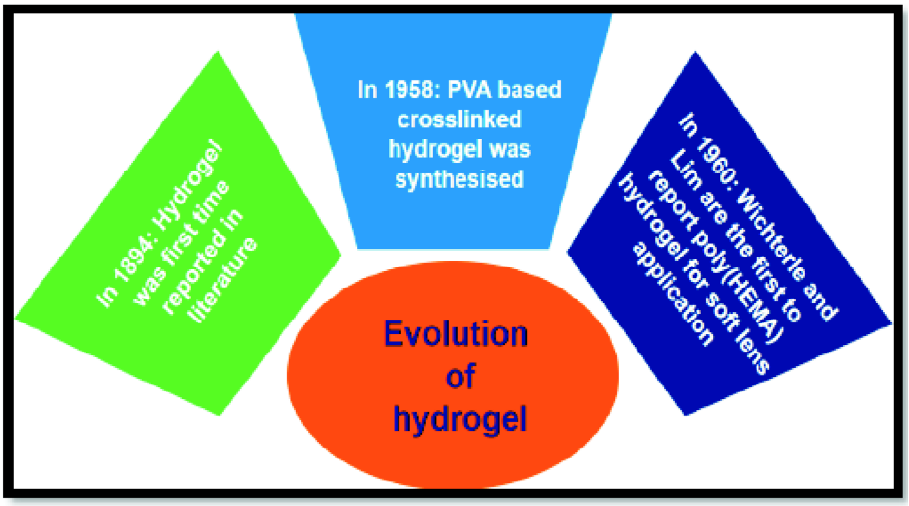

**Fig. 1.** Evolution of hydrogel.

Hydrogels are usually hydrophilic, physically/chemically crosslinked, three-dimensional polymeric networks, which can absorb a large amount of water and get swelled with maintaining their structural integrity[6]. They have found potential applications in diversified fields (Fig. 2).

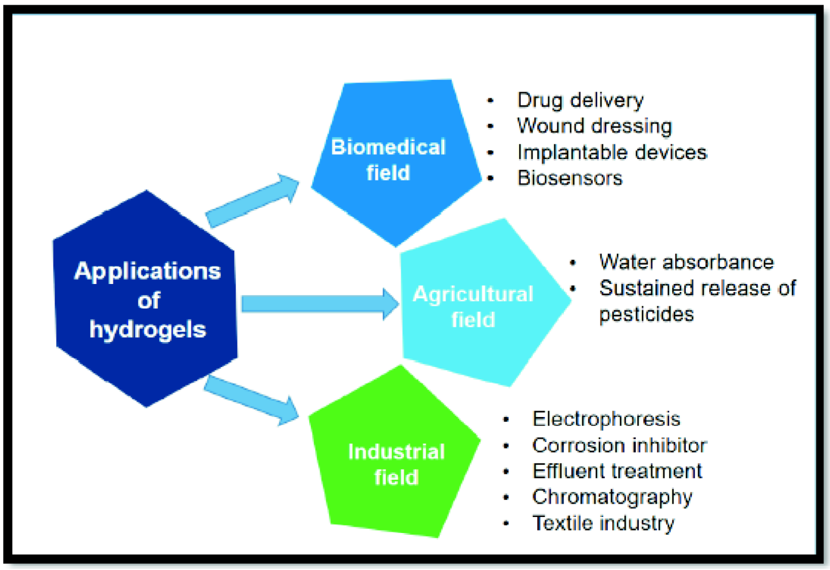

**Fig. 2.** Applications of hydrogels.

Various efforts have been made to synthesize different polymeric hydrogels with several advantageous features like 3-D network morphology, adequate functionality, stimuli-responsive characteristics, excellent mechanical characteristics, enhanced water absorption capability, biocompatibility, and so on. All these properties are vital for a smart device to be used in different fields of biomedical applications, specifically in the field of controlled drug delivery. Although several synthetic polymer-based hydrogels have already been reported as drugs carrier, however, their biodegradability and biocompatibility are of concern for real-life application. In this context, natural polymer-based hydrogels, which are biodegradable, cytocompatible, and non-toxic, are worthy alternatives as matrices for the controlled release of different drugs.

Polysaccharides are considered to be one of the most essential biopolymers obtained from natural resources. The use of natural polysaccharides in controlled drug release applications has increased drastically owing to their inexpensive, easy availability, non-cytotoxic and biodegradable nature[7]. However, in their pristine form, polysaccharides seem incompetent as promising therapeutic carriers, because of their shortcomings: such as low water absorbing capability, water solubility, and limited functionality. The chemical modification of polysaccharides to develop polysaccharide-based hydrogels may lead to an efficient drug carrier with tailor-made properties. There are various techniques to modify natural polysaccharides to develop hydrogels with improved characteristics to a certain standard so that they can be of real importance. However, it is important to remember that for oral administration of drug delivery, safe, noncytotoxic, biocompatible, biodegradable matrices are essential. In this regard, the modified polysaccharides, synthesized via grafting of synthetic hydrophilic polymers on natural polysaccharide backbone, followed by crosslinking are a great choice (Fig. 3). Hence the developed graft copolymeric hydrogels contain a basic

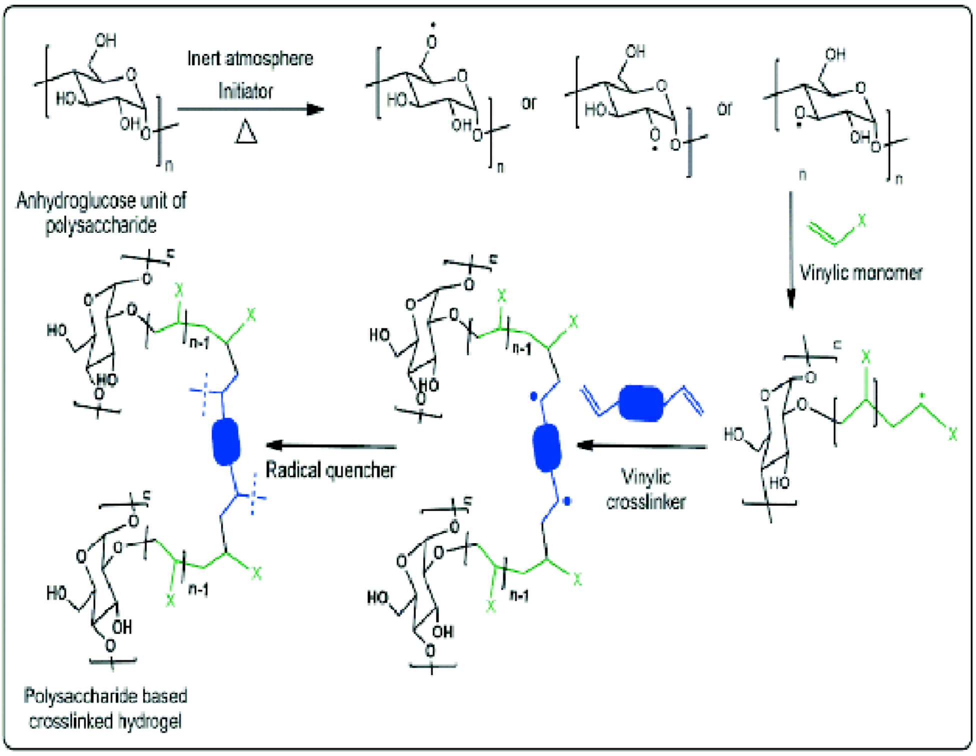

**Fig. 3.** Schematic representation for the preparation of polysaccharide based crosslinked hydrogel.

polysaccharide backbone, which provides biodegradability. Then the grafted hydrophilic polymeric chains increase the hydrophilicity of the entire macromolecule and ensure the enhanced interaction with water. Finally, the chemical crosslinking between the grafted chains provides the desired mechanical strength and also makes the hydrated polymeric material to be insoluble in water. Because of the advantageous properties, the crosslinked copolymers absorb an extensive amount of water and swell to form a gel, when introduced to an aqueous media. Various polysaccharide-based chemically crosslinked hydrogels have been developed in the authors' laboratory[8].

The synthesized polysaccharide-based hydrogels are found to be biocompatible and non-toxic, offer better bioavailability of drugs and demonstrate excellent compatibility between the drug and matrix. Moreover, they reveal sufficient drug stability in tablet formulations, provide unique characteristics like reducing burst release effects and prolonged drug release behavior.

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# An introduction to composite material

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Conservation of the natural resources of our planet has become an issue of prime importance all over the world. Due to rapid urbanization, metal and wood are abundantly use in industry for development of building and household furniture. Metal is limited where as wood is renewable but to grow it requires huge time. For this reason, we are facing scarcity of metal as well as wood (not only used as building material but majorly used in furniture industry, paper industry and several other purposes). Global environmental consciousness induced us to use the other materials which are not metal and wood but have equivalent properties like metal and wood, called composite – a material. Most of the metals are non-biodegradable and they need huge energy for production and process. On the other hand wood collect from tree has a great roll on the ecosystem. In this situation fiber reinforced polymer matrix composite plays great roll as substitute of metal and wood in numerous applications because of its some extraordinary strength properties. Here, a preliminary and easy attempt has been taken for development of different composite materials, there properties, application, merits and demerits as substitute of metal and wood. Due to its high specific stiffness and strength, composite could be an ideal solution of metal and wood which indirectly will save our natural wealth and forest reserves.

Keywords: Metal, wood, material, composite, matrix, reinforcing agent.

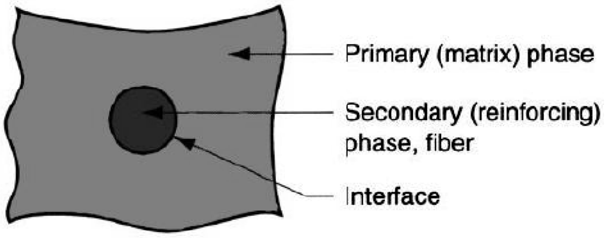
## Introduction

Due to continuous increase in gap between demand and supply of metal and wood, we are passing through a critical state as they are not only limited in this world at the same time play a massive roll in our ecosystem. Due to unbound use of metal for building multistoried housing system, the earth magnetic field pulls upwards and causes massive destructive effect in our health. On the other hand, unplanned cutting of forest in past century leads to increasing global warming and effect on the climate, rainfall as well as on biodiversity. This situation leads to uplift composite as wood and metal substitute. The role of matrix material in a fiber reinforced plastic (FRP) composite is three-fold to transfer stresses between the fibers, to protect the fiber surface from mechanical abrasion along with preventing fiber or fiber dislocation and to provide protection of the reinforcing fiber from the attack of chemical environments[1]. Composite materials are composed of two or more components that differ in physical and chemical properties to provide desirable characteristics. Mechanical characteristics of fiber reinforced polymer composites depend primarily on the mechanical properties of matrix and fiber materials, the surface of the fiber and the nature of the fiber-resin bonding. There is a greater awareness of the need for materials in an expanding world population and increasing affluence. Beside of several synthetic fiber, there are vast supplies of agricultural fibre residues like bagasse, jute, straws, and sisal appear to hold the most promise for continued development[1,2]. In general, lignocellulosic non-wood fibers are a relatively inexpensive alternative to higher quality wood fibers. Composite manufacturing using bagasse furnish is an option for utilization in areas where this material is abundant. Due to its large production of sugarcane and other agronomic crops, Louisiana is an ideal place in the U.S. for development of agro-based composites. Bagasse is a fibrous by-product from sugar cane processing and has been used to produce hardboard (HB) and insulation board[3]. Composites made from agro-fibers are typically somewhat poorer in quality than those made of wood fibers. Surface modification, thermal and chemical treatments can be done to improve comparable mechanical and physical properties to medium density fiber board (MDF)[4]. Laminates, grass board, particle board, plywood, block board molded plastic door car body, airplane body and Kevlar fiber reinforced bullet proof jacket are results of composite material.

### Materials science

Materials science deals with the study of preparation, properties of solid materials and correlation of those properties with a material's composition and structure. It is associated with research and study of the structures and chemical properties of various natural and synthetic composite materials including metals, alloys, rubber, ceramics, semiconductors, polymers and glass. In our everyday life the widely used materials are mainly metal, ceramics, wood, plastic, glass, synthetic fibers and different composites.

**Composite:** Composite materials are made from two or more different component materials when combined together become stronger than those individual components. Simply, composites are a combination of two or more components. Composites are combinations of mainly two materials in which the binding material is called the matrix phase or primary phase which exists in the form of polymer, resin adhesive, ceramics etc. On the other hand second material is called the reinforcing phase or secondary phase which exists in the form of metals, fibers, or particles. These reinforcing agents are normally used in two forms. One is flake or particle or powder or dust form and the other is thin or thick fiber but having thread form. Reinforcing materials are normally strong with low densities while the matrixes are usually ductile or highly viscous. Composites could be natural or synthetic. Wood is a good example of a solid type natural composite, combination of cellulose fiber as reinforcing agent and lignin as matrix. The cellulose fiber provides strength and the lignin is the glue that is the binding matrix and stabilizes the fiber. Bamboo is also a very efficient hollow type composite structure. The components are cellulose and lignin. This result produces material of very light in weight and comparatively stiff structure. The ancient Egyptians and Aryans of Indus valley manufactured composites likes Bricks. Mud, rice husk and straw combination forms a natural composite that is stronger than the component materials which provides strong and beautiful surface finish wall in the housing system in villages. Synthetic composites are made by using matrix materials like thermoplastics or thermosetting polyester like epoxy (80 of reinforced plastics), fluorocarbon, silicon, melamine and phenolic resin with reinforcing agent like glass, graphite, boron, and Kevlar commercially called polymer matrix composites (PMC), fiber reinforced plastics (FRP)[5,6], glass fiber reinforced plas-



Structure of composire

tics (GFRP), graphite reinforced plastics (CFRP). The fibers have high specific strength (strength with respect to weight) and specific stiffness (stiffness strength with respect to weight). Composites obtained from proper designed and fabricated reinforcement with combatable and suitable matrix provides desirable properties, strength and toughness which are not available in any single conventional material.

### Why fiber reinforced composites are important for survive in future?

Due to rapid urbanization, community interest, building development and industrialization consumption of metal and wood causes not only scarcity of those materials but also affects our environment violently. Global environmental consciousness induced us to use the materials like metal and metals products but, most of them are associated with huge energy consumption for production and process. On the earth surface there exists a magnetic field. This magnetic field is important for our health. Metal uses for building purpose as reinforcing agent in concrete pulls the magnetic field upward from earth surface. This situation creates bad effect on our health. At the same time to fulfill the huge demand of wood, deforestation cases a massive environmental disorder. In this situation fiber reinforced polymer matrix composite got considerable attention as substitute of metal and wood in numerous applications because of its some extraordinary strength properties. The superior advantages are comparatively low cost, low weight, less damage to processing equipment or mould, high relative physic-mechanical properties such as flexural modulus, tensile modulus and improved surface finish of molded composite, use of renewable resources, biodegradability, being abundant flexibility during processing, and least health hazards. Composite preparation is associated with utilization of fast growing, renewable fiber resources[7–12] like jute, bamboo, sun hemp, baggase, coir which will generates of employment from plantation to production of biodegradable composites. Due to its high specific stiffness and strength composite could be an ideal substitute of metal and wood which indirectly save our natural wealth and forest reserves.

**Polymer:** A substance which has a molecular structure built up partly or completely from a large number of similar units of same or different monomers bonded together to form macro molecule with high molecular mass. Many natural and synthetic organic, inorganic materials are used as polymer[13–15].

**Difference between macromolecule, polymer and resin:** Macromolecules are large sized single molecules and having high molecular mass. Examples are stearic acid, sodiumdodecylsulphonates (SDS), Tweens, butter etc. Polymer describes the material at a macromolecular level where repeating of huge number of single or more than one monomer units with high molecular mass. So all polymers are macromolecule but all macromolecules are not polymer.

**Filler:** These are solid particles of different size or solid powder used to fill the pores of the reinforcing agent and make a strong bridge between matrix and reinforcing agent. Precipitated silica, $CaCO_3$, marble dust, carbon dust, French chalk, wood fiber and coconut shell flower are used as filler[16] in industry for composite preparation.

**Extender:** These are solid particle of starch or proteinous materials[17,18] soluble in resin adhesive increase mass, volume and viscosity of adhesives as a results lower the glue cost.

**Glue:** All types of polymers, adhesives are low viscous and absorbed through the pores of porous reinforcing agent causing weaker bond. When filler and extender are mixed in definite proportion with polymer and adhesives it helps to increase viscosity to a certain extent called glue. It prevent penetration of matrix through pores improve surface bonding.

**Different polymer used in industries:** Polymer matrixes used in industries are basically two types – (a) aqua based polymer and (b) solvent based polymer. Examples of aqua based polymer are Phenol Formaldehyde (PF), Melamine Formaldehyde (MF), Urea Formaldehyde (UF) resin. The solvent based polymer is Alkyd resin. The well known alkyd resin have commercial name general purpose (GP), Polyester, epoxy etc.

### Phenol formaldehyde (PF) resin (Resol type – High strength and rigid)

**Material:** Phenol:formaldehyde = 1:1.5–1.8 by weight ratio and NaOH solution 50%.

**Procedure:** For the preparation of PF resol type resin we need 180 kg of formalin solution (37% to 40%), 100 kg of liquid phenol (98% to 100%) follow by required amount of NaOH solution 50% to maintain pH 9 to 10 in resin kettle. Stir and raise the temperature slowly up to 60°C. Exothermic reaction raises temperature slowly to 88°C to 90°C. Cook these materials in resin kettle for 45 to 50 minutes at (90±2)°C temperature. Polymeric chain growth is checked through water tolerance test by adding 1 or 2 drops of resin into cold clear water. A milky cloud formation indicates polymeric chain growth occurs. This resin is called resol. Resol is used for preparation of Bakelite, pressure cooker handle, post office box, marin grade ply board, panel and board for thermal and electrical insulator.

### Novoloc type (soft and flexible)

**Material:** Phenol:formaldehyde = 1.5–1.8:1 by weight ratio, NaOH solution 50% and acetic acid solution 35%.

**Procedure:** For the preparation of novolc type resin we need 180 kg of formalin solution (37% to 40%), 100 kg of liquid phenol (98% to 100%) follow by required amount of NaOH solution 50% to maintain pH 9 to 10 in resin kettle. Stir and raise the temperature slowly up to 60°C. Exothermic reaction raises temperature slowly to 88°C to 90°C. Cook these materials in resin kettle for 45 to 50 minutes at (90±2)°C temperature. Polymeric chain growth is checked through water tolerance test by adding 1 or 2 drops of resin into cold clear water. A milky cloud formation indicates polymeric chain growth occurs. This resin is called novoloc. Novoloc is used for preparation of laminates, flexible ply board, flexible panel and flexible board for thermal and electrical insulator.

### Melamine formaldehyde (MF) resin

**Material:** Melamine:formaldehyde = 1:1.5–1.8 and NaOH solution 35% (Maintain pH of reaction 8.5–9 or add borax 1.5% w.r. to melamine).

**Procedure:** For the preparation of MF type resin we need 180 kg of formalin solution (37% to 40%), 100 kg of melamine powder follow by require amount of 50% NaOH solution to maintain pH 9 to 10 in resin kettle. Stir and raise the temperature slowly up to 90°C. Cook in resin kettle for 40 to 45 minutes at (90±2)°C Polymeric chain growth is checked through water tolerance test by adding 1 or 2 drops of resin into cold clear water. A milky cloud formation indicates polymeric chain growth occurs. This resin is called MF resin. MF resin is used for preparation of marin grade ply board and making tray, plate, dishes sculptures, toys etc.

### Urea:formaldehyde (UF) resin

**Material:** Urea:formaldehyde = 1:2.4, 35% acetic acid solution and NaOH solution 35%.

**Procedure:** For the preparation of UF type resin we need 240 kg of formalin solution (37% to 40%), require amount of 35% NaOH solution to maintain pH 9 to

9.5 followed by 90 kg of urea powder in resin kettle. Again check and maintain pH 9 to 9.5 (by adding 35% caustic solution). Stir and raise the temperature slowly up to 90°C. Cook in resin kettle for 90 minutes at (90±2)°C temperature. During this process check and maintain pH 9 to 9.5 (by adding 35% caustic solution) at 10 minutes interval. After 90 minutes cooking maintain pH 4.5 to 5 by adding require amount 35% acetic acid solution. Polymeric chain growth is checked through water tolerance test by adding 1 or 2 drops of resin into cold clear water. A milky cloud formation indicates polymeric chain growth occurs. Again maintain pH 9 to 9.5 (by adding 35% caustic solution). Cool the whole material to 70°C and add rest 10 kg of urea. After 10 minutes, cool it to room temperature.

### Solvent based alkyd resin (GP/polyester/epoxy)

### Alkyd resin

**Material:** Linseed oil:glycerol = 380:200, 1 kg dry Calcium acetate, 50 kg and pthalic anhydride 400 kg.

**Procedure:** For the preparation of alkyd type resin we need linseed oil 380 kg and glycerol 200 kg in a kettle, stir and raise temperature to 180°C. When temperature reaches 180°C add 1 kg dry calcium acetate. Then raise temperature upto 240°C. Cook for 10 minutes. Monoglyceride (MG) formation test can be done by adding 1 ml of polymer into three ml of methanol. A crystal clear solution indicates MG formation is completed. Stop heating, temperature slowly cool downs to 180°C. After reaching temperature 180°C, add maleic anhydride 50 kg and pthalic anhydride 400 kg into the kettle. Again raise temperature up to 200°C. Polymeric chain growth is checked through string formation by taking a small part of prepared material on glass rod and touch on a glass plate. String formation indicates polymeric growth occurs. Start cooling and upto 50°C and add 190 kg [20% of the total mass (950 kg) of alkyd resin] cello solve (2-ethoxy ethanol).

### Different composite materials

**Metal Matrix Composites (MMCs):** MMC composites made from mixture of ceramics and metal or cemented carbides. Examples are: (a) Tungsten carbide: it is used as cutting tools and rock drilling bits. (b) Titanium carbide: it is used as cutting tools and rock drilling bits and in high temperature application like gas-turbine nozzle. (c) Chromium carbide: it is used as gage block, spray nozzle, valve liners.

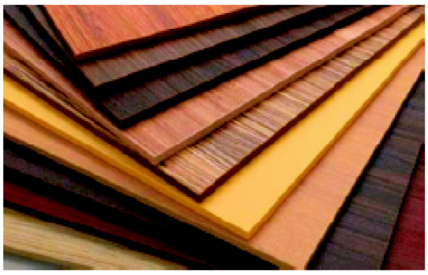
**Ceramic Matrix Composites (CMCs):** CMC composites are made from mixture of ceramics mainly $Al_2O_3$ and SiC and polymer. It is used in high temperature and high voltage applications.

**Fiber reinforced polymer matrix composite (FRP/PMCs):** FRP composites made from different thermoplastic and thermosetting polymers, adhesives as matrix with glass fiber are most common and the least expensive, high strength, low stiffness and high density materials as reinforcing agent. Other abundantly available natural reinforcing agents are Jute, Bamboo, Banana, Baggas, Sanhemp, and synthetic reinforcing agents are Nylon, Dacron, Orlon, Cotton and Asbestos. These materials are used for making light weight composite application. Examples are plastic molding compound, rubber reinforced with carbon black and fiber reinforced plastics (FRPs).

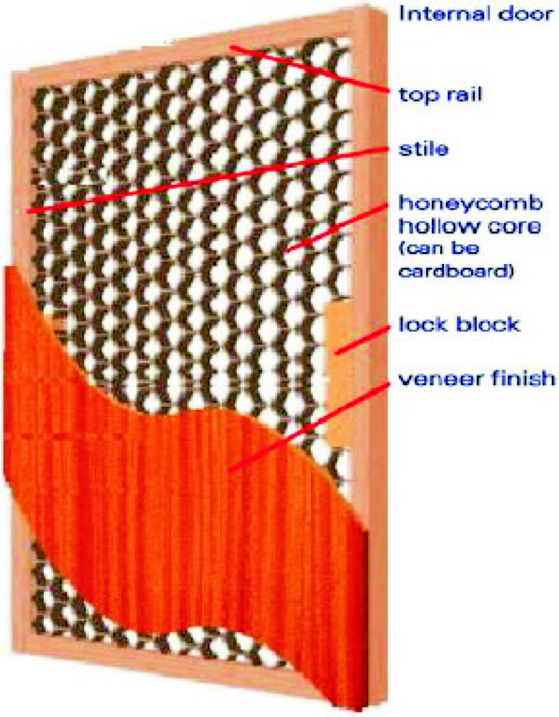
### Different fiber reinforced composites

Fiber reinforced composites are mainly three types: (a) solid core composite (b) hollow core composite and (c) particle board composite.

**Solid core composite:** Whole composite[19] is a solid material. Used as table top. Load bearing floors.



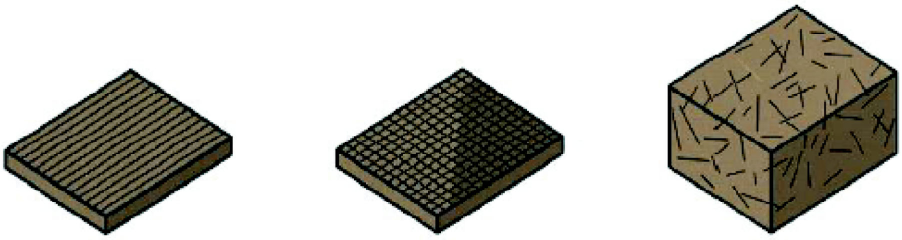
**Hollow core composite:** In this composite[1], a hollow core is sand witched from both side using matrix impregnates fiber. Such composites are light weight material. Used as toilet door, partition wall.



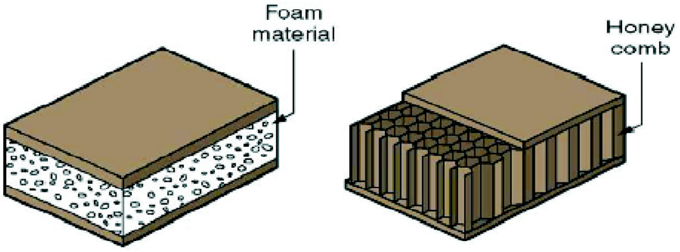
**Particle board composite:** In this composite[1,20] particles are impregnated by resin matrix and then hot pressed of desire thickness. Particle board composite are used for false ceiling and table top.

**Orientation of reinforcing agent in solid core composite:** Four types of orientation of fiber and fiber grain along different direction for the preparation of composite material. The strength properties of composites are very much dependent on this orientation fiber.

- **(a) One dimensional orientation:** Fiber grains of every layer are oriented in a one direction to get the strength of composite in a particular direction and the composite can be rolled in a particular (parallel to fiber grain) direction. Examples are flexi material like flexi ply board, flexible sheet.
- **(b) Two dimensional orientations:** Fiber grains of every layer are oriented in alternate direction to get the strength of composite[20–24] uniform in all direction and the composite cannot be rolled. Examples are normal ply board, roofing sheet.
- **(c) Three or random orientation:** Fiber grains of every layer are oriented haphazardly or randomly along three directions to get uniform and better strength of composite[25–27] in all direction. Examples are load bearing composite bridge, glass fiber reinforced plastic.


(a) (b) (c)

**(4) Hollow core composite:** In this composite, a hollow core is sand witched from both side using matrix impregnates fiber. Three layers sandwich structure for the preparation of thermal and sound insulation composite board.



(b) (c)

**Particle board:** Particle boards are mainly three types: (a) single layer, (b) three layers and (c) laminated particle board.

**Single layer particle board:** Such types of particle boards are made by using uniform size particle as reinforcing agent with matrix. Such type particle boards are used for filling core or gap of costly wood.

**Three layers particle board:** Such types of particle boards are made by using comparatively larger particle at the middle of thick layer and very thin layer on both sides by using smaller sized particle as reinforcing agent with matrix. Surface of such type particle boards are very smooth and used directly as false ceiling.

**Laminated particle board:** Such types of particle boards are made by using design paper or plastic paper on both sides of three layer particle boards. Use as table top, false ceiling, partition wall.

**Properties of composites:** The physical properties of composite materials are mainly test of mechanical properties. These mechanical properties are tensile strength, modulus of rupture (MOR), modulus of elasticity (MOE), abrasion, tear, humidity, impact indentation, nail fixing, water absorption with time, screw withdrawal, swelling in water. The chemical properties are itching test by using acetic acid.

### Applications

Composite prepared from high stiffness fiber reinforcement with high acting resin systems are widely used in house hold as well as in industrial application from a wide range of low cost to expensive purpose. Its application starts from different type of laminates, all items for military including light weight, thermal resistant, composite housing for military and army shelter at high altitude area. It is also used in aerospace industry for commercial aircraft. These materials have also been adopted for use in different kinds of sporting goods, where high-performance equipment such as golf clubs, tennis rackets, fishing poles, and archery equipment, benefits from the light weight high strength offered by advanced materials. It is used in automobiles sectors for preparation of car bodies, false ceiling, car tire etc.

### Advantages

Composites have a higher specific strength (strength-to-weight ratio) than many other materials. A most important advantage of composites over other materials is the ability to use many combinations of matrix and reinforcements with enhanced physic-mechanical properties with tuff, durable, light weight high strength easy to prepare, easy transportable and cost-effective. Most of the composites are acts as electrically and thermal insulator.

### Disadvantages

Composites are used as substitute of metal but some composites are comparatively weak and brittle with respect to metal. Most engineering structural materials are homogeneous. Composites are extremely anisotropic in nature. The strength properties of composites vary with the direction of reinforcing arrangement. Maximum composites are non-biodegradable in nature.

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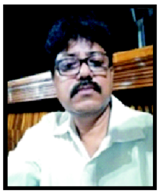

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# Basics of foam-Raman spectroscopic characterization

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Wet foam is a very common example of soft matter. In wet foam, molecules are more structured than in liquids but more random than they are in solids. Recently, the physics of foam has become a rapidly developing branch in science and engineering. A deeper understanding is crucial for many technological applications of wet foam. Hence, in this article, the basic structure and properties of the foam are reviewed based on the literature survey of published research work. Some research works, available in the literature, in which optical probes have been used to study the structure, properties, and dynamics of foam. In this article, wet foam is used to study the basic structure and properties of foam for better understanding. Raman spectroscopy and diffusing wave spectroscopy have been used on wet foam to establish its structure and properties are also reported. Finally, in conclusion, recent scientific, technological, and commercial applications and future prospects of wet foam are proposed to build impulse on the wet foam science more to enrich our day to day life with the modern concepts of nanofoam technology. Recently, due to rapid increase of nanotechnology, different metallic (Cu, Au, Ni, Pt, Pd, etc.) or nonmetallic (Carbon), solvent-assisted nanofoam has modernized the structure, properties of foam science, and hence have accelerated its day to day technological applications.

Keywords: Wet foam, rheology, coarsening, liquid drainage, collapse, Raman spectroscopy, diffusing wave spectroscopy, nanofoam.

## Introduction

Imagine opening a carbonated cold drink bottle or a soda can after shaking it: almost instantaneously, gas bubbles rise and crowd together at the surface of the liquid forming a soft foam. Inside the bottle or can, carbon dioxide is dissolved in liquid at high pressure. Shaking of the container results in the creation of a large number of little bubbles as the agitation unbinds the carbonation from the solution. By opening the container, these gas bubbles rise to the liquid surface to release carbon dioxide into the surrounding air. A similar incident also occurs at the time of washing or shaving with soap. These are the common examples of sort-lasting wet foam. the history of foam can be traced from the publication in 1873 titled *Statique Experimentale et Theorique des Liquides soumis aux seules Forces Moleculaires* by the Belgian physicist Joseph Antoine Ferdinand Plateau[1]. This book summarizes the previous history of foam research and also presents the author's work, which laid the foundation for future studies. Soft foam is a very common example of soft matter (a matter which is neither liquid nor solid, but something in between). In foam, molecules are more structured than in liquids but more random than they are in solids. Foam physics has become a rapidly developing branch in science. This is because the physics of foam is, as yet, ill-understood. Further, a deeper understanding is crucial for many technological applications of foam. There are several models are available in the literature to simulate the bubble growth in foam in two or three dimensions, its bubble size distribution, and most essential properties of foam[2–14]. There are also a lot of experiments with wet foam in the literature to establish its essential properties[15–19]. Recently, carbon nanofoam is one of the lightest solid materials known today, having a density of ~2 mg/cm$^3$. It has an extremely high surface area and is a good electrical insulator. It is fairly transparent, quite brittle, and can withstand very high temperatures. Highly uniform samples of carbon nanofoam from hydrothermal sucrose carbonization were studied by helium ion microscopy (HIM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy[20]. Facile synthesis of Ni nanofoam using aqueous solutions at room temperature is studied for flexible and low-cost non-enzymatic glucose sensing[21]. Once more, hierarchical $NiCo_2O_4$ nanosheets are grown on Ni nanofoam as high performance electrodes for supercapacitors[22]. Cu nanofoams are also fabricated using a simple powder-metallurgy method which is useful for potential energy applications[23.]. Bimetallic Pd/Pt nanostructure deposited on Cu nanofoam substrate by galvanic replacement is also fabricated as an effective electrocatalyst for hydrogen evolution reaction[24]. Gold nanofoams were synthesized in the Deep Eutectic Solvent (DES) with no templates, seeds, or additives[25]. Thus, there is much such foam with different advanced technological applications are reported in recent literature, but this article is focused to study the basic structure and properties of the foam.

### Basic structure of foam

Foam is a two-phase cellular structure either of gas and liquid (liquid foam) or of gas and solid (solid foam). Here, in this article, we shall concentrate only on liquid foam. Liquid foam consists of a collection of gas bubbles surrounded by thin liquid films. A typical microscope image of wet foam (Gillette shaving foam) is shown in Fig. 1. For better stability, some surface-active substances (i.e. surfactants) are used while preparing liquid foam.

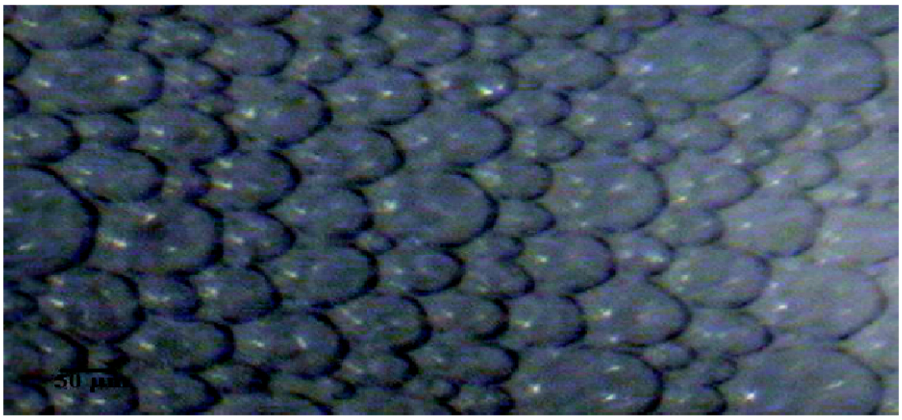

**Fig. 1.** A typical microscope image of Gillette shaving foam.

There are mainly two types of liquid foam depending upon its liquid content: (a) *dry foam* has less liquid and consists of thin films between bubbles. These bubbles take the form of polyhedral cells and have a poly-disperse distribution and (b) *wet foam*, which has high liquid content. All bubbles in the wet foam are spherical in shape and nearly mono-disperse at the initial state. A statistical analysis of bubble size distribution using Gillette shaving foam shows coarsening of bubbles and the change in bubble size distribution in wet foam with aging. It also shows an increase in polydispersity of foam with aging and the growth of larger bubbles at the cost of the smaller bubbles, during aging[17]. In a foamy network, the three liquid films from three nearby bubbles meet to form a scalloped-triangular channel, which is known as the Plateau border. Only four Plateau borders meet at a region shared by four neighboring bubbles making equal angles and this region is known as the vertex. In foam, the Plateau borders and vertices form a continuous network. The law of Plateau defines few rules, which are necessary to obtain an equilibrium configuration of a foamy network. These rules are:

**Rule 1:** For dry foam, three films of three nearby bubbles intersect at a time with an angle of 120° to each other. In two dimensions, this applies to the lines, which define the cell boundaries.

**Rule 2:** For dry foam, four bubbles meet and form asymmetric tetrahedral vertex. The angle between the films is called the Maraldi angle.

**Rule 3:** In wet foam, the Plateau border joins the adjacent films by smooth surfaces.

Typical schematic diagrams of dry and wet foam with the construction of the corresponding Plateau border network are shown in Fig. 2.

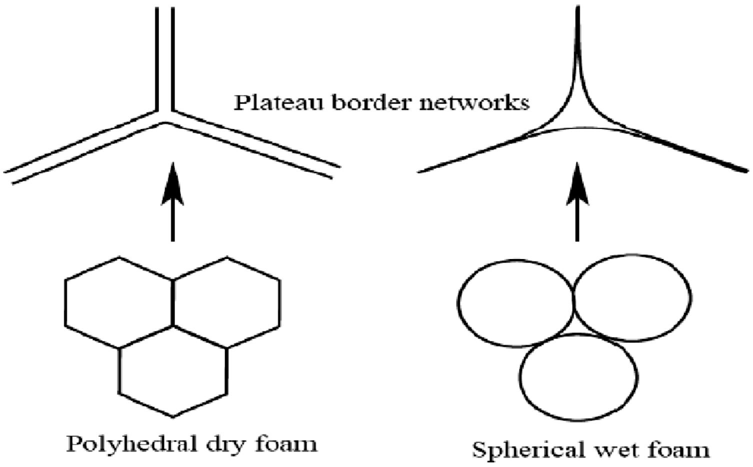

**Fig. 2.** Schematic representations of dry and wet foam with Plateau border network.

In dry foam, the polyhedral bubbles are with slightly curved edges and faces. Any polyhedron (whose closed surface is topologically equivalent to that of a

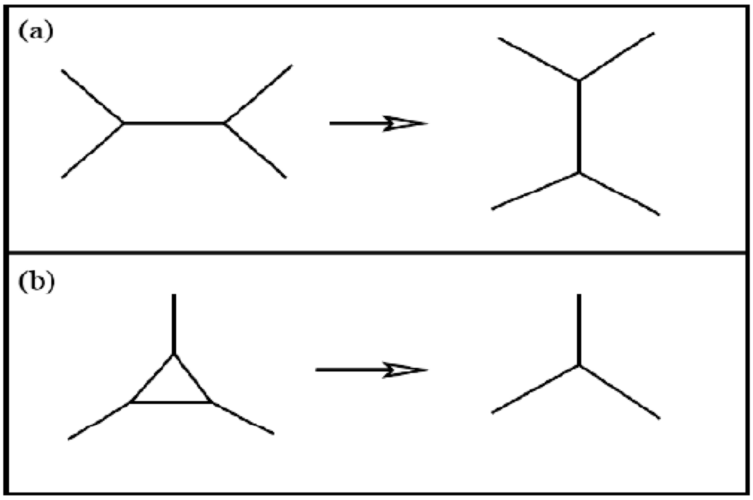

**Fig. 3.** Schematic representations of topological changes in liquid foam via (a) T1 process and (b) T2 process[26].

sphere) in three-dimensional space obeys Euler's theorem, $U - E + F = 2$, where, $U$, $E$, and $F$ are the number of vertices, edges, and faces of the polyhedron, respectively. For dry foam bubbles, the polyhedral geometry is further restricted by Plateau's rules. The coordination numbers of Plateau's laws enforce $2E = 3U$ and therefore, $E = 3F - 6$ follows for any foam polyhedron. In other words, for polyhedra in foam any of the three quantities $U$, $E$, and $F$ determine the other two. The fascinating properties of foam arise from its topological changes via T1 and T2 processes. While in the T1 process, a fourfold vertex dissociates into a stable three-fold vertex (Fig. 3(a)), a three-sided cell may disappear by the T2 process, as shown in Fig. 3(b)[26]. With this introduction to the basic structure of wet foam, its essential properties are discussed in brief below.

## Properties of foam

To study the properties of foam, we have chosen wet foam for easy understanding. In the following sections of this article, the four most essential properties of foam: (i) Rheology, (ii) Coarsening, (iii) Liquid drainage, and (iv) Collapse, are briefly reviewed. A study about the structure and dynamics of wet foam using optical probes is also reported in the following sections.

### Rheology

Foam has unique rheological properties. The mechanical response of liquid foam to an applied force is complex, exhibiting both elastic and viscous character[27]. Under low applied shear stress, foam behaves like an elastic solid. However, with an increase in stress, it becomes progressively plastic; beyond certain yield stress, the foam flows along with topological changes. The flow is intermittent and mediated by non-linear rearrangement events in which several neighboring gas bubbles suddenly hop from one tightly packed configuration to another. Such characteristics of foamy structure strongly depend on the bubble size, liquid fraction, viscosity, and interfacial tension. The schematic stress-strain relation for the liquid foam is shown in Fig. 4. Both two and three-dimensional foam can be accurately simulated using various models[28]. The computer simulation results provide the correlation between the shear modulus and gas/liquid fraction in the tightly packed gas bubbles[29–32]. For example, the model based on bubble-bubble interaction takes into account the pair-wise quadratic potential energies for con-

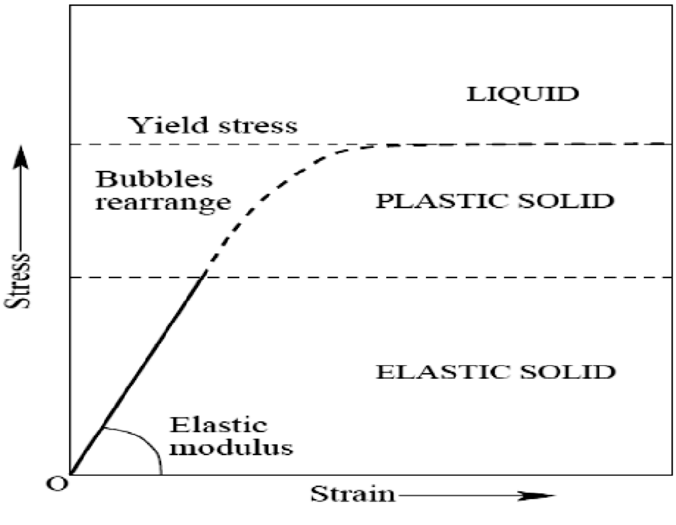

**Fig. 4.** A schematic diagram of the stress-strain relation for liquid foam.

necting bubbles in the low compression limit. The bubble-scale model, proposed by Durian and his co-workers, explains the foam mechanics by solving the equation of motion of the individual disk (two-dimensional projection of spheres) and assuming a harmonic potential for interaction between the bubbles[33,34].

The effect of liquid flow under low shear has been taken into account by including the viscous term. The model provides a connection between the complex macroscopic rheological behavior of foam and its underlying microscopic structure. Other models are also available in the literature, in which, the various aspects of the stress-strain relation have been dealt with[35–39].

### Coarsening

Foams are of broad scientific interest for their ability to fill space efficiently with a random packing of bubbles and for the coarsening of this disordered structure with time. Coarsening is the gradual change of foam structure due to gas diffusion through the films from smaller bubbles to larger bubbles following the well-known Laplace-Young law. This law relates the pressure difference to the mean curvature for a surface in equilibrium. From Laplace-Young law, the balance in pressure difference inside a bubble, $\Delta P$, can be expressed as $\Delta P = \frac{2\alpha}{r}$; where $\alpha$ is the surface tension of liquid film and $r$ is the mean local radius of curvature of the film surface. $r$ is related to the two principal curvatures $r_1$ and $r_2$ as:

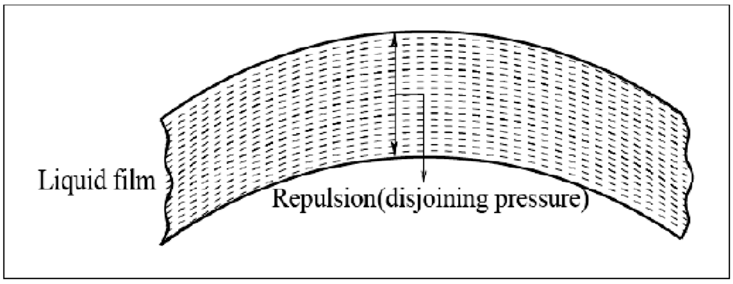

**Fig 5.** The mutual repulsion (disjoining pressure) between the two surfaces of a thin liquid film.

$\frac{2}{r} = \frac{1}{r_1} + \frac{1}{r_2}$. For wet foam, the bubbles are spherical, and hence $r_1 = r_2$. At equilibrium, the Laplace pressure is balanced by the disjoining pressure of the films, which originates from the mutual repulsion between the two surfaces of the thin liquid film (see Fig. 5). In the case of wet foam, the gas diffusion takes place only through the liquid films, not through the Plateau borders[40]. The increase in the average bubble size with time can be obtained from the fact that the rate of change of a bubble's volume is proportional to its surface area and its Laplace pressure difference concerning a certain mean or critical bubble radius $r_c$. Thus,

$$\frac{dr^{d}}{dt} \propto r^{d-1}\left(\frac{1}{r_c} - \frac{1}{r}\right)$$

for any dimension $d$. for $d = 3$,

$$\frac{dr}{dt} \propto \left(\frac{1}{r_c} - \frac{1}{r}\right)$$

Thus, the large bubbles, $r > r_c$, grow in size, whereas the smaller bubbles $r < r_c$ shrink. If $r_a$ be the average bubble radius, then we have

$$\frac{dr_a}{dt} \propto \frac{1}{r_a},$$

which implies that $r_a(t) \sim t^{1/2}$. In general, the time-scale of the evolution of the average bubble radius can be expressed as:

$$r_a \propto (t - t_0)^{1/2}$$

where $t_0$ is an initial constant. For an infinite foam network, the coarsening process has no end. Thus, one can identify the asymptotic scaling behavior of foam with aging. In 1952, von Neumann demonstrated that the time evolution of bubbles in a two-dimensional foam only depends on the number of its sides, $n$, rather than on the size or shape of the bubbles[41]. The rate of change of area, $A_n$, of the $n$-th bubble, is given by von Neumann's law

$$\frac{dA_n}{dt} = \frac{2\pi}{3}\alpha k\,(n - 6)$$

where, $\alpha$ and $k$ is the permeability constant and surface tension for the liquid films. The significance of the above equation for $n = 6$, is that the area of the hexagonal bubbles remains constant until they encounter a topological change. Many models are available in the literature to simulate the bubble growth in foam in two or three dimensions[29,35,42–44].

## Liquid drainage

The liquid between the bubbles can drain out in response to gravity or due to adjacent film rupture to settle into an equilibrium profile. This phenomenon is known as drainage. For fairly dry foams, the liquid is distributed in (a) the flat films that separate two neighboring bubbles, (b) the long Plateau borders, and (c) the scalloped-tetrahedral vertices[45–47]. During drainage, the flow of liquid out of foam is assumed to be confined to the network of Plateau borders and/or vertices and it slows down as equilibrium is approached. Due to the density mismatch between gas and liquid, the bubbles rise and collect at the top and the liquid accumulates at the bottom. The liquid also flows because of the capillary effect, which is related to the gradient of liquid fraction in a column of foam. Such a gradient of liquid fraction implies an existence of a pressure gradient in the liquid foam. Thus, a capillary flow is induced by bringing liquid from high liquid fraction regions to regions with low liquid fraction. Liquid drainage in a column of wet foam has been modeled by a non-linear partial differential drainage equation, which expresses liquid conservation as it flows in response to gravity, capillarity, and viscous forces[47–49]. However, the analytical solutions of the nonlinear equation can only be obtained by ignoring the capillary term. Durian *et al.* designed an experiment, minimizing the capillary effect during drainage, to verify the drainage equation[50]. A generalized drainage equation for the arbitrary shape of the container is also available in Ref.[50]. The complex draining action in a wet foam prompted many experiments in which the drained liquid has been measured as a function of time. In the experiments based on ‘forced drainage’, constant input of external liquid at the top of the foam column maintains a constant flow of liquid throughout the foam. On the other hand, for ‘free drainage’ experiments, no external liquid is added on the top of the foam surface. Free drainage is the unavoidable fate of aqueous foams under earth’s gravity[45,46]. Drainage of liquid in wet foam has been studied using various optical techniques, like absorption or transmission measurements. A detailed review is available in Ref.[51]. Free drainage with slow as well as fast coarsening of gas is a coupled phenomenon in wet foam[51,42]. Despite a thorough endeavor to understand the free drainage process in wet foam, the problem is still not well understood[53].

### Collapse

Usually, most liquid foams do not last for long, as the bubbles collapse by the rupture of the exposed liquid films. Many factors like liquid drainage, coarsening, evaporation, impurities, and additives are responsible for foam collapse. The study of foam collapse has great practical importance because it deals with the stability of the film. Topological change in foam structure due to the bubble growth by film rupturing is less studied in the literature and remains very poorly understood. A crucial feature of liquid foam is that it irreversibly evolves with time. The spherical bubbles in fresh foam take the form of polyhedra while minimizing the energy of the system. The evolution of the bubbles in foam with time can be described by the above four mutually coupled mechanisms.

### Measurement of properties of wet foam with light

The structure and properties of foam have been probed extensively using various optical techniques. Here we mention some of the earlier works, where light has been used to measure the size, wetness, and movement of bubbles and other properties of the foam. Diffusing wave spectroscopy (DWS) is the most commonly used optical tool to study the behavior of foam[54–57]. This technique is an extension of the dynamic light scattering technique for a strongly scattered medium, where the propagation of light is described by the diffusion approximation[58]. The autocorrelation function of the multiple scattering of light is calculated by dividing the photons into separate diffusive paths. The distribution of these paths and the probability that the photon will follow a path of a given length is determined through the diffusion equation of light. The total correlation function is then determined by summing the contributions from all possible paths with weighted probabilities, assuming that each path is uncorrelated with the other path. The fluctuations of the transmitted scattered light result from the variation in total optical path length. The decay of the temporal autocorrelation function of the intensity of the scattered light, which reflects the temporal evolution of the path length, provides the dynamics of the medium. DWS has been extensively used to study bubble size and liquid fraction in wet foam. Using this technique the static transmission coefficient ($T$) of light through the foam of a given thickness has been measured. Diffusion of light is characterized by the transport mean free path, $l^*$, of the transmitted light. It has been shown

$$T \approx \frac{5l^*}{3L}$$

that (Considering the large thickness of the foam, $L$, and no absorption of light by foam). Using this relation, the average bubble diameter $d_a$ can be estimated from the relation $l^* = (3.5\pm0.5)d_a$ [53]. The scaling behavior of the bubble growth, discussed in the above Section-3, has been verified experimentally with the average bubble diameter growing in time as $t^z$, with $z = 0.45\pm0.05$[60]. It is reported that the changes in the packing conditions during the coarsening process give rise to a dynamic process that also exhibits temporal scaling. In Ref.[61], Vera *et al.* used the multiple scattering of light by aqueous foam to study the coupling between drainage and coarsening mechanisms. Other than confirming the fact that the transport mean free path is proportional to the bubble diameter, authors have shown that the liquid fraction in foam is proportional to $\frac{1}{l^*}$. Furthermore, DWS is a potential tool to study the viscoelastic behavior of foam[62]. The technique has also been applied to model foam subjected to shear stress. The observed data reflect the local rearrangement events in the foam[63,64]. Along DWS, various other optical techniques have been used to study the behavior of wet foam. The change in the degree of depolarization of collimated, polarized incident light on non-absorbing foams has been studied by Wong *et al.*[65]. It is observed that the denser media (with a large number of bubbles) tend to depolarize the incident beam more. The degree of depolarization can be correlated to the bubble size distribution in wet foam. Durian and his co-workers used photon channeling experiments to study the absorptivity and liquid fraction in foams[66]. The authors added a dye to the continuous liquid phase for the absorption of diffuse photons in the aqueous foams and studied the absorption mechanisms under different experimental conditions.

### Study wet foam by Raman scattering

In this thesis, we have studied the properties of the soft Gillette shaving foam, using an optical spectroscopic technique, based on Raman scattering. Raman spectroscopy is a powerful noninvasive tool to probe the structure and dynamics of a system at the molecular level. We aim to investigate if this technique can be used to study the effect of aging on molecular structure and to characterize the stability of the wet foam. In addition, Raman scattering is caused by the deformation/stretching of different vibration bonds of molecules. Thus, if macroscopic and macroscopic properties in foam are related, one expects that the analysis of

Raman line profiles can be used to probe the elastic properties of wet foam, indirectly, by studying its molecular behavior. The main hindrance in using Raman spectroscopy to probe wet foam arises due to multiple scattering of light within the bubbles, which masks the Raman signal from the foamy structure, to a large extent. The signal-to-noise ratio in the spectrum is always poor in this case. Thus, in the literature, we do not find too many articles on Raman studies of wet foam. The most significant one is by Goutev and Nickolov[67], where the authors have studied the microstructure of stable three-dimensional foam based on its molecular behavior. Based on Raman measurements of foam, authors have shown that (a) two distinct phases can exist in wet foam a lamellar phase (with an ordered multilayer structure of surfactant molecules) and an isotropic phase, (b) in fresh foam small bilayer lamellae are dispersed in foam films and with aging they self-organize around the bubble in large shell-like bilayer structures. It is to be noted that the quantitative estimates of the structure and properties of liquid foam depend on the liquid fraction and the chemical constituents. However, the generic features are expected to remain the same for all. Since, the other groups have worked on various aspects of foam using Gillette shaving foam as their sample[59,60,64,67], it is preferable to use the same material for further investigation while using a new experimental technique. Therefore, we have chosen the Gillette foam in our work. The basic ingredients of Gillette shaving foam are triethanolamine stearate with a small amount (< 1%) of sodium lauryl sulfate (SLS), Polyethylene glycol glycidyl lauryl ether and emulsified liquid hydrocarbon gases. These ingredients are kept in an aqueous solution under high pressure. The foam is produced after the expansion of the above mixture in the air. It is reproducible and stable over the duration required for optical measurement. For Raman measurements, this commercial foam offers an extra advantage|when laser light is incident on the foam it undergoes multiple scattering. To obtain the optimum Raman signal, the mean free path, $l^*$, [$\cong$ 3.5× average diameter of the bubbles ($d_a$)] of light within the foam should be comparable with the slit-width of the spectrometer collecting the scattered light[68]]. The mean diameter of bubbles in fresh Gillette shaving foam is close to 30 μm and the maximum diameter, which we have studied, is $\approx$ 350 μm|comparable with the slit-width of our spectrometer ($\cong$ 100 μm) in order of magnitude. Below we discuss the basic principle of Raman scattering and also the instrument used by us for the Raman measurements. Different recent researches on wet foam have explained the gross properties of wet foam in light of its characteristic molecular structure using Raman spectroscopy. They have related the observed shift in the low-frequency Raman peak position of the methylene rocking mode with the variation in internal stress in the system. The analysis of Raman data over the range between 1000 $cm^{-1}$ and 1450 $cm^{-1}$ indicates the gradual structural change of wet foam from all-trans conformation to crystalline structure with aging[27]. Drainage of water from wet foam is discussed and in addition to free water molecules, which drain out with the aging of foam, water clusters of only a few water molecules are also present in foam. It is also shown that the correlation between the internal stress and the characteristics of a vibrational mode in wet foam. Thus the capability of the Raman spectroscopy to reveal the crystallinity in foamy materials is established[18,19].

## Conclusion

In conclusion, the basic structure and properties of the wet foam are reviewed in the light of present scientific literature to reveal interesting essential properties of wet foam. The optical probes (especially, Raman spectroscopy and Diffusing wave spectroscopy) used to study the wet foam are also briefly discussed. There are huge applications of solid foam compared to wet foam reported in the literature. Similarly, recent researches suggest that wet foam has also huge possibilities in different technological applications like fire extinguishing, food processing, commercial chemicals and cosmetics, agricultural fields, biomedical fields, environmental safety and toy-making industries, etc.[68–70]. Recently, the higher density foams like carbon nanofoam, however, show an advanced graphitization degree and a stronger $sp^3$-type electronic contribution, related to the inclusion of $sp^3$ connections in their surface network[20]. Again, by employing Ni nanofoam flexible and highly sensitive glucose sensors have been produced on a plastic substrate with excellent performances[21]. A high-performance electrode for supercapacitors is also designed and synthesized by growing electroactive $NiCo_2O_4$ nanosheets on conductive Ni nanofoam[22]. Again, Cu nanofoams are also very much useful for potential energy applications[23]. The gold nanofoams with no capping agents have more catalyst active sites and excellent catalytic efficiency[25]. The main objective of this article is to review the structure and properties of foam to attract more research attention towards foam technology and develop this field for more scientific, technological, and commercial applications for our day-to-day life. Diffusing wave spectroscopy and Raman spectroscopy are quick and non-invasive tools to measure the strain and hence, the stability of a wet foam[18,19], and hence, these spectroscopic techniques can act as an optical probe to study the properties of the foam. Some papers use Gillette shaving foam to study wet foam characteristics. But, the composition of commercial shaving foams (like Gillette foam) is quite complex and its physicochemical properties are ill-defined; it is worth studying the wet foam using simple foamy materials with well-controlled composition, specially made in a laboratory. Further experiments on known surfactants will also indicate if the observed behavior of the wet foam originates from the characteristics of the surfactant itself or its foamy structure[38,71,72]. Furthermore, using the experimental method stated in Ref.[18] at different heights of the column of foam, one can experimentally study the coupling between coarsening and drainage of liquid in wet foam.

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# Crystal engineering: The chemistry behind molecular structure

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Crystals are formed by the aggregation of molecules in solution. This phenomenon encourages several questions. Among them few are, how do these aggregations happen to form crystals? Why do the same molecules adopt more than one crystal structure? Why does solvent occupy some crystal structures? How does crystal structure can be designed with specified coordination of molecules and/or ions with a specified property? What are the relationships between crystal structures and properties, for molecular crystals? At present several queries are being resolved by the crystal engineering community; a larger community constructed by organic, inorganic, and physical chemists, crystallographers, and solid-state scientists. This article provides a brief idea to provide a basic introduction to crystal engineering and this fascinating and important subject that has moved from the fringes into the mainstream of chemistry.

## Introduction

What is Crystal engineering?

The modern definition according to Gautam Desiraju, is “the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties[1]. So it offers a good opportunity the design molecular crystals for a wide variety of physical and chemical purposes. Crystal engineering is quite resembling organic chemistry based on two components, analysis, and synthesis. For designing a crystal and predict the structure experimentation and computation are equally important[2]. Because with the help of experiment, structural information of supramolecular architecture could be obtained by further application of single-crystal X-ray diffraction and computational approach could be helpful to enumerate the interactions for crystal packing in terms of thermodynamically stable product.

The formation of crystals is governed by recognition processes in supramolecular aggregation. Principally it is classified into two main categories; molecular recognition in solution is denoted as supramolecular chemistry and periodic self-assembly in the solid-state as crystal engineering (Fig. 1)[3]. At the supramolecular level, molecular recognition is complementarity; even the functional groups of for same molecules are interacting differently. Hydrogen bonds are formed when an electropositive hydrogen bond donor approaches an electronegative acceptor ($D^{\delta}—H^{\delta+}\cdots A^{\delta-}$), cation···anion electrostatic interaction in salts and metal complexes ($M^+X^-$), and bumps in one part of the molecule fit into hollows of another portion (hydrophobic interactions), and so on. Using the Crystal Engineering approach several types of solids are reported so far, such as co-crystals, polymorphs, individual API, Co-crystal polymorphs, metal-organic frameworks (MOFs)[4], etc. The packing of all the solids can be analyzed by supramolecular synthons.

This article is part of a special issue to celebrate the Education in Chemical Science and Technology in the Annual Convention of Indian Chemical Society. This article aims to provide a brief idea of basic introduction to this fascinating and important subject that has moved from the fringes into the mainstream of chemistry[5]. This article is mainly helpful to the new researchers who are interested to work in this field.

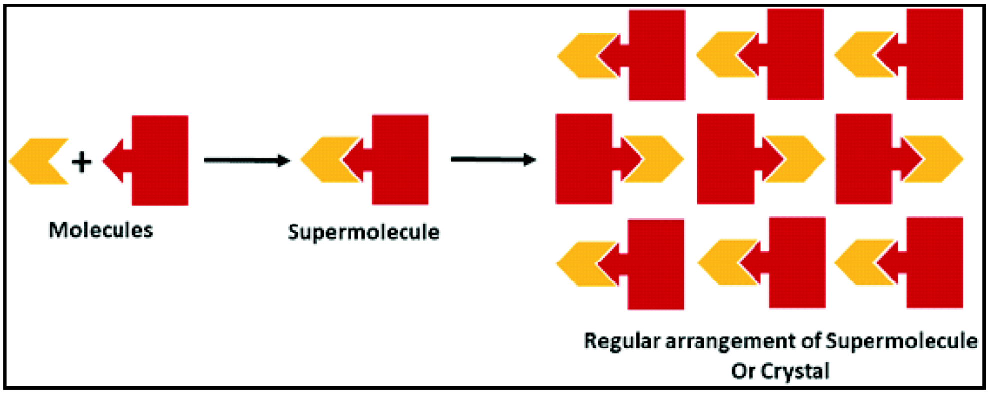

**Fig. 1.** Molecular recognition of molecules to give supermolecule and periodic arrangement of supermolecules in a crystal lattice. Note the complementary shape and bonding feature of interacting molecules[3].

## Intermolecular interactions

The analytical component of crystal engineering consists of studies of the various intermolecular interactions that are responsible for crystal assembly and of the systematic exploration of families of crystal structures that are based on particular interactions of choice. The research on crystal engineering has been expanded by extensive interests like intermolecular interactions which are used in the formation of solid-state structures. Modern crystal engineering originated from the arrangement of molecules in the solid-state and now the subject continues to be motivated by the understanding of intermolecular interactions and their use in trying to control solid-state structures. Among several types of intermolecular interactions hydrogen bonds and coordination bonds are widely studied. Well-known strong hydrogen bonds are N—H···O and O—H···O and are now routinely used for crystal architecture. Weak hydrogen bonds such as C—H···O bonds in crystal structure design are still in their infancy but the early results hold much promise for the future[6]. Another type of bond C—H···$\pi$ interaction is sure of the hydrogen bond type if the donor group is sufficiently acidic[7]. In the same way, C—H···X (X is halogen) hydrogen bonds are significant[8,9]. The energy of different intermolecular interactions is given in Table 1.

**Table 1.** Strength scale of different intermolecular interactions and hydrogen bonds[3]

| Interaction type | Energy (kcal mol$^{-1}$) | Examples |
|---|---|---|
| Very strong H bonds | 15–40 | O—H···O$^-$, F—H··· F$^-$ |
| Strong hydrogen bonds | 5–15 | O—H···O$^-$, N—H··· O$^-$ |
| Weak hydrogen bonds | 1–4 | C—H···O$^-$, O—H···$\pi$ |
| Coordinative bonds | 20–45 | M—N, M—O |
| van der Waals interactions | 0.5–2 | $CH_3$···$CH_3$, $CH_3$···Ph |
| Heteroatom interactions | 1–2 | N···Cl, I···I, Br···Br |
| $\pi$-stacking | 2–10 | Ph···Ph, nucleobases |

## The strategy of synthesis

The best synthetic strategy is the combination of methodology with imagination and perception. There are so many reports seen that describe the use of hydrogen-bonded supramolecular synthons as a primary tool for crystal engineering[10–17]. By using bis-isophthalic acid derivatives as building blocks, some of the supramolecular links were replaced in the parent trimesic acid network with stable intramolecular links[18]. When trimesic acid is linked with 4,4′-bipyridine reveals an expanded hexagonal 2D network[19]. An inventive strategy was used to form a square hydrogen-bonded network structure for 4,4′-sulfonyldiphenol[20]. This is a doubly interpenetrated corrugated two-dimensional structure, contains two hydrogen bond donors and acceptors. Another report on perylene was cocrystallized with electron-deficient species, tetracyanohydroquinone, formed a hydrogen bonded network by optimizing $\pi \cdots \pi$ interactions.[21] Weak $\pi \cdots \pi$ interactions are another type of dominant interaction that can control 3D crystal structure. For supramolecular synthesis, knowledge of both molecular and supramolecular levels is necessary, and increasing complexity at the molecular level can bring with it a high degree of supramolecular specificity. In this context, crystal engineering might not be relaxed as synthetic chemistry to prepare target-molecule. Universally, chemist sees a telescoping of the organo-physical, synthetic and application-oriented branches of crystal engineering in a manner that was unknown and unnecessary in the slower-paced times that witnessed the growth of molecular organic chemistry[22].

### Types of solids

Continuous development has meant that there is considerable encouragement to design solids with very specific physical or chemical properties. Functionalization or various type of solid indicates that investigation of different forms will dominate research efforts shortly and already many reports emphasize the idea of ‘solids with a purpose’[22]. A major type of solids with nonlinear optical (NLO) properties such as second harmonic generation (SHG). Perhydrotriphenylene is known to form channel-type inclusion compounds and many long polarizable molecules have their dipoles parallel rather than antiparallel in the channels of the host material leading to bulk SHG[23].

Crystal engineering also covers the fullerene chemistry domain which is an interesting topochemical metathesis reaction; the bis-adduct of anthracene and $C_{60}$ has been obtained from the mono-adduct. Schmidt imagined this combination of crystal engineering with solid-state topochemical control and opens routes to highly specific fullerenes and, in general, to ‘programmed’ molecular synthesis[24].

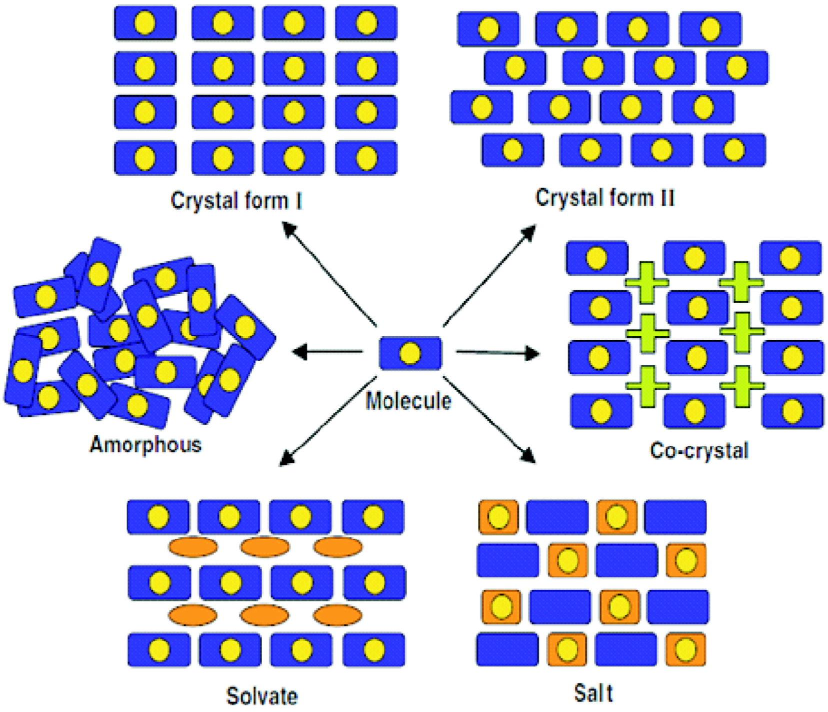

**Fig. 2.** Structural relationship between "true" polymorphs, solvates, co-crystals, salts, and the amorphous phase[31].

Crystal engineering is highly connected with pharmaceutical solids[25] such as co-crystal, polymorph, solvate, etc.

**Co-crystal:** The definition of **co-crystal** has been a topic of debate in recent years. G. R. Desiraju defined it as "multi-component crystals with clearly defined intermolecular interactions, i.e., non-covalent, interactions between the component molecules, be termed "molecular complex"[26]. J. D. Dunitz[27] also agree with that.

Bond suggested that "co-crystals" are composed of multi-component, stoichiometric and neutral molecular species, that themselves each exists as a solid under ambient conditions[28].

Michael J. Zaworotko states pharmaceutical co-crystals, as "co-crystals that are formed between a molecular or ionic API and a co-crystal former that is a solid under ambient conditions”[29].

**Polymorph:** It was first recognized by Mitscherlich[30]. Polymorphs are different crystalline forms of the same pure substance in which molecules have different arrangements and/or different molecular conformation.

**Solvate/hydrate:** If a solvent molecule comes into the crystal structure as one component of a crystal, then the solid is called solvate[31]. When water replaced the solvent molecule in a crystal structure, is called hydrate.

## Conclusions

Behind molecular structure, there is always nice chemistry which is mostly unknown to most people. For example, why is a particular organic molecule consisting of a particular type of packing arrangement? There are a lot of factors that work such as hydrogen bond (both strong and weak), electrostatic interactions, van der Walls forces, $\pi\cdots\pi$ interactions, solvent effect, temperature, etc. So organic chemistry deals with molecule-based but crystal engineering is supermolecule-based. Communications and networks between molecular and supramolecular structures lie at the core of the subject. Such transforms are the most useful of supramolecular synthons to identify the particular form. To predict the crystal structures from molecular structures with or without partial crystallographic information, computational studies are conveniently carried out with programs such as Cerius[32] from Molecular Simulations; from the crystal engineering viewpoint, these approaches are of significance for many materials where structure cannot be obtained from single crystals for X-ray diffraction studies.

The ultimate goal of this article is to provide a piece of knowledge about different types of interactions in crystalline solids and how they work. It is expected from the analysis and synthesis of crystalline supermolecules to lead to new families of designer solids with truly tuneable properties. We might surely expect progress in these related areas soon.

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# Adsorption performance of Indian Neem leave powder for removal of cationic Methylene Blue dye from dying industry effluents: Kinetics and isotherms

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Industrial effluents containing hazardous chemicals and complex metal dyes are highly toxic and carcinogenic. Being toxicological, these dyes not only harm humans, even more, but they also bio-accumulate in wildlife and build hazardous situations in water and thus contaminate the eco-system. Many dyes used in dying industries are stable to light and resistant to aerobic digestion. Thus, the elimination of complex dyes from dyeing industry effluent is a most challenging problem today. To find out a cost-effective and eco-friendly bio-adsorbent have growing demand to save the environment. In this paper Neem leaf powder (NLP) obtained from the local area has been used for the removal of Methylene Blue (MB) dye. The effect of solute concentration, adsorbent amount, contact time, pH, and temperature on the removal of dyes has been observed. It was observed that a higher amount of adsorbent and lower concentrations of dyes favor the higher percentage of adsorption. The applicability of the rearranged Langmuir isotherm model for this adsorption process shows the maximum adsorption capacity of the activated NLP was 188.7 mg/gm. Helfferich first order kinetics and pseudo-second order reaction kinetics has also been fitted to find out the reaction constants for these adsorption process. Results confirmed that Indian NLP has excellent potential as a low-cost adsorbent for the removal of carcinogenic and complex dyes from various industrial wastes.

Keywords: Adsorption, Neem leaf, Methylene Blue, Freundlich isotherm, Langmuir isotherm.

## Introduction

Among the different pollutants of aquatic ecosystems, synthetic dyes are a very important group of industrial chemicals that are used in many industries like paints, pharmaceuticals, paper, leather, cosmetics, plastics, waxes, and especially textile materials[1]. These dyes are highly toxic and carcinogenic and are responsible to harm the skin, liver, kidney, heart, etc. Hence it is recommended to remove these poisonous toxic materials from effluents, before their release to the environment[2]. Several technical processes like coagulation, chemical precipitation, electrochemical degradation, biological stabilization, ion exchange membranes, photo-assisted-biological treatment, membrane filtration, micellar enhanced ultrafiltration, photocatalytic degradation, reverse osmosis, solvent extraction, solar photo-Fenton, biological processes, and sonochemical degradation have been verified and evaluated for dye bearing effluents treatment. Many of these processes are expensive, specific and may need additional care and infrastructure facilities. Adsorption is found to be highly cost-effective among all these treatment processes. Adsorption by activated charcoal and various agricultural wastes has been studied by many researchers. Activated carbon is a good adsorbent due to its high porosity, large surface area, and intrinsic adsorption properties, but it is expensive in contrast to naturally obtained leaves and agriculture wastes. Thus, effective utilization of natural Neem Leaf Powder as a low-cost bioadsorbent for removal of hazardous heavy chemicals and carcinogenic dyes from dying industry effluents and to investigate its adsorption characteristics is a challenging problem to the investigators.

Hardwood, sawdust, and charcoal as adsorbent was used for color removal from textile effluent were tried by various researchers[1,3]. Removal of hexavalent Cr and various dyes by sawdust was performed by Sibonil *et al.*[4], Das *et al.*[5,6], and Mohan *et al.*[7]. Chen *et al.*[8] studied the adsorption of Methylene Blue from aqueous solution using poly(cyclotriphosphazene-co-4,4-sulfonyldiphenol) nanospheres. Bhattacharya *et al.*[9] studied the adsorption performance of NLP for removal of Brilliant Green and Neem sawdust was used by Khattri *et al.*[10] for the elimination of Malachite Green dye from wastewater. Yao *et al.*[11] investigated the adsorption behavior of Methylene Blue on carbon nanotubes. Activated carbon derived from *Borassus aethiopum* flower biomass was used for removal of Malachite Green dye by Nethajia *et al.*[12].

The present study shows the adsorption characteristics of Neem leaf powder (NLP) as a potential adsorbent to remove Methylene Blue (MB) from its aqueous solution. Effect of solute concentration, pH, adsorbent amount, time, and temperature on removal of dye has been investigated. Applicability of Freundlich isotherm and rearranged Langmuir model for this adsorption process has been observed. Special emphasis has also been given to find out the first order and second order reaction rate constants for this sorption process.

## Materials and method

*(a) Materials:*

Neem leaves were collected from the different trees from local areas of the college campus. Methylene Blue (Chemical formula: $C_{16}H_{18}ClN_3S$, mol. wt. 319.85 gm/mol) of analytical grade was purchased from Merck Specialties Pvt. Ltd. (Mumbai). Laboratory grade NaOH (Fisher Scientific, Kolkata) and HCl was used in this experiment.

*(b) Experimental:*

The collected leaves were first washed repeatedly using distilled water to remove the impurities and were then dried at room temperature followed by heating at 80–100°C for 4–6 h till it became crispy. Grounding of these dried leaves was done followed by screening by 120–250 $\mu$m mesh size. Prepared leaves were stored in an airtight glass bottle and kept in the refrigerator. The detailed preparation method of NLP is given in our earlier work[13]. Experiments were carried out using various quantities of adsorbents 3 to 10 gm/L of NLP and MB solution having 10 to 100 mg/L concentration at various pH and temperature. Experiments were done at a constant temperature shaker which was running at 280 r.p.m. for a different contact time of 10–150 min. The percentage removal of dye was determined by spectro-photometrically at the wavelength of 660 nm. The amount of MB adsorption per unit mass of adsorbent, NLP (Q), and the dye removal efficiency (R) may be calculated using eq. (1):

$$R = 100 \times \frac{C_o - C_t}{C_o} \qquad (1)$$

## Results and discussion

*(a) Characterization study:*

In a nutshell, the scanning electron microscopy (SEM) images of NLP revealed the irregular macro-pores with fibrous material. The Energy (electron) Dispersive X-ray analysis (EDX) found that Neem leaf powder consists of carbon, oxygen, and calcium at varied proportions. The results obtained from FTIR spectra of the Neem leaf powder observed the presence of a large number of constituents. The characteristic feature of NLP is discussed in detail in our earlier work[13].

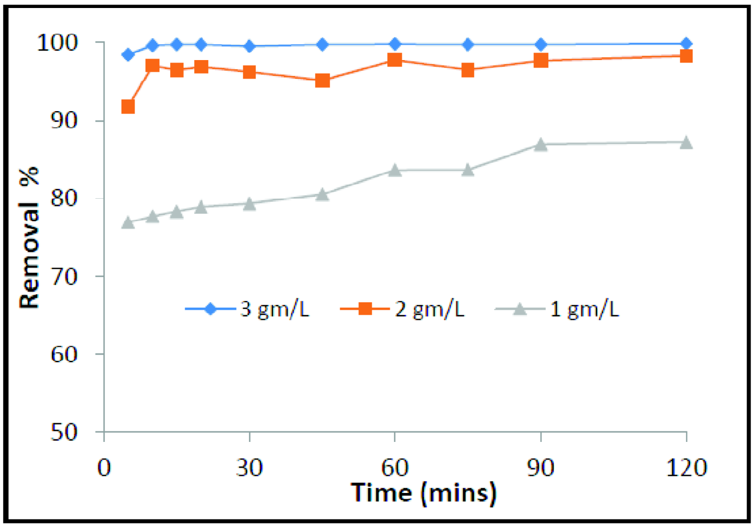

**Fig. 1.** Effect of amount of adsorbent (NLP) on removal of Methylene Blue dye (solute concentration: 20 mg/L, T: 303 K, pH: 7.0).

*(b) Effect of adsorbent amount:*

Fig. 1 shows the effect of adsorbent, NLP amount, and contact time on the removal of MB from its solution having a concentration of 20 mg/L. It was found that the removal of MB increases from 82% to 98% for the change of adsorbent amount from 1 gm/L to 3 gm/L. Results also indicate that this sorption process increases with time and reached equilibrium concentration after 120 min.

*(c) Effect of solute concentration:*

The influence of solute concentration on the removal of MB dye has been depicted in Fig. 2. Results indicate that the removal quantity of dye decreases with an increase in solute concentration. It is seen that with increasing dye concentration dye removal percentage decreases. The reason can be ascribed to the fact

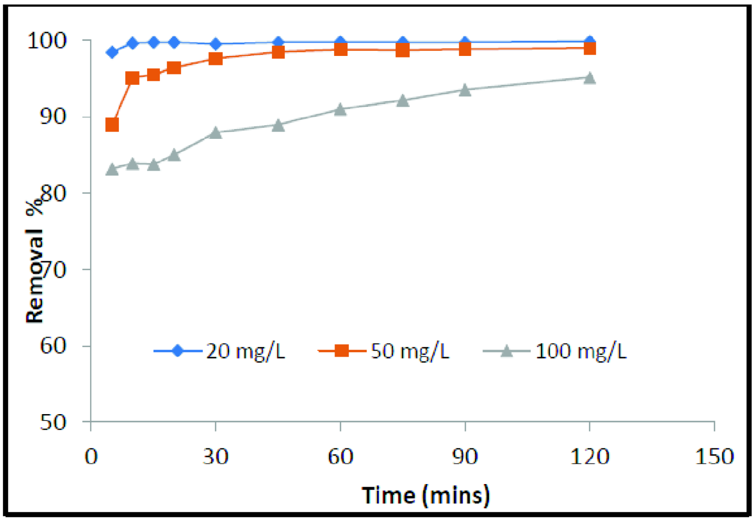

**Fig. 2.** Effect of solution concentration on removal of MB dye (NLP: 3 gm/L, T: 303 K, pH: 7.0).

that at lower dye concentration the ratio of the available surface area of the adsorbent to the moles of solute will be higher. Similar nature of adsorption properties has been reported by other researchers also[1,4].

*(d) Effect of temperature:*

The removal of MB dye was affected by the change of temperature has been shown in Fig. 3. From the experiment, it was noted that with the increase of temperature removal percentage of MB increases. Which indicates that the reaction is endothermic.

*(e) Effect of pH:*

The influence of pH on the removal of MB dye has been described in Fig. 4. It has been seen that at lower at higher pH adsorption increases significantly. The MB removal increases from 65% to 95% for change of pH from 2.9 to 7.0 and 10.2 from the solution containing 50 mg/L MB.

*(f) Studies on regeneration of adsorbent:*

Regeneration is a process to restore, renew or revitalize a substance to it's sources of energy and materials, enabling the recycling of those materials a re-

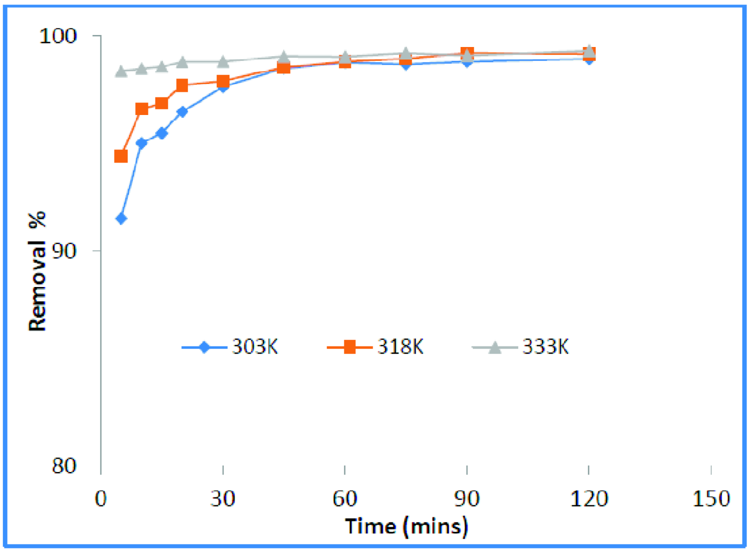

**Fig. 3.** Influence of temperature on removal of Methylene Blue dye (solute: 50 mg/L, NLP: 3 gm/L, T: 303 K, pH: 7.0).

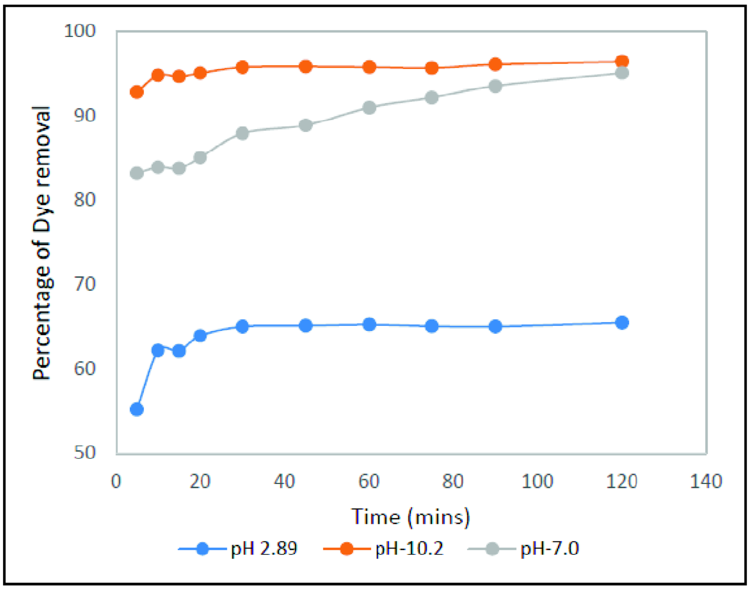

**Fig. 4.** Effect of pH on removal of MB (solute: 50 mg/L, NLP: 3 gm/L, T: 303 K).

peated number of times. In this observation, a regenerative study was conducted in which the dye-stained NLP was collected during various batches of an experiment, which was further boiled with 1 ml of 5 *N* HCl for 10 min, twice. Then the adsorbent was washed using distilled water another 4 times till a clear liquid was obtained. This absorbent was further dried for 2 h in an oven at 70–80°C. The results using regenerated NLP study of MB dye solution is shown in Fig. 5.

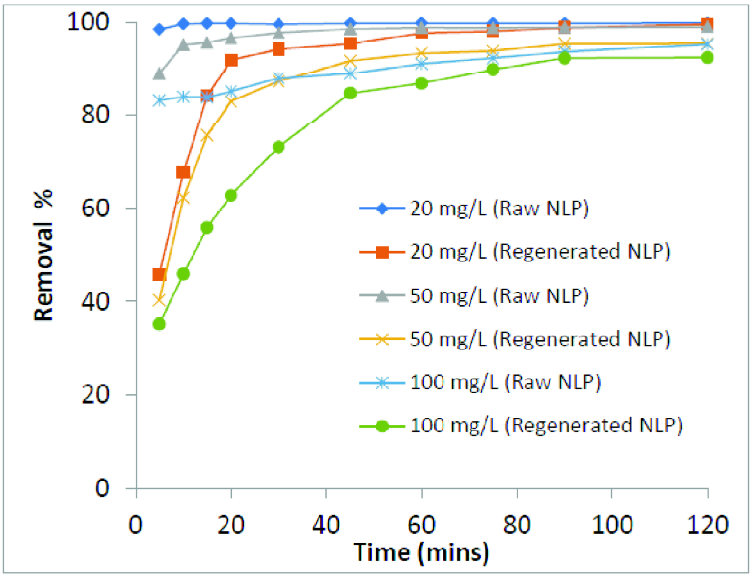

**Fig. 5.** Performance of regenerated NLP for removal of MB dye (NLP: 3 gm/L , T: 303 K, pH: 7.0).

### Adsorption kinetics

The kinetic model for this adsorption process is very important for the removal of dye from industrial effluents or aqueous solutions. Various reversible models may be tested as follows.

Considering MB dye “A” is absorbing from solution on adsorbent “B” NLP, in a reversible reaction

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

If $C_{A0}$ be the initial dye concentration of MB dye in the solution, in moles/liter, $C_A$ as the concentration of MB in the solution at any time " t", in moles /liter, and $C_B$ is the concentration of dye adsorbed on the adsorbent, NLP at a time "t", in moles/liter. If $C_{Aeq}$ and $C_{Beq}$ are the equilibrium concentration of MB in the solution and on the adsorbent, then the rate equation may be written as

$$-\,dC_A/dt = K_1C_A - K_2\,C_B \tag{1}$$

$$K_C = K_1/K_2 = C_{Beq}/C_{Aeq} \tag{2}$$

$$C_B = C_{A0} - C_A \tag{3}$$

From eqs. (1 and 5) the rate equation for the above reaction can be written as

$$-\,dC_A/dt = K_T\,(C_A - K_2/K_T.C_{A0}) \tag{4}$$

where $K_T$ is $(K_1 + K_2)$.

Integrating the eq. (4) with limit $C_{A0}$ to $C_A$ for time "0" to "t" we get

$$\text{In}\,[(C_A - K_2/K_T.C_{A0})/C_{A0}\,(1 - K_2/K_T)] = -\,K_T.t$$

Since, $C_{Beq} = C_{A0} - C_{Aeq}$

So, $\text{In}\,[1 - U(t)] = -\,K_T.t$ (5)

where U(t) is the fractional attainment of equilibrium and is given by $(C_{A0} - C_A)/(C_{A0} - C_{Aeq})$, $K_T$ is the sum of $K_1$ and $K_2$, where $K_1$ and $K_2$ are the rates constant for adsorption and desorption respectively, $K_C$ the equilibrium constant, $C_{Beq}$ and $C_{Aeq}$ are equilibrium concentrations of dye on the adsorbent and in solution respectively in moles/liter.

Helfrich first order kinetics at different dye concentration, Lagergren pseudo-first order, and pseudo-second order reaction kinetics has been presented in Fig. 6 to Fig. 8. Results show that reaction rate constant K decreases with the increase of solution concentration, which also agrees with the experimental observation.

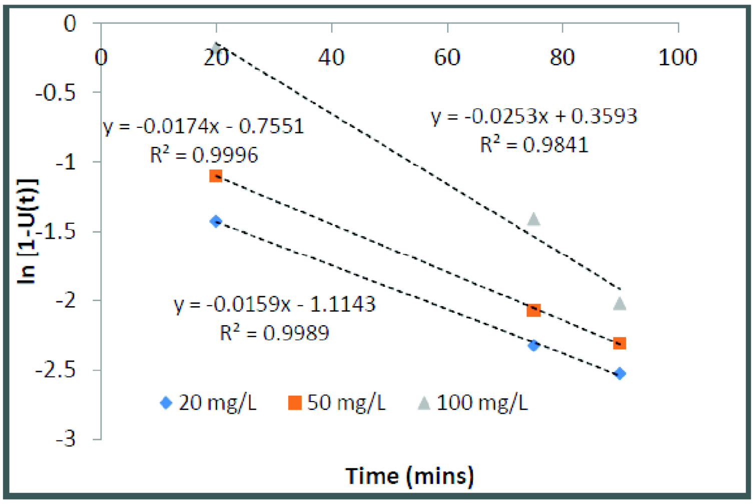

**Fig. 6.** Helfferich first order kinetics for MB dye solution (NLP: 3 gm/L, T: 303 K, pH: 7.0).

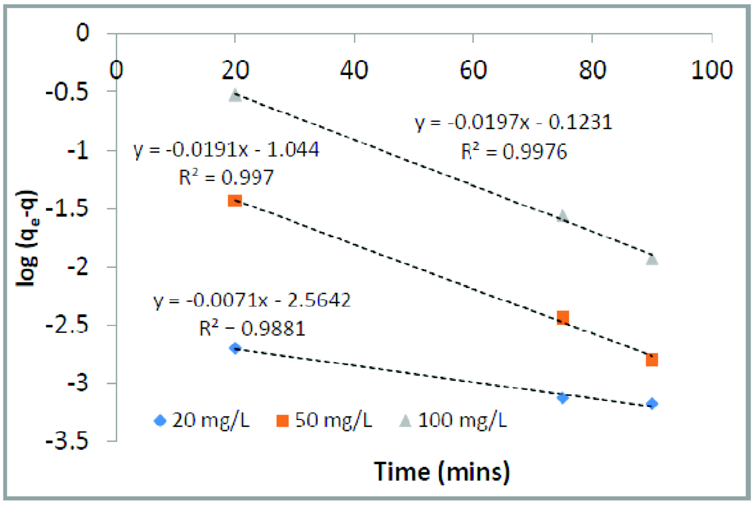

**Fig. 7.** Lagergren pseudo-first order reaction kinetics for various dye solution (NLP: 3 gm/L, T: 303 K, pH: 7.0).

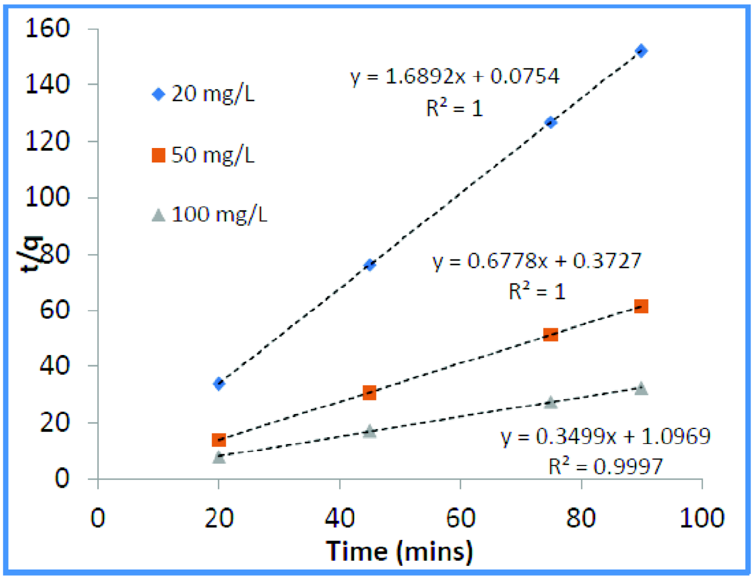

**Fig. 8.** Pseudo-second order reaction kinetics for various dye concentration (NLP: 3 gm/L, T: 303 K, pH: 7.0).

## Adsorption isotherms

*(a) Langmuir isotherm model:*

The results obtained from adsorption of MB with various concentrations using NLP as and correlated with the rearranged Langmuir model of adsorption.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L\, q_m}$$

where $q_e$ is the amount of dye adsorbed per gram of adsorbent at equilibrium (mg/gm), $C_e$ is the equilibrium concentrations (mg/L.) of dye, $K_L$ and $q_m$ are Langmuir constant (L/mg), and maximum adsorption capacity in mg/gm respectively. Fig. 9 indicates the maximum adsorption capacity $q_m$ of the prepared NLP is 188.7 mg/gm and the value of $K_L$ is 0.043 L/mg.

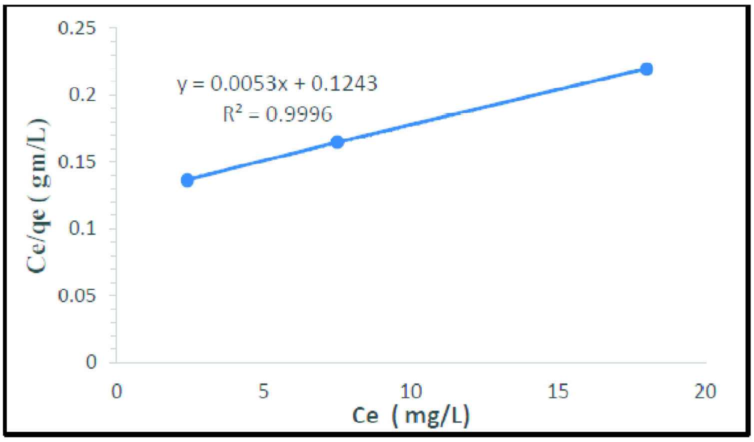

**Fig. 9.** Langmuir isotherm model for MB dye adsorption Using 1 gm/L NLP at 303 K.

## Conclusions

The present study confirmed the potentiality of Indian Neem leaf powder (*A. indica*) as a low-cost bio-adsorbent for the removal of MB dye from aqueous solution or industrial effluents. The maximum adsorption of MB on activated NLP was 188.7 mg/gm and maximum removal of 96% dye may be achieved from 100 mg/L using only 3 gm/L of activated NLP. The adsorbent was characterized by Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Energy Dispersive X-ray (EDX) techniques. The kinetics of adsorption followed second-order rate expression. The linear plot and the satisfactory values of correlation coefficients ($R^2$) suggest the applicability of Langmuir's model for this sorption process. It was found that the process was endothermic in nature and adsorption was favored at a higher temperature. Thus, it can be concluded that NLP has an excellent capacity for waste management by removing various hazardous dyes from industrial effluents.

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# Protein structure, dynamics and stability in alcohols

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## Introduction

Proteins, the most abundant biological polymers of living systems are made of amino acid residues that are connected through peptide bonds (CO–NH). There are four levels of structural organization in proteins namely, primary, secondary, tertiary, and quaternary structure[1] as shown in Fig. 1. The sequence of amino acids in proteins determines its structure and biological function[2]. The primary structure of the protein is the simplest one made up of the linear amino acid sequence, which undergoes twist and turns to form local structural conformations such as, turn, α-helix or β-sheet to develop the secondary structure.

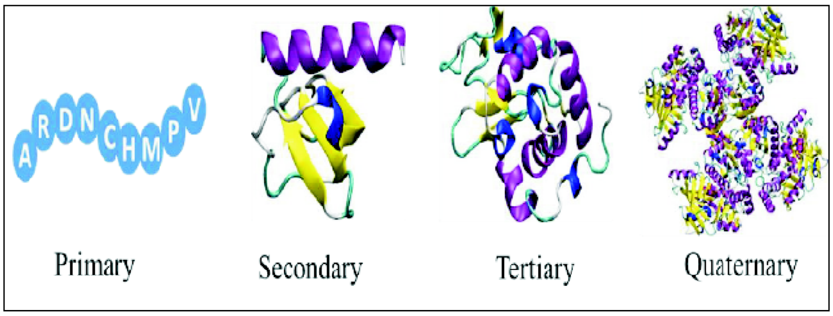

**Fig. 1.** The four levels of structural organization in proteins.

The three-dimensional tertiary structure of protein forms through several non-local interactions such as hydrogen bonds, disulfide bonds, and hydrophobic and ionic interactions. The quaternary structure of a protein is a result of polypeptide subunits associated in a geometrically specific manner. In an aqueous medium, the three-dimensional structure of protein majorly regulates its biological activity. Thus it is necessary to acquire the correct three-dimensional structure to maintain the functional form of a protein. Elucidation of protein structure and dynamics is, therefore, an important and active area of research.

The physical stability of proteins is hampered with the change of environmental conditions such as pressure, temperature, as well as with the solvent's physiochemical properties resulting from the disturbance in balancing the forces between the intra-protein interaction and protein-environment interactions. In such a scenario, the native folded state of protein can attain the denatured/unfolded state (see Fig. 2). In this context, it may be noted that protein denaturation or unfolding is a process where a protein loses its stable native state through disruption of its folded native secondary/tertiary/quaternary structure.

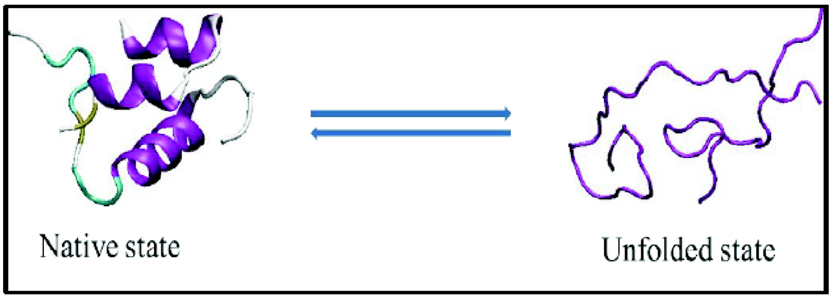

**Fig. 2.** Equilibrium between native conformational state and unfolded state of a protein.

Alcohol, among many, is an important co-solvent. It is amphiphilic and has diverse effects on cellular processes, immune responses, etc.[3–5]. Alcohol-water binary mixtures have been of interest among biologists, physicists, chemists, and engineers due to their relevance in many areas such as the pharmaceutical industry, biofuels, and protein aggregation. It was reported that the water-alcohol binary mixtures disrupt the tertiary structure of proteins whereas it stabilizes protein's secondary structural units[6]. Thus protein dynamics are markedly affected in presence of alcohols in the solution.

### How to determine protein structure and dynamics

Protein's structure and dynamics in solutions can be probed by using several experimental techniques, such as, Fourier Transform Infrared (FTIR) spectroscopy, 2D-IR spectroscopy, Circular Dichroism (CD) spectroscopy, Isothermal Titration Calorimetry (ITC), Differential Scanning Calorimetry (DSC), Gel Filtration, Nuclear Magnetic Resonance (NMR) spectroscopy, Dynamic Light Scattering (DLS)[7–9]. Apart from experimental techniques, computational studies using computer simulation techniques are widely used to probe the microscopic behavior of protein's structure and dynamics in solutions and its detailed motions of individual atoms[10–12].

### Understanding the role of alcohols on protein structure and dynamics

The explicit effect of alcohol on the structure of the protein can be described in two broad ways: (1) the stabilization of secondary structures of the protein, (2) the breaking of compact tertiary structures through destruction of hydrophobic interaction[6,13]. Further, the structure and dynamics of proteins in alcohols depend on several factors (a) the concentrations of alcohols, (b) alkyl chain lengths, (c) substitution and branching in the alcohols[14–19]. The presence of a small amount of alcohol in solution can favor a more compact structure whereas at high concentrations, unfolding of proteins may occur[20]. There can be an appearance of several partially unfolded states depending on the alcohol concentrations, which give rise to the multistage dynamics. It was reported that denaturing potency of alcohol increases with the increase in alkyl chain lengths and decreases with the branching in the alkyl chains. The presence of halogen groups in alcohol promotes the unfolding transition depending on their type and number and generally the effectiveness of alcohols follows the trend: hexafluoroisopropanol > 2,2,2-trifluoroethanol > isopropanol > ethanol > methanol[21,22]. Generally, fluoro alcohol destabilizes the backbone exposure and induces non-native helix formation[23].

A lot of experimental and theoretical studies showed that the aggregation or self-association of alcohols occurs on the protein surface (see Fig. 3)[19,24,25]. The

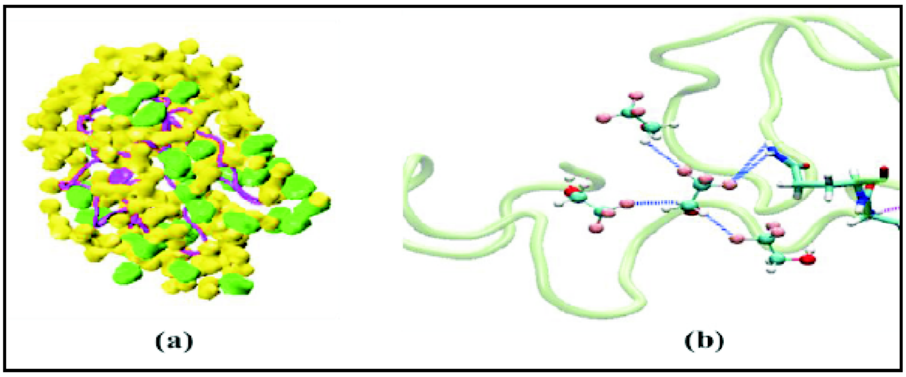

**Fig. 3.** (a) Mixed water (yellow) and alcohol (green) solvation layer[18]; (b) self-aggregation of alcohols in solution and a representative snapshot of protein-alcohol hydrogen bonds[19].

hydration layer of protein in the water-alcohol binary mixture forms a strong water-alcohol mixed solvation layer [see Fig. 3(a)][18]. Further, the formation of alcohol-cluster is one of the important factors for the stability of the secondary structures of protein[26]. The alcohol clusters accommodate a solvent matrix that assists side chain-side chain interactions of proteins, as a result of which the conformational entropy of the side chains decreases which accelerates helix interactions[27]. To maintain the tertiary structure of the protein, intramolecular hydrogen bonding between the side chains is one of the key factors. In presence of alcohol, such hydrogen bonds break down, due to the formation of protein-alcohol hydrogen bonds (see Fig. 3(b)), as a result, the unfolding of proteins takes place[28]. Further, alcohols can destroy the hydrophobic core of the proteins resulting in denaturation[29].

## Summary

Alcohol as a cosolvent plays an important role in the structure and stability of proteins. Alcohol effects are concentration-dependent, which further varied with the substitution, branching, and length of alkyl groups. Alcohols are known to disrupt the tertiary structures of protein. It was reported that the self-association behavior of alcohols slowed down their mobility in the protein surface due to the formation of hydrogen bonds and hence promote denaturation. The mechanistic study on alcohol-protein interactions would be effective to describe several biological processes and therefore it is still an active area of research at present.

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