

Chapter

Recent Developments on the Removal of Antibiotics Using Carbon-Based Nanocomposites: A Mystic Approach in Nanoscience

By Anita Kongor, Mohd Athar, Manoj Vora, Keyur Bhatt, Vinod Jain

Book [Novel Applications of Carbon Based Nano-Materials](#)

Edition	1st Edition
First Published	2022
Imprint	CRC Press
Pages	19
eBook ISBN	9781003183549



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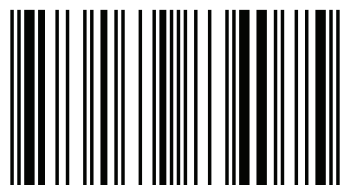
The study explains different methods for isolation & maintenance of yeasts. In addition, methods that can be used to determine probiotic potential are also explained along with necessary formulas. Present study includes isolation of yeasts from local dairy products collected from different dairy shops from across Gujarat, India. The yeast isolates were identified on the basis of biochemical characters (such as ability to ferment different sugars, assimilation of carbon-nitrogen compounds and growth in different conditions) as well as rRNA gene sequence. Yeasts were identified as belonging to genera *Kluyveromyces*, *Saccharomyces* and *Schwanniomyces*. Among yeast isolates, it was found that yeast belonging to *Kluyveromyces* sp. exhibited excellent probiotic potential as compared to *Saccharomyces* sp. and *Schwanniomyces* sp. Probiotic properties that were studied and found appropriate for yeasts from *Kluyveromyces* sp. includes bile tolerance, acid tolerance, cell surface hydrophobicity and certain other characteristics. All the characteristics of yeasts related to probiotic potential were also compared to yeast *Saccharomyces boulardii* which is utilized as probiotic supplement now a days.



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Probiotic Attributes of Yeasts Isolated from Dairy Products



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Chapter - 5

Biocontrol Agent: A Promising Tool towards Sustainable Agriculture

Ushma Joshi, Mrunali Patel, Nehal Rami, Dhvani Patel and Kruti Dave

Abstract

Biocontrol can be defined as the control of the type of living organisms with the application of another. The use of Biocontrol agents are also called biological control and are mainly used for the reduction of pest population and produce yields that are free of any pests. The biocontrol methods are a long-term method and most importantly, a self-sustaining one that helps in the control of invasive species of plants. Nowadays, Plant and Microbes based biological control is considered to be a rapidly developing natural phenomenon in research area with implications for plant yield and food production. They may help to maintain the quality of crops, food and feeds and reduce the undesirable usage of chemical pesticides and toxic chemicals. The present study includes the current progress of biological control by using molecular docking and understanding about the mode of mechanism.

Keywords: Biotic stress, abiotic stress, biocontrol, molecular docking

1. Introduction

1.1 Role of agriculture in India

India has achieved remarkable place in the sector of Agriculture from past 30 years; this has become possible because of number of families of farmers and scientists working in the field of agriculture. This tremendous growth sector is flourishing and contributing Indian agriculture with help of research and analysis of crop, government policies for crop production. Trading and export of agricultural products is a key factor for an economical growth of any region; specifically developing Nation. Export of such agricultural products can effectively balance the economical investment done by any country like India for petroleum products, capital goods and any other product necessary for sustained growth. Agriculture plays very important role in the Indian economy and over 70% of the rural household depends on agriculture, which contributes sixty per cent to the total population and about seventeen per cent to the total GDP [1].

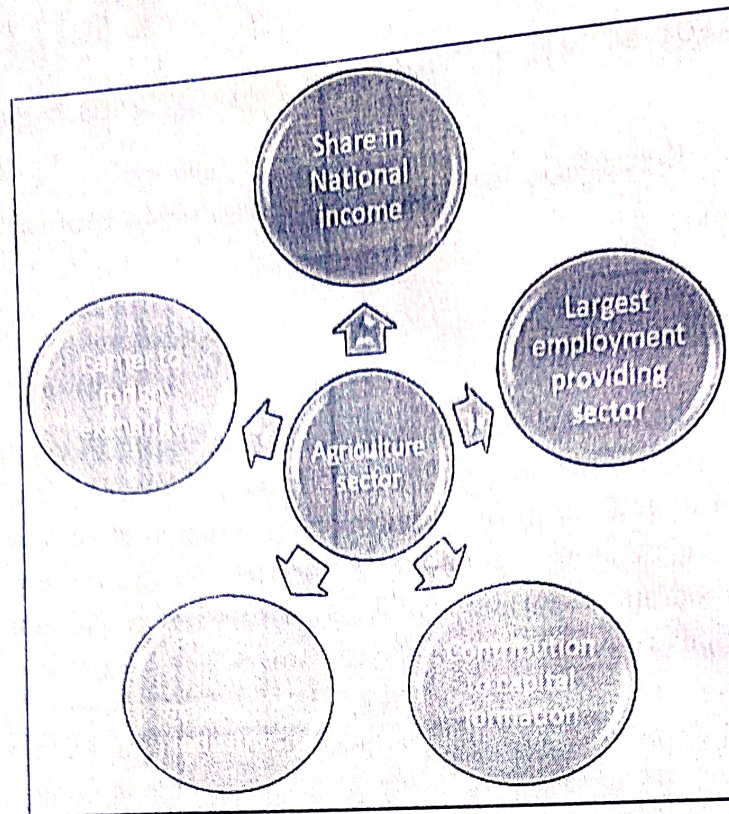


Fig 1: Role of Agriculture in Indian economy

1.2 Problem in agriculture sector

Plant crop during their growth life cycle faces many challenges which cause stress during their growth period. These factor causing plant growth are majorly categorized into biotic stress and Abiotic stress.

1.2.1 Abiotic stress

A variety of environmental factors like Alkalinity, drought, salinity, temperature, pH, nutrient deficiency, high light are the major abiotic factors that affects the plant growth and its metabolic activity. Abiotic stress affects plant via various mechanisms like change in the salt concentration results in decrease of vacuolar and cytosolic volumes, when amount of available free water decreases in soil it causes drought condition in plant system and affects plant growth by disturbing biochemical reactions. Concentration of certain metals like Cu, Zn, Ni, Ag, Mg plays very important role as their unavailability can hinder plant growth as they play role as cofactor in various enzymatic reactions and their excessive amount can have some toxic effect. Difference in temperature can have adverse effect on crop yield; low temperature can have some freezing effect on cytosol of temperate crop and increase in temperature leads to disturbance in plant metabolic activity [2].

1.2.2 Biotic stress

On a global scale, plant diseases have drastic impact on social, economical and ecological impact. Potato late blight and chestnut blight are

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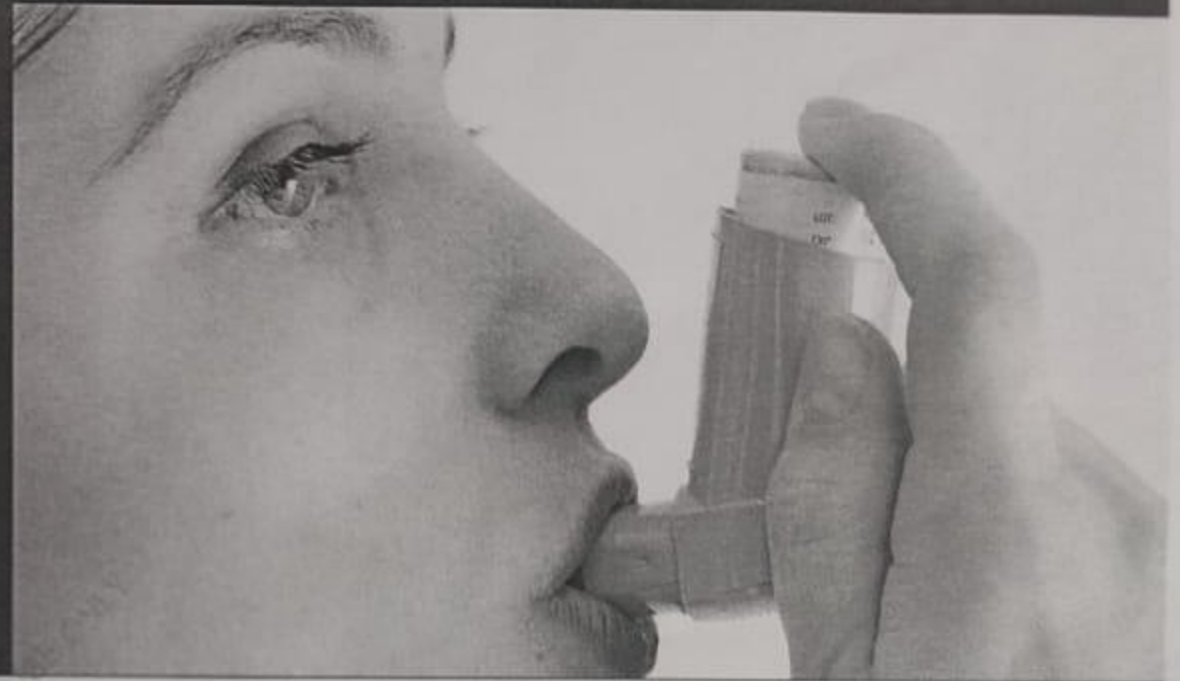
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Dry powder inhalers (DPIs) are the system in which devices used to administrate a dry powder formulation of an active drug is delivered for local or systemic effect via the pulmonary route. DPIs have several advantages over other methods of pulmonary drug delivery, for example, direct delivery of the drug into the deep lungs utilizing the patient's respiration and are increasingly being explored as a mechanism for the delivery of systemic drugs. Successful delivery of drugs into the deep lungs depends on the integration between powder formulations and the device performance. Development requires that current DPIs demonstrate in vitro performance and reliability. However, questions remain about the ability to interchange DPIs and the effects of different clinical states and patient characteristics.



Keyur Bhatt
Mayur Raval



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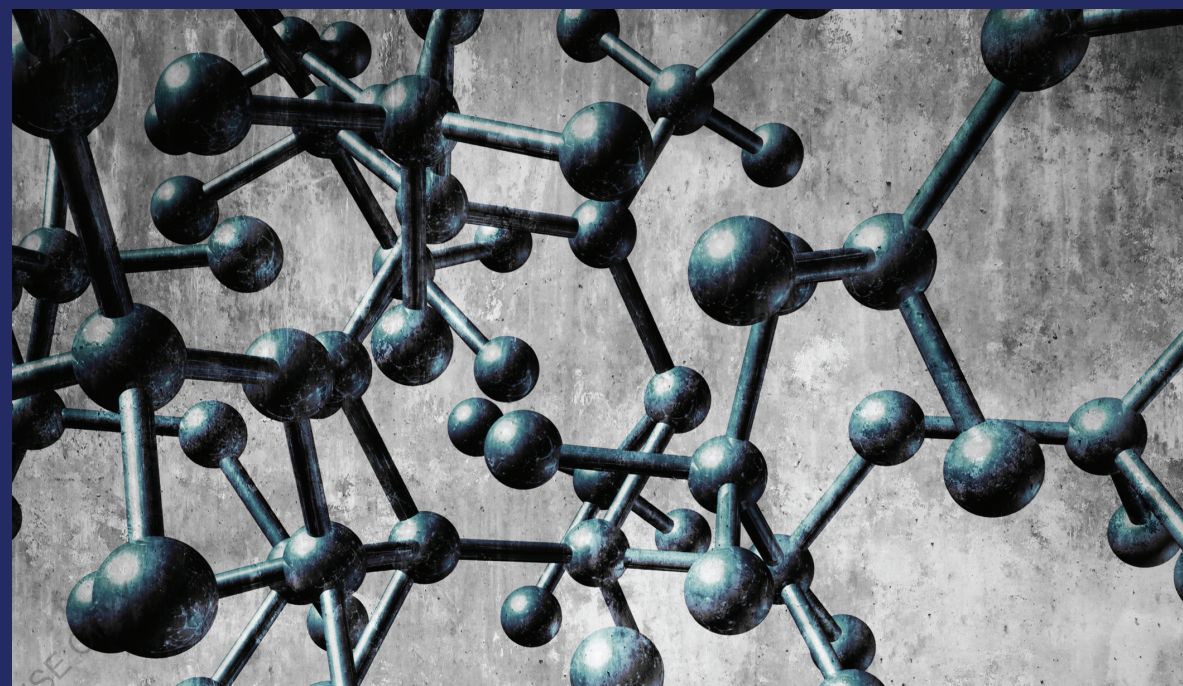


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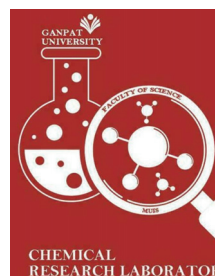
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The writing on calixarene has been extensively looked into. A Elevation in the synthesis and functionalization of calixarene is introduced. Different utilizations of calixarene as fluorescent sensors and nanocatalyst are secured. The aim and scope of the current work is additionally talked about. Macrocyclic chemistry is an exceptionally interdisciplinary field of science that covers the physical, chemical and biological highlights of concoction types of more noteworthy intricacy than particles themselves that are held together and composed by methods for intermolecular (non-covalent) restricting communications



Keyur Bhatt
Nihal Patel
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Chemistry of Macrocyclic Compound and its Applications



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17 Meldrum Street, Beau Bassin 71504, Mauritius

Printed at: see last page

ISBN: 978-620-3-84655-3

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Chemistry of Macrocyclic compounds and its Applications

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Abstract

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Abbreviation

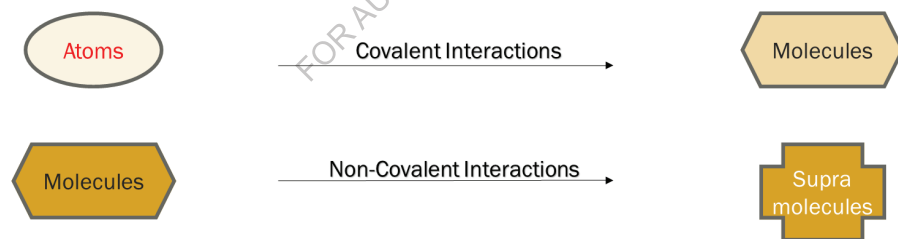
C[4]A	Calix[4]arene
TC[4]A	Thiacalix[4]arene
UV-VIS	Ultra-Violet visible spectroscopy
UV	Ultra-Violet
mp	Melting point
nm	Nanometer
ml	Milliliter
Fig	Figure
TMS	Tetra Methyl Silane
NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared Spectroscopy
TLC	Thin layer chromatography
DMF	N, N'-Dimethyl Formamide
HPLC	High Performance Liquid Chromatography
DMSO	Dimethyl Sulphoxide
ppm	Parts per million
DMF	Dimethyl formamide

1. INTRODUCTION OF SUPRAMOLECULAR CHEMISTRY

This kind of Chemistry has outperformed basic particles and built up its power over non-covalent interaction [1]. It has built up another measurement, whose objective is to pick up predominance over the intermolecular bond. The intricacy (complexity) has expanded past atoms and towards super-molecules and sorted out poly-molecular arrangement in chemistry [2].

Supramolecular chemistry is an exceptionally interdisciplinary field of science that covers the physical, chemical and biological highlights of concoction types of more noteworthy intricacy than particles themselves that are held together and composed by methods for intermolecular (non-covalent) restricting communications. This moderately youthful research region has been characterized, conceptualized, and organized into a rational framework. Supramolecular chemistry is quickly expanding at the boundary of chemical science involving physical and biological events. There has been an excellent development in supramolecular science that has pulled in the consideration of numerous researchers from different fields, for example, chemical and biological science [3]. There have been noteworthy evolution in supramolecular components during the last decade in various fields such as, catalysis, molecular folding, molecular recognition, self-assembly and nano-medicine etc. With such extensive applications researcher recognize that supramolecules are the chemical building blocks of the future. Supramolecular structures are not only additive but also outcome of co-operative interactions, with hydrogen bonding, hydrophobic interaction and co-ordination and their properties are frequently better than some of properties of each individual block.

Supramolecular chemistry is as yet a youthful field, implying that it tends to be somewhat hard to characterize precisely what it envelops – in fact it is a field that has grown quickly because of commitments from an assortment of related fields. Thusly, the subject should be handled from different perspectives. In this book, supramolecular science is grouped into three classes: (I) the science related with an atom perceiving an accomplice particle (sub-atomic acknowledgment science); (ii) the science of atoms worked to explicit shapes; (iii) the science of sub-atomic get together from various particles. This order is profoundly identified with the size of the objective sub-atomic framework. Sub-atomic acknowledgment (Molecular recognition) science for the most part manages the smallest supramolecular frameworks (systems), furthermore, incorporates collaborations between only a couple particles. In contrast, the chemistry of atomic gatherings can incorporate sub-atomic frameworks made from countless quantities of molecules. [4]



A supramolecular assembly possesses amazing structural flexibility and illustrates the binding or a complexation event that takes place between a host and a guest. Supramolecular chemistry includes various types of molecular receptors such as crown ethers, cryptands, spherands, porphyrins, and calixarenes. Supramolecules can be classified by their generation of time scale

as (a) first generation (cyclodextrins) (b) second generation (crown ethers) and (c) third generation (calix[n]arenes). From the different type of supramolecular receptors calixarenes have created raise interest in both applied and fundamental chemistry [5].

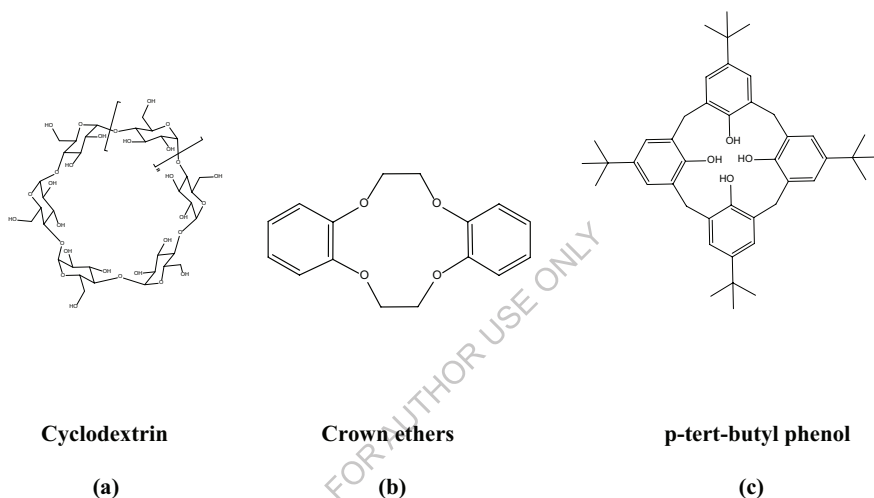


Figure-1 Generation of supra molecules

The non-covalent interactions supporting the two and three-dimensional structure are key challenge as well as very significant in chemical and biological sciences. Supramolecular chemistry “chemistry beyond a molecule” provides one such platform to study the non-covalent interactions of systems, the chemistry of system where molecules are able to self-organize, self-assemble, and self-control into systems. Supramolecular Chemistry has grown significantly in a broad range of fields of research and has been employed in many multidisciplinary applications such as biology, physics, engineering, medicine and chemistry. Over last few years significant

developments in the areas of supramolecular chemistry took place including molecular devices, molecular recognition, catalysis, self-organization, ensembles and nanochemistry. Among these, molecular recognition chemistry aims at the design and synthesis of molecular receptors which are useful to understand and mimic nature's specific interactions towards various guest molecules by non-covalent interactions. For a molecular receptor to be an effective host, molecular scaffold should be easily synthesized undergoing chemical modification with designed recognition behavior.

In addition, there are some phenomena which belong to Supramolecular Chemistry which can be classified into two major categories as below (i) Molecular recognition in solution (lock and key), which generally deals with the smallest supramolecular systems. It is based on the design and the preorganization of supramolecules as well as implementing information storage and processing. Therefore, results in suitable structural and chemical features able to form a selective and strong binding of a guest (molecule or ion) with a host molecule (receptor).

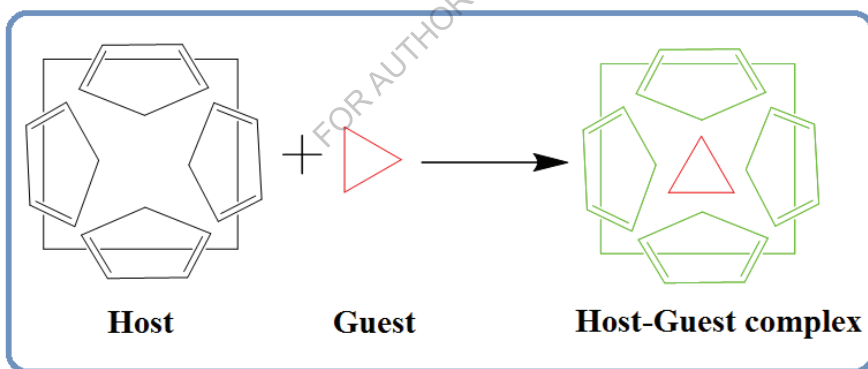
(ii) Organized self-assembly which is a process resulting from the association of two or more components through selection to form diverse and suitable structures (membranes, liquid crystals)

Third generation supramolecular receptor Calixarenes given by C. D. Gutsche in 1978 is a class of cyclic phenolic compound derived from Greek word, '*calix*' meaning *vase* or *cone* shaped conformation Calixarenes with various cavity sizes have been designed in which each of having conformational isomers as well as modified phenolic hydroxyl groups. These structural characteristics allow us to create various structural modifications leading to modified calixarene derivatives. When organic moiety attached is pyrrole, furan, pyridine etc. they are known as **Hetero-calixarenes**. These hetero-calixarenes possess unique supramolecular characteristics

with interesting chemical and physicochemical properties as well as wide applications. Calix[4]pyrrole belongs to the family of hetero-calixarene macrocycles, which phenolic units are replaced with four pyrrole units instead of.

Cram introduced to the term 'host-guest' in 1970. Solid state host-guest chemistry is a subclass of Supramolecular Chemistry where host molecule accommodates small guest molecule via non-covalent interaction. Binding sites of host components converge in the complex while binding sites of the guest component i.e. molecule or ion diverge in complex.

Main focuses in the host-guest chemistry is on the development of synthetic host that binds with a guest as target species via non-covalent interaction as well as the molecular recognition between a synthetic receptor and its substrate leading to the 'host-guest' complex or supramolecule called as "a target species complex"



Host-Guest complexation

4. Different techniques for synthesis of calix

Calix can be synthesized mainly using four techniques:

4.1 One-pot [1+1+1+1] condensation

4.2 [2+2] Condensation

4.3 [3+1] Condensation

4.4 State of the art approach

Among these, one-pot approach is most popular for preparing simple calix[4]pyrrole.

4.1 one-pot [1+1+1+1] condensation

Condensation of pyrrole(s) and ketone(s) in 1:1 ratio in the presence of an acid catalyst is known as one-pot synthesis of calix[4]pyrrole. Hydrochloric acid, methane sulfonic acid, trifluoroacetic acid, and boron trifluoride diethyletherate act as acid catalyst in one pot synthesis. Methanol, ethanol, acetonitrile, and dichloromethane can be used as solvent, but in some reactions ketones itself used act as both reactant as well as solvent for condensation with pyrrole. One-pot condensation can be categorized into two types on basis of pyrroles or ketones are used in the reaction i.e. a) homo-condensation and b) mixed condensation.

4.2 [2+2] Condensation

Acid-catalyzed condensation of two dipyrromethane units in a predictive step from pyrrole and a ketone, with two ketone units (normally different from those used in the synthesis of the dipyrromethanes) refers [2+2] Condensation. This [2+2] approach represents an important means of constructing a variety of calix[4]pyrrole macrocycles, which otherwise cannot be obtained by one-pot condensation.

4.3 [3+1] Condensation

[3+1] Condensation involves the reaction of a tripyrrane or its derivative with a pyrrole or its derivative in the presence of an acid catalyst. Due to the poor stability of most tripyrranes in the presence of an acid, the reaction products are generally obtained in low yield. Infact, no true calix[4]pyrroles have been synthesized using this method.

4.4 State of art approach

Synthesis of calixpyrroles in high yield by an environmentally clean process is of topical interest so as to meet the increasing demand for reducing the pollution hazards caused by the usage of homogeneous acid catalysts. Heterogeneous catalytic synthesis is known to be one of the most effective ways to the selectivity of calixpyrroles with high yield and it has the potential to be scaled up at relatively low cost. The synthesis of calixpyrroles over mesoporous materials, such as MCM-type silica and alumina catalyst has highlighted the future application of these materials for the synthesis of macrocycles. The same author recently prepared porphyrins and calixpyrrole macrocycles using zeolite based molecular sieves catalyzed synthesis in liquid phase under microwave irradiation.

2. Chemistry of Calixarenes

Calixarenes are the third generation of this supramolecular host molecules and among with this three generation calixarenes are simple to synthesize & modified with comparison of crown ethers and cyclodextrins [26]. Calixarenes were grown later than crown ethers and cyclodextrins yet have still been extensively investigated. Calixarenes with different hole (cavity) sizes have been planned, every one of which has conformation isomers, and their phenolic hydroxyl groups are frequently changed. These primary qualities permit us to make calixarene subsidiaries with different structural alterations [4]. Calixarenes which are cyclic oligomers in structure composed

of phenolic (Ph-OH) units related with methylene group and clearly shown conformational properties and cavity that can accommodate different guest species. Calixarenes are synthesized by the base-catalyzed condensation reaction of p-alkylphenols and it can be modified by some functionalization of its upper and lower rime [27, 28]. calixarenes are in this manner known as macro cycles with unlimited prospects that are not contemplated other regular hosts [29]. utilizing these kinds of manufactured parts various calixarene-based receptor have been integrated and their capacities have been used in different manners, for example, in chromatography, sensory, and partition chemistry applications [5]. Further calixarenes are characterized in to two classes one is Heterocalixarenes and second is Heterocalixarenes; In (i) Heterocalixarenes, in which hetero atoms for example, N, S, and O replace the scaffold methylene group; and (ii) Heterocalixarenes, in which heterocyclic moiety , for example, Furan and Pyrroles replace the phenolic group [30].

3. Chemistry of Thiocalixarenes (TCA)

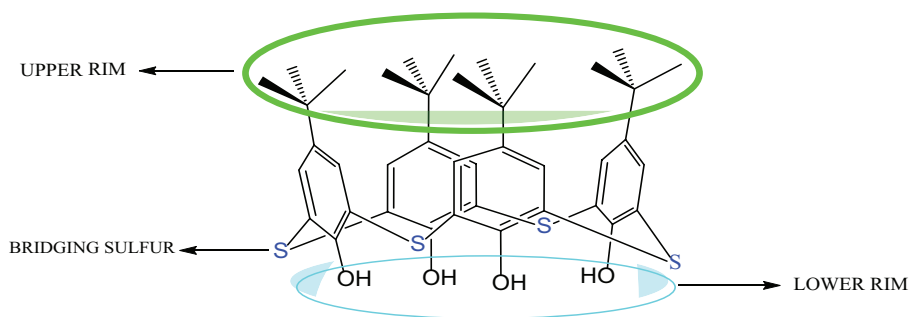


Figure-2 Functionalization of TCA

In Heteracalixarenes, that are less talked about in the substance writing, the carbon linkages between aromatic units are supplanted by heteroatoms [31]. Thiacalixarenes are arranged as heteracalixarene elements since they contain sulfur atoms instead of the typical methylene gatherings [32, 33]. Thiacalix[4]arene (TCA) rose in 1997 as individuals from the heteracalixarene family and have since gotten extensive consideration from the supramolecular network [30]. Miyano et al. [34] revealed a further secondary class of calixarene family, the *p*-tert-butylthiacalix[n]arenes (where, $n = 4, 6, 8$), in which all the methylene scaffolds of the calixarene were relieved by sulfide bonds. Thiacalixarenes have additionally been investigated as atomic stages for fascinating likely applications, for example, the consideration of an assortment of guest molecules, the acknowledgment (recognition) of metal particles, chiral acknowledgment, novel anion receptors and novel dendritic-shelled sub-atomic receptors [35]. Until 2006, different surveys [16] [36] [37] accentuated the amalgamation of upper-edge functionalization, conformational conduct considers and the elements of metal complexation on thiacalix[4]arenes, and numerous extra new perspectives identified with derivatization and application have not been investigated up to this point. Along these lines, we have completely explored the work on thiacalixarenes, focusing in fundamentally on new derivatives and functional groups with applications identified with new examination areas, for example, fluorescence, drug and biochemical applications.

In contrast with the basic qualities of the traditional calix[4]arene moiety, thiacalix[4]arene is progressively alluring because of the accompanying reasons; (1) the size of the ring of thiacalix[4]arene than that of calix[4]arene is 15% bigger due to the more drawn out bond length of carbon-sulfide bridge, when contrasted with Carbon-Carbon(c-c) [38] (2) the ring linkages affiliating sulfur(S) with the phenolic oxygen's may act agreeably after restricting metal particles

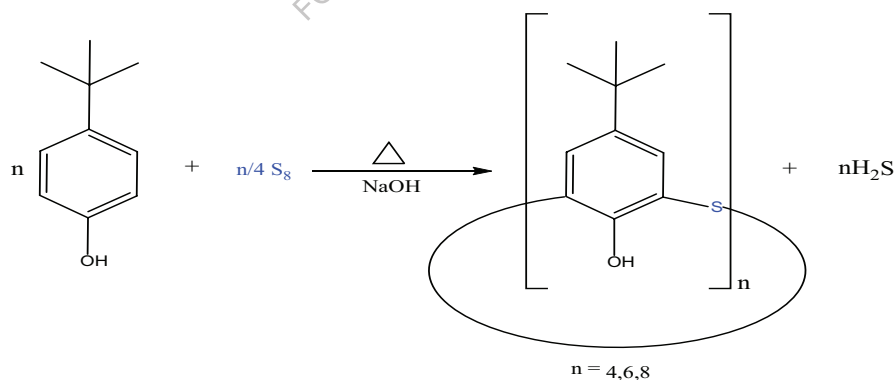
(3) simple change in sulfide bridge by the oxidation to form a sulfoxide and sulfone derivatives can change the properties of cavity form by the structures of calix benzene rings.

3.1 Synthesis of Thiocalixarene (TCA)

Straightforwardness in the procedures of thiocalixarene has encouraged availability to gram-scale amounts of these compounds thiocalix[4]arenes are popular due to their changed cavity sizes and extra binding sites that gave by the nearness of sulfur molecules. Adequate techniques are being created for the derivatization of thiocalixarenes, in which the conformational results become significant.

General method

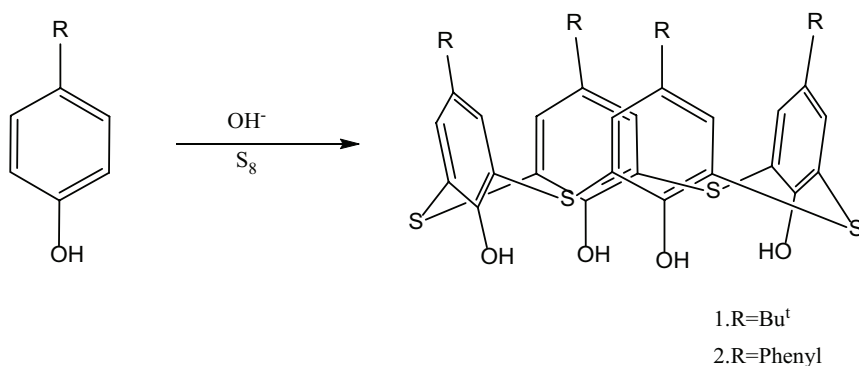
Thiocalixarenes 1 ($n = 4,6,8$) are cyclic oligomers gotten under Basic conditions from p-tert-butylphenol and natural sulfur (S_8), i.e., for the substitution of the methylene scaffold in traditional calixarene by sulfur(S) molecules (Scheme 1).



Scheme-1 General synthesis method of TCA

3.1.1 Single-step method

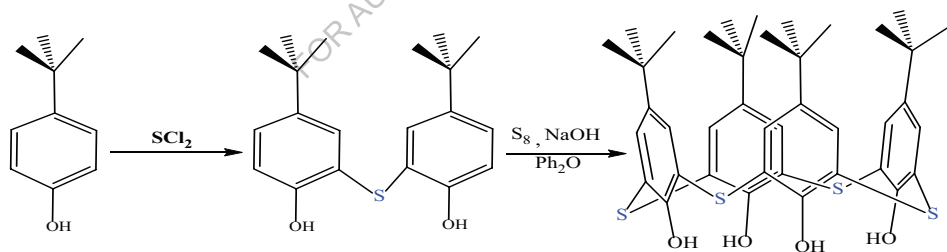
In 1997, **Kumagai et al. [30]** revealed single-step method for the amalgamation of TCA by continuously warming a blended mixture of p-tert-butylphenol (64.5 g, 0.43 mol), elemental sulfur powder (S_8) (27.5g, 0.86mol) and sodium hydroxide (NaOH) pellets in tetra-ethylene glycol dimethyl ether (tetraglyme) as solvent below nitrogen condition to 230°C temp. Over a time of four hours and afterward keeping up this temp. For an extra three hours with concurrent expulsion of the developing hydrogen sulfide (H_2S) by a moderate flow of nitrogen gas. The yield was 54%. Different salt metal hydroxides along with CsOH, NaOH, KOH, and LiOH were inspected as the impetus in the response, among which NaOH gave the best outcome as far as the yield of (1) tert-butylated TCA. This may propose that the sodium cation goes about as a layout for the development of the thiacalix[4]arene (1). **Lahotak et al. [39]** determined another thiacalix[4]arene, called 4,11,17,23-tetraphenyl thiacalix[4]arene (2), utilizing biphenyl-4-ol with sulfur powder (Scheme 2).



Scheme-2 Single-step synthesis method of TCA

3.1.2 Two-step method

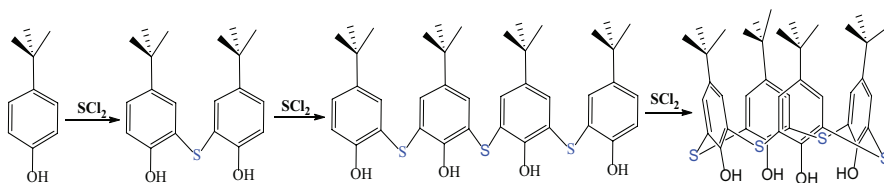
Sotaro et al. proposed a helpful two-step system [40] in which a sulfur-bridged over straight dimer of p-tert-butylphenol is arranged first and utilized as the beginning material for cyclocondensation with sulfur to incredibly improve the yield of TCA (83%). The beginning dimer (3) was acquired in acceptable yield (75%) by treating p-tert-butylphenol with SCl_2 in dry CHCl_3 . The base-catalyzed response was practiced with the beginning direct dimer (3) and sulfur in diphenyl ether utilizing NaOH as the base in a round-bottomed flask furnished with an attractive mix bar. After slow warming of the reactants in a proportion of 1:2:1, separately, to 130 °C Over a time of 2h, then to 170°C for 2 h lastly to 236°C for 3 h, the response blend was portrayed by HPLC to contain a perplexing blend of numerous oligomers of p-tert-butylphenol connected by sulfur, among which were the cyclic oligomers, TC[n]A including n=4,6, and 8 (Scheme 3).



Scheme-3 Two-step synthesis method of TCA

3.1.3 Three-Step method

Sone et al. [41] announced the principal combination of this class of heterocycles in 1993 [42] by means of a stepwise procedure. Analogs of p-tert-butylcalix[4]arene contained sulfide bridge in the spot of the methylene linkages. Be that as it may, p-tert-butylthiacalix[4]arene was gotten in poor yield by cyclization of a straight tetramer [43] with sulfur dichloride (SCl₂) (Scheme 4).



Scheme-4 Three-step synthesis method of TCA

3.2 Conformers of TCA

The thiacalix[n]arene platform as customary calix[n]arene has two edges. The phenolic groups (Ph-OH) containing restricted edge is also known as the 'lower rim', while para-substituents of platform is more extensive segment is known as the 'upper rim'. The four potential adaptations displayed by thiacalix[4]arenes "cone", "partial cone", "1,2-alternate" , "1,3-alternate" as appeared into figure-3 are conceivable from the direction of the phenolic units concerning one another. E. Graf et al. [38] reported the first X-beam structure of tetra-thiacalix[4]arene and confirmed that TCA adopted a cone conformation with actual C₄ symmetry establish by means of a cyclic layout of hydrogen bonding consist of four phenolic units. This X-ray analysis gives information about bond length between bridging group and aromatic residues is 15% more large

than corresponding calix[4]arene is indicating the larger cavity of thiacalix[4]arene as compare to traditional calix[4]arene [32].

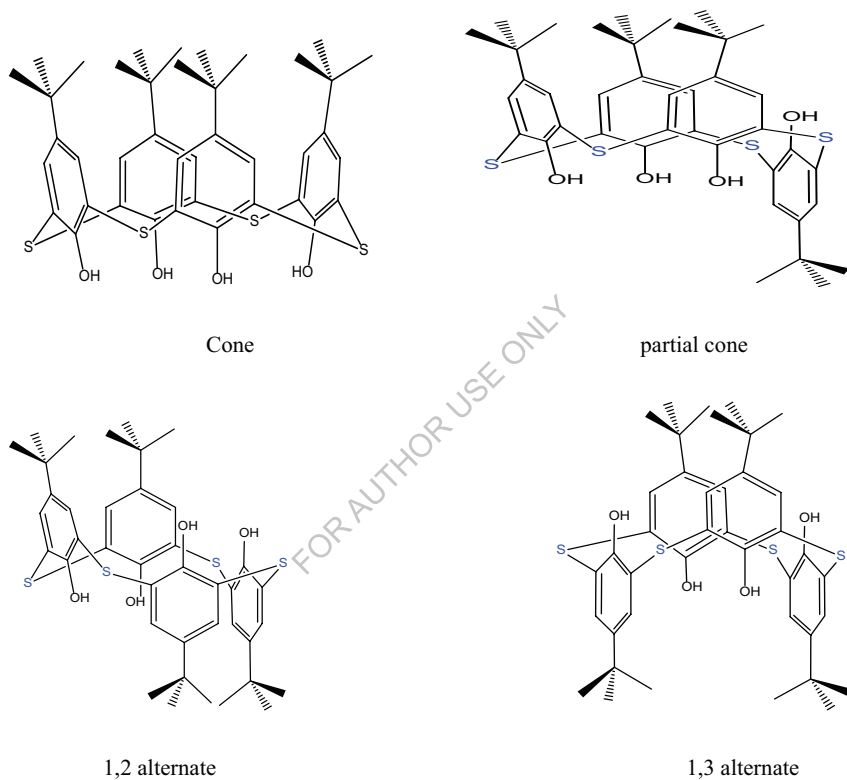
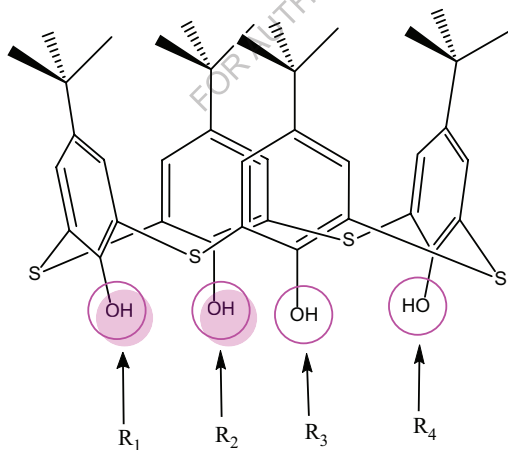


Figure-3 Conformers of TCA

4. Functionalization of TCA

4.1 Lower rim functionalization

For the modification of thiacalixarenes there are wide range of variety in the methods have been reported here to before. For the functionalization of lower rim important method is 'modification of hydroxyl's groups (phenolic hydroxyl groups). Hydroxyl groups are dynamic species and can experience responses with various reagents. With an abundant number of different ether and ester groups thiacalixarenes have been substituted. Different conformers can be discriminated because of incompatible groups are sufficient to prevent interconversion. Normally two types modification in reaction method of thiacalixarenes are undergoes (1) alkylation and (2) esterification.



4.1.1 Alkylation

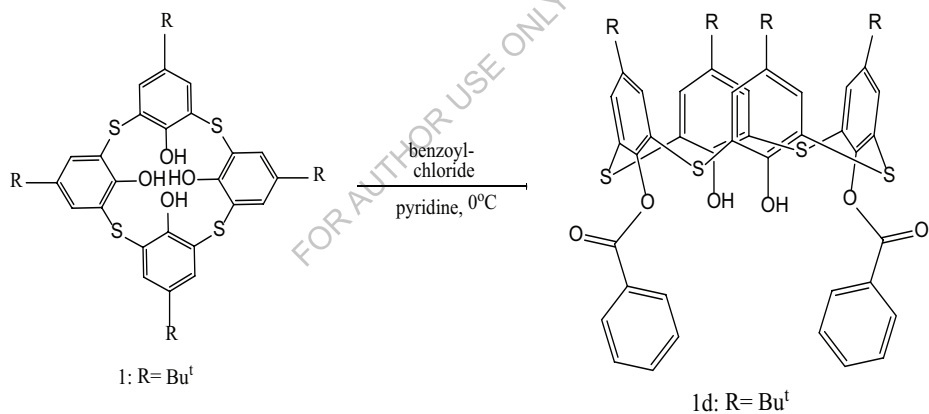
The alkylation with simple halo-alkanes and ethyl bromo-acetate of thiacalix[4]arenes are occurs in presence of various metal carbonates (M_2CO_3 , where $M= K^+, Na^+, Cs^+$) give various products with different conformations like cone, partial-cone, 1,2alternate, 1,3alternate [16]. With the halo-alkanes (RX ; $X=I, Br$; $R=C_2H_5, Me, nPr$ and nBu) alkylation of thiacalix[4]arenes gives production like tetra alkylated and partially alkylated product with the presence of metal carbonates (M_2CO_3 ; $M= K^+, Na^+, Cs^+$). Because of various metal template effect of M_2CO_3 ($M= K^+, Na^+, Cs^+$) Conformer gradation of thiacalix[4]arenes is varied from traditional calix[4]arenes.

4.1.1.1 Alkylation with propyl-iodide: Alkylation of classical calix[4]arene with the propyl iodide in the presence of K_2CO_3 (metal carbonate) in acetone gives partial cone conformation product as main product and 1,3 alternate conformation as side product in small amount. Now, if we change the base and solvent, we get different product conformations. Here, we take NaH (sodium hydride) or KH (potassium hydride) in to DMF , we get cone conformation as main product with them. Now, as compare with product of alkylation of thiacalix[4]arenes with this classical calix[4]arenes product we get different conformations products from classical. The alkylated products of thiacalix[4] with propyl iodide presence K_2CO_3 gives **1a and 2a** in the 1,3-alternate conformation as main product (**scheme1**) [44]. Now, As we show in alkylation of classical calix[4]arenes give cone conformation product with changing of base from K_2CO_3 to NaH or KH in DMF but as for thiacalix[4]arene does not produce the requisite cone conformation. With the use of two step method of dialkylation-dialkylation in high yield of cone conformer of the tetra-alkylated result **1c** of thiacalix[4]arene **2** has been prepared (**scheme 5**) [45]. In any case, the two-advance alkylation didn't work for p-tert-butylthiacalix[4]arene, yet

4.1.2 Acylation

The acylation of thiacalix[4]arene(TCA) at lower rim is not find out as broadly as compare with alkylation of thiacalix[4]arene.

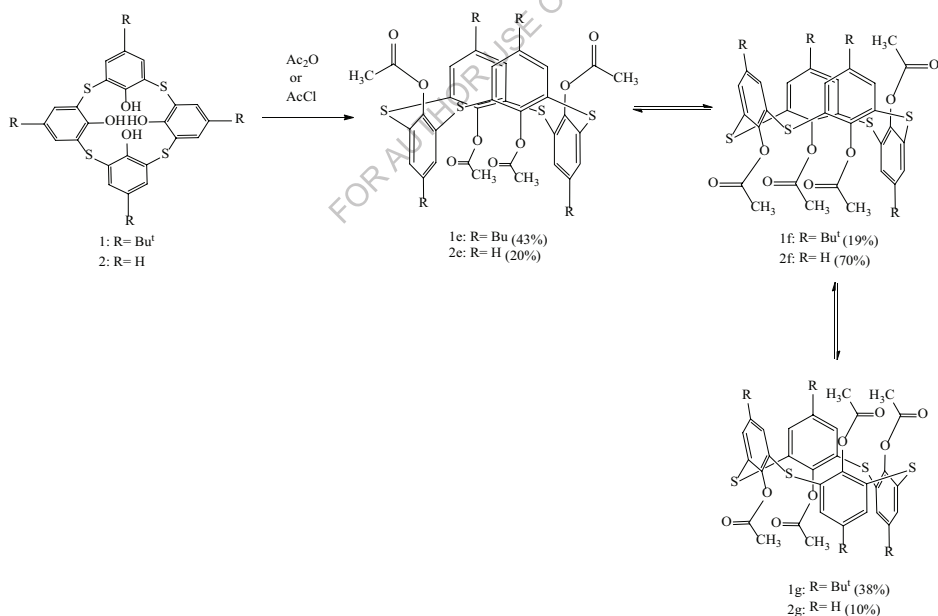
4.1.2.1 Acylation of TCA with benzoyl chloride: Acylation of thiacalix[4]arene with benzoyl chloride in pyridine presence at 0°C is given di-benzoylated derivative(39% yield) (**scheme 6**) [46].



Scheme-6 Acylation of TCA with benzoyl chloride.

4.1.2.1 Acylation of TCA with acetyl Chloride (CH_3COCl) or acetic anhydride (CH_3CO) $_2\text{O}$:

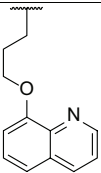
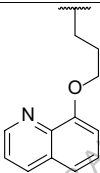
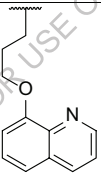
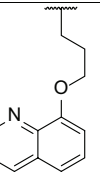
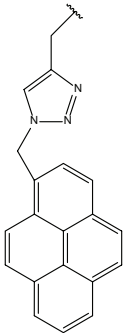
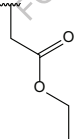
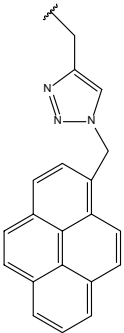
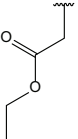
Acylation of thiacalix[4]arene with acetyl chloride gives tetra-acetoxy derivatives with functional conduct of various conformation at room temperature (**scheme 7**) [47]. And upper-rim substitution is responsible for this different type of conformations. Now, acetylation of p-tert-butylthiacalix[4]arene with acetyl chloride gives 1,3-alternate conformations **1e** (43%) and 1,2-alternate conformation **1g** (38%) of tetra-acetoxy derivatives as main products. But in other case when unsubstituted thiacalix[4]arene **2** gives partial cone conformation **2f** (70%) as main product. This type of concern between conformation selection and upper rim substitution is not establish in normal acylation of classical calixarenes and it gives static lower-rim of tetra-acetoxy derivatives with compare to thiacalix[4]arenes [48].

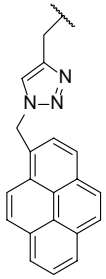
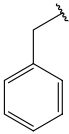
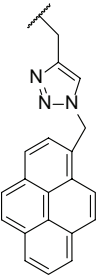
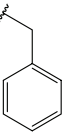
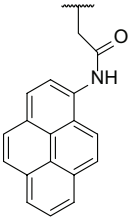
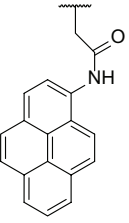
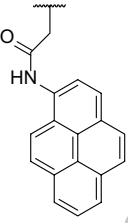
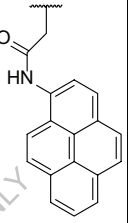
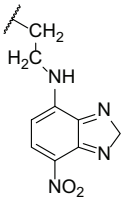
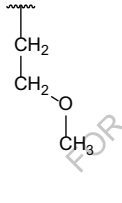
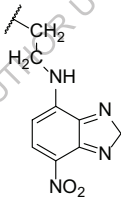
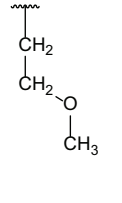
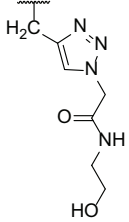
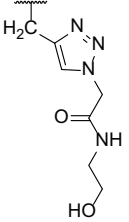
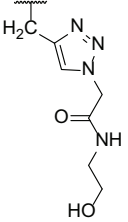
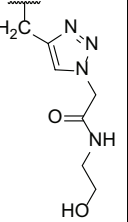


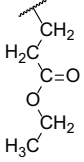
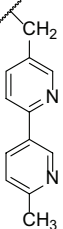
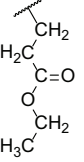
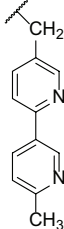
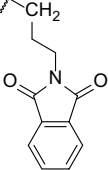
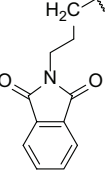
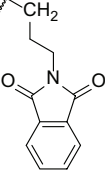
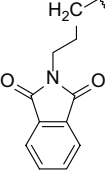
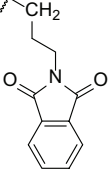
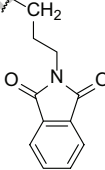




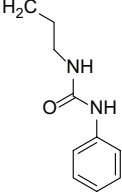
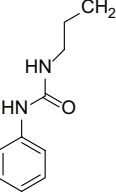
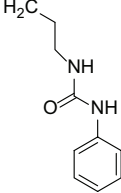
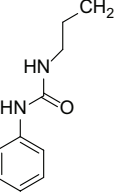
Scheme-7 Acylation of TCA with Acetyl Chloride.

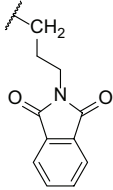
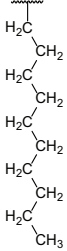
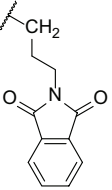
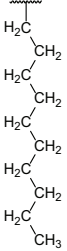
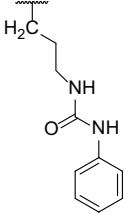
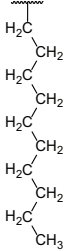
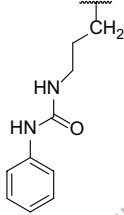
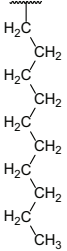
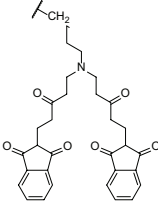
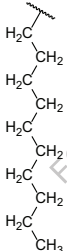
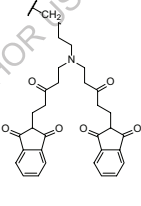
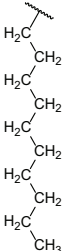


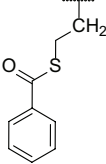
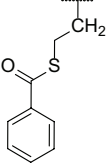
Thiacalixarenes have been substituted with a tremendous number of various ester and ether gatherings. At the point when the substituent bunches are sufficiently huge to forestall interconversion, distinctive conformers can be separated. The proportions of the conformers are subject to a wide scope of boundaries, for example, the temperature of the response, the idea of any base utilized, the size and steric imperatives of the alkyl gathering, and the idea of the leaving gatherings (Table 1). Different subsidiaries of thiacalix[4]arenes with lower-edge functionalization and their stereoisomers are momentarily recorded in the accompanying table.

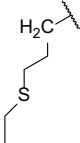
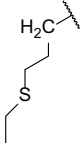
Table 1

Sr. No.	R ₁	R ₂	R ₃	R ₄	Conformers	Ref.
1					1,3-Alternate	[49]
2					1,3-Alternate	[50]

3					1,3- Alternate	[51]
4					Cone	[52]
5					1,3- Alternate	[53]
6					Cone	[54]

10					1,3-Alternate	[56]
11					1,3-Alternate, Cone	[57]
12		H	H		Cone	[57]
13					1,3-Alternate, Cone	[57]
14					1,3-Alternate, Cone	[57]

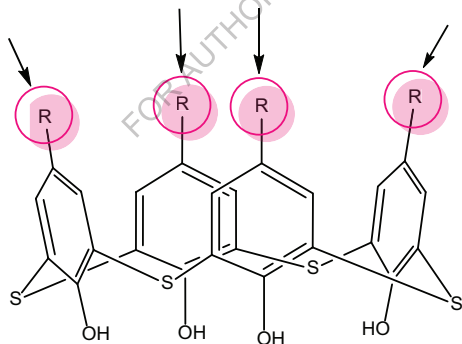
15					1,3- Alternate	[57]
16					1,3- Alternate	[57]
17					1,3- Alternate	[57]
18		H		H	Cone	[58]
19		H		H	Cone	[58]

20		H		H	Cone	[58]
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4.2 Functionalization of TCA at upper rim

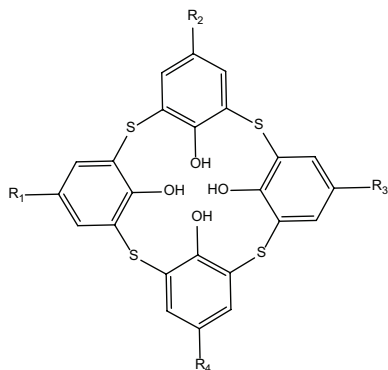
Functionalization at the upper rim of TCA have been done principally by means of two methods

- (1) Electrophilic aromatic substitution (SEAr) reaction at para-position of phenolic groups [36]
- and (2) ipso-substitution by electrophilic group at tert-butyl groups.



4.2.1 Friedel-Crafts Dealkylation

The Friedel–Crafts dealkylation of the tert-butyl group at the upper position of rim is the initial step for the electrophilic aromatic substitution. p-tert-butylthiacalix[4]arene can be changed over in the completely de-tert-butylated product with 51% yield under reflux conditions utilizing phenol/ AlCl_3 /toluene, as per the built up system in the traditional calixarene chemistry [38] with cone conformation as thiacalix[4]arene. Sometimes because of this tendency it gives different variety of results in particular on a large scale reactions. **Kumagai et al.** have improved this technique for large scale methods. In this process they take thiacalix[4]arene with 10.5 equiv. of aluminium chloride (AlCl_3) at 80 °C with phenol and it gives 80% yield [59]. Now, for the regio-selective partial dealkylation of thiacalix[4]arene was occurs using 7.1 equiv. of aluminium chloride (AlCl_3) at lower reaction time for the production of mono-, di-, and tri (p-tert-butyl)thiacalix[4]arene with 7%, 20%, and 21% yields [59]. fractional de-tert-butylated thiacalix[4]arenes embrace the cone conformation in arrangement and in the solid state like p-tertbutylthiacalix[4]arene [60].



$R_1=R_2=R_3=R_4=H$ (51%)

$R_1=R_2=R_3=H, R_4=Bu^t$ (7%)

$R_1=R_2=H, R_3=R_4=Bu^t$ (20%)

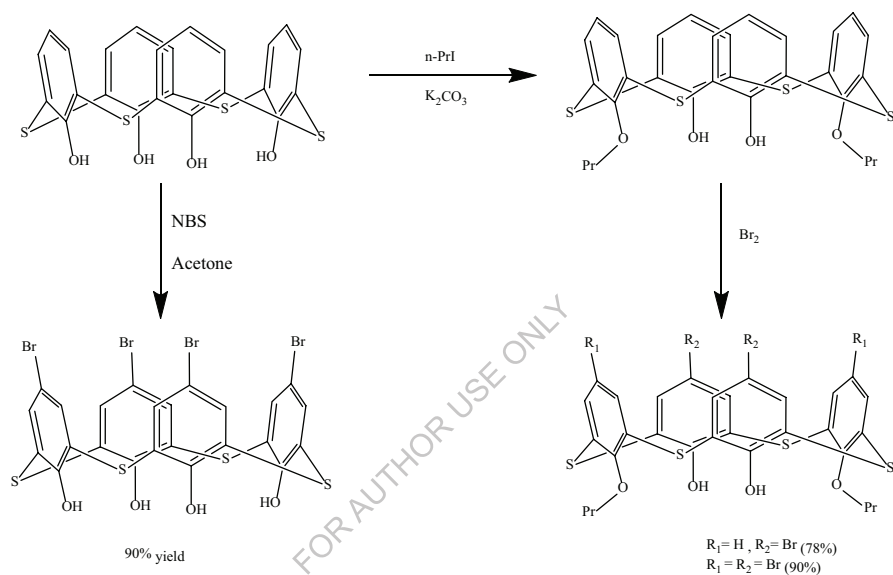
$R_1=R_2=R_3=Bu^t, R_4=H$ (21%)

Scheme-8 De-tert-butylated structures of TCA

4.2.2 Bromination of TCA

Tert-butyl thiacalix[4]arene (TCA) is modified with different reactivity by various electrophilic aromatic substitution reactions as compare to tert-butyl calix[4]arenes. Bromination of tert-butyl thiacalix[4]arene is the widely investigated substitution reaction with compare to classical tert-butyl calix[4]arenes. Bromo substituted derivatives are very useful intermediates in many synthetic applications. Here dibromo and tetra bromo derivatives can be synthesized by the bromination of dipropoxy-thiacalix[4]arenes [61] at room temperature for 24 hours. Here dibromo derivative is synthesized by use of 6 equiv. bromo for gating 73% yield and 12 equiv. of bromo gives terta-bromo derivatives with about 90% yields [62]. Now, The Bromination of

thiacalix[4]arene with the presence of NBS (in acetone) for 4 hours gives tetrabromo derivatives of thiacalix[4]arenes with 90% yield [63].

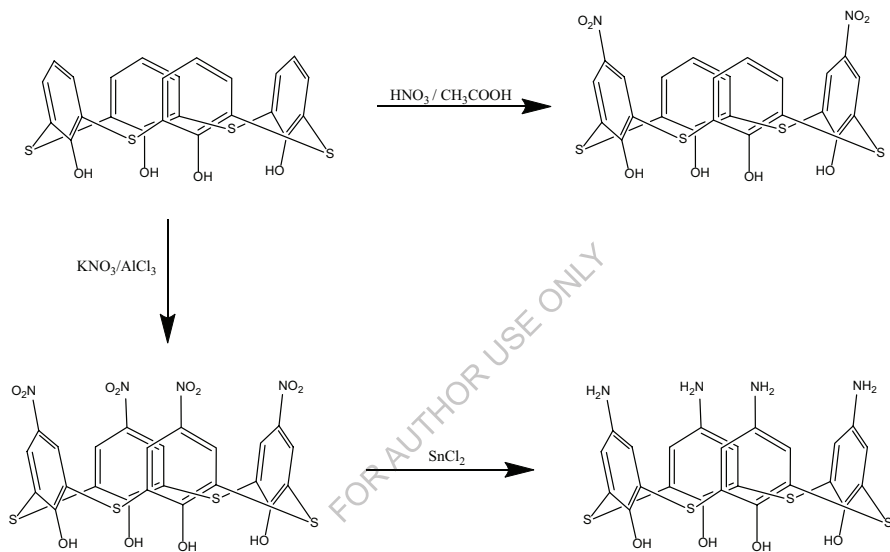


Scheme-9 Synthesis of bromo derivatives

4.2.3 Nitration of TCA

Nitration of given de-tert-butyl thiacalix[4]arene is occurs with the presence of KNO_3 and AlCl_3 gives tetranitro derivatives with 67% of yield [64]. Selection of solvents is very important for reactions occurs in in-situ formation as it establish the active electrophilic species NO^+NO_3^- . Some nitrating solvents are not able to get nitration's products. **Hu et al.** [65] reported on further

reduction tetra-nitro derivatives with SnCl_2 gives tetra-amino-thiacalix[4]arene derivative (93% yield) which is very useful for further synthesis. **Y. Li et al. [46]** reported about the synthesis of di-nitro-thiacalix[4]arene derivative (71% yield) with the presence of HNO_3 and CH_3COOH .

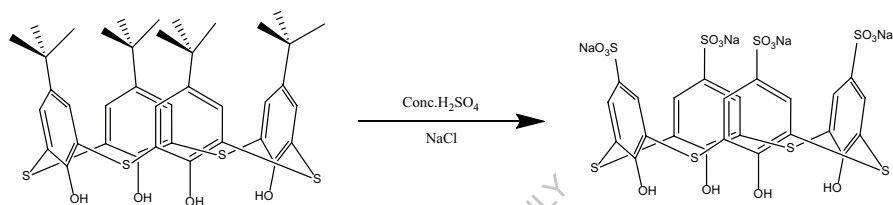


Scheme-10 Synthesis of nitro derivatives

4.2.4 Sulfonation of TCA

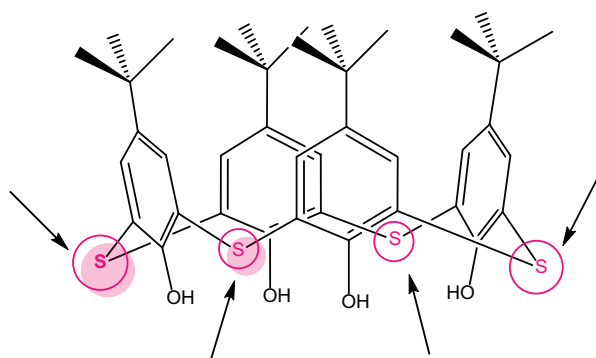
Sulfonation of thiacalix[4]arene is important for the study of thiacalix[4]arenes derivatives in to the aqueous medium because of insolubility of thiacalix[4]arenes in to the water. Introduce the sulfo group on the upper side of thiacalix[4]arene is help to take more application of compound derivatives into aqueous solutions. Here we introduce ipso-sulfonation of thiacalix[4]arene

because of direct sulfonated compounds are not possible. **Fujimoto et al. [66]** introduce ipso-sulfonation of p-tert-butylthialix[4]arene with the presence of concentrated H_2SO_4 and NaCl gives p-sulfonatothialix[4]arene (4-sulfonic acid salt) derivative with good yield (81%).



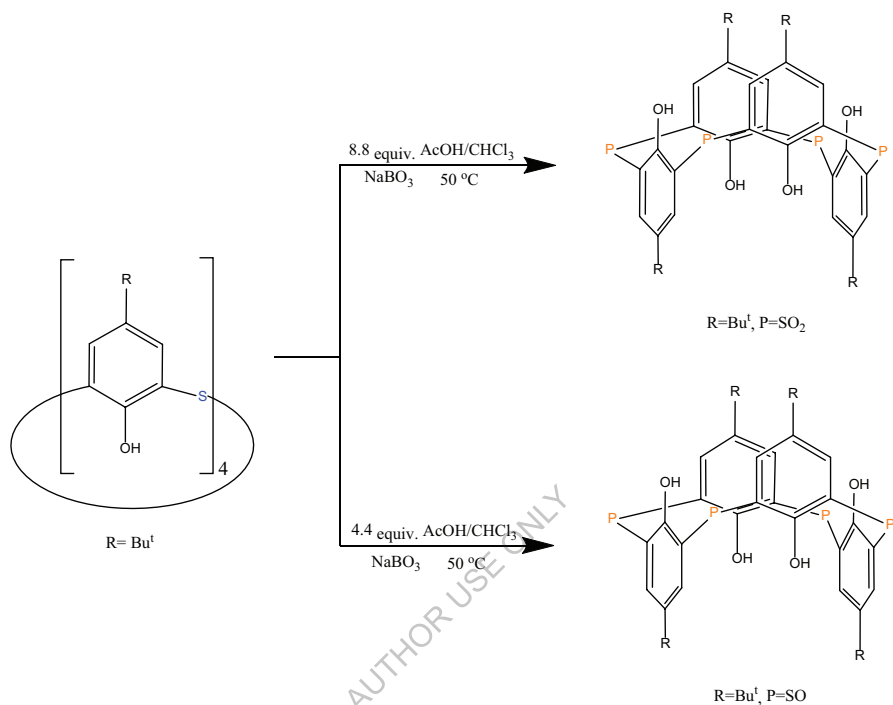
Scheme-11 Synthesis of ipso-sulfonation of TCA

4.3 Functionalization of Sulfide Bridges



With compared to traditional calix[4]arene presence of sulfide groups in thiacalix[4]arene is exclusive characteristic of it which can go through oxidation to sulfonyl and sulfinyl functions. Because of sulfur atom in the place of methylene bridged it can be undergo with some unique-applications. Which cannot applicable on traditional calix[4]arenes. Now, oxidation of thiacalix[4]arene with the presence of some oxidant like H_2O_2 (hydrogen peroxide) or NaBO_3 (sodium perborate) or TFA (trifluoroacetic acid) in some organic solvents gives sulfone derivatives and sulfoxide derivatives; which are the result of conversion sulfide bridge to sulfone and sulfoxide derivatives [67, 68]. Hosseini et al. reported that sulfonyl derivatives and sulfoxide derivatives have 1,3 alternate conformation [69, 70]. Sulfonyl derivatives has hydrogen bonding between phenolic hydroxy group and sulfonyl oxygen.

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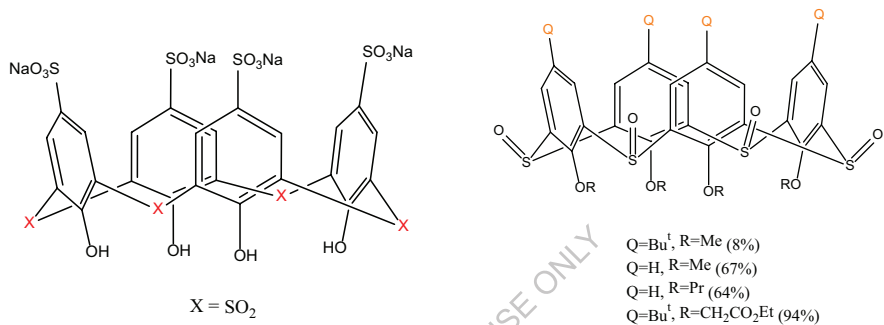


Scheme-12 Oxidation of TCA at Sulfide Bridges

The oxidation of p-sulfonato thiacalix[4]arene conduct sulfony derivative [71] while **P.Lhotak et al. [72]** observed distinctive novel building blocks utilizing thiacalix[4]arene tetra-acetate in the cone conformation, which was stereo-selectively and regio-selectively oxidized to various sulfoxide subordinates. These creators found that no nitrated item was framed while endeavoring the ipso-nitration of tetraacetate, yet the sulfoxide subordinates were recognized. The Regio- and

stereoselective oxidation of the sulfide to sulfoxide was too detailed in 2003 by **I. Stibor et al.**

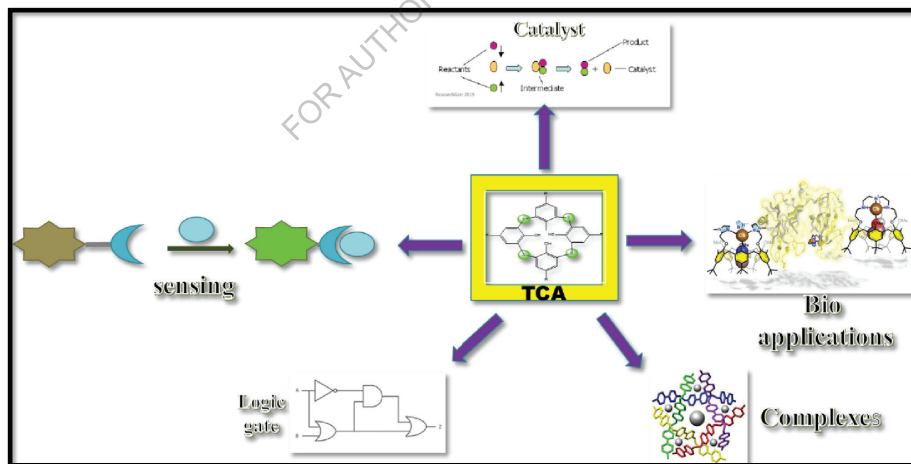
[73] utilizing a mix of $\text{NaNO}_3\text{-CF}_3\text{COOH}$, which fills in as a fantastic oxidizing agent.



Scheme-13 Stereo controlled Oxidation

5. Application of TCA

TCA have so many advantages for functionalization at lower rim, upper rim, and sulfide bridges. Now, with compare to traditional calixarene thiacalix[4]arene have good biding ability with metal ions because of sulfide group present at bridging position. Thiacalix[4]arene have functionalized for good binding affinity with soft and hard metal ions with incorporation of oxygen. TCA have been functionalized for the detection of various anions, cations and neutral analytes. In other applications of thiacalix[4]arenes have been reported as self-assembled coordination networks, molecular switches, magnetic materials, logic gates and luminescent materials.



5.1 Spectroscopic sensors (UV/Fluorescent sensors)

5.1.1 Cationic recognition

C. Redshaw et al. [50, 51] reported fluorescent sensor which is functionalized from lower edge of thiacalix[4]arene having triazole ring as cationic binding sites with 1,3 alternate conformation with specifically bind Ag^+ particles with huge improvement of the monomer emissions of pyrene with ratiometric fluorescence conduct. This all report suggested that triazole moiety is responsible for the good affinity with Ag^+ ion because presence of nitrogen atom on it and coordination by the ionophoric cavity and sulfur atom of TCA.

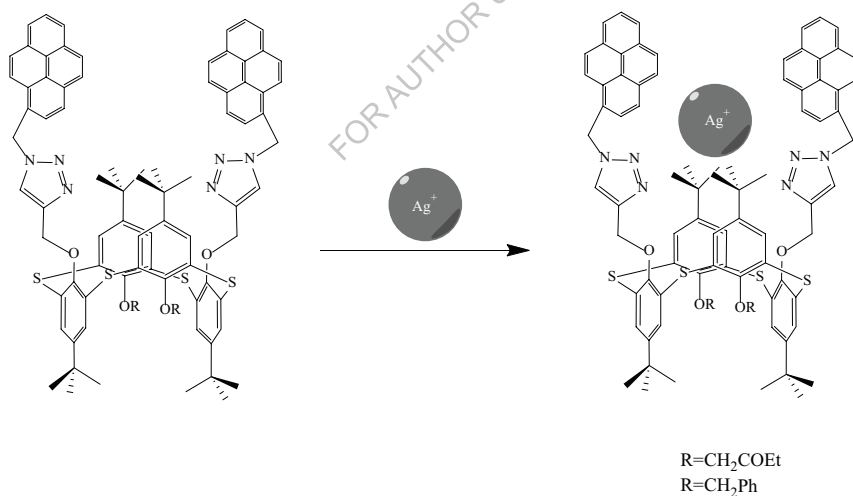


Figure-4 Fluorescent mechanism of compound with Ag^+

Kumar et al. [52] reported tetra pyrene-appended chemosensor in cone-conformation of thiacalix[4]arene. In aqueous medium it gives compliance behavior with metal ions. The chemosensor indicated high selectivity to Fe^{3+} particles by fluorescence extinguishing of excimer emission of pyrene units because of reverse photoinduced charge transfer to carbonyl oxygen from pyrene units. In presence of any variant cations, anions, amino acids, blood serum or bovine serum albumin (BSA) the selectivity is not affected. That's why it used as selective sensor in living cells (PC3 cells) for Fe^{+3} ions.

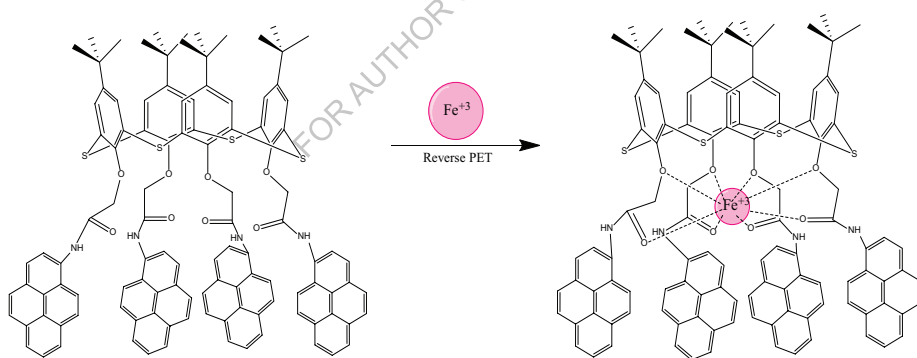


Figure-5 Fluorescence binding mechanism of compound with Fe^{3+} ions

Luo et al. [74] reported p-tertbutyl thiacalix[4]arene (with diagonal 8-hydroxyquinoline moieties) derivative in very stable complex formation of ligand with Co^{2+} , Zn^{2+} and Ni^{2+} ions by UV-Vis and fluorescence spectroscopy and ^1H NMR titration. Stoichiometries of Co^{2+} , Zn^{2+} and Ni^{2+} , were 1:2, 1:2 and 1:1, respectively and it gives very stable complexes with this three metal ions shown by results. We accept that the p-tert-butylthiacalix[4]arene (diagonal 8-hydroxyquinoline moieties) derivative may have the hypothetic use as the change metals fluorescent test and natural light-emitting diodes.

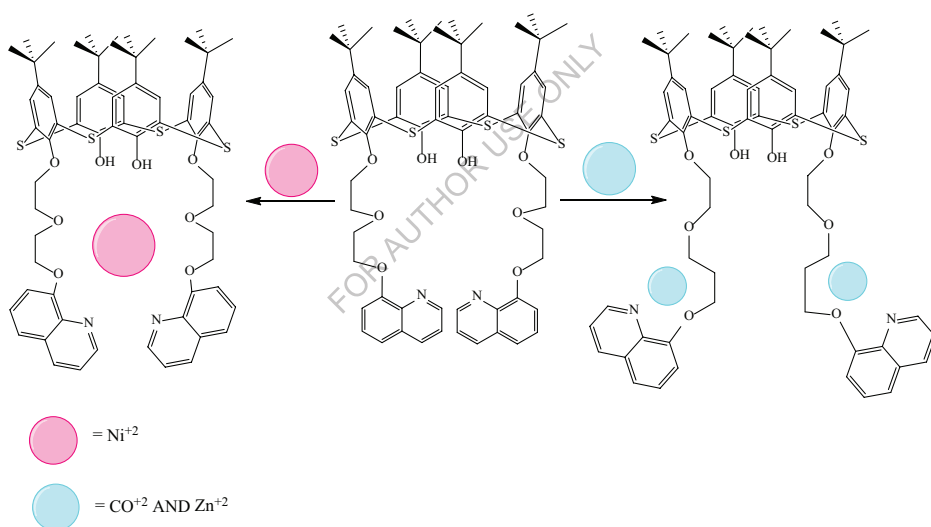


Figure-6 Fluorescence binding mechanism of compound with Ni^{2+} , Co^{2+} and Zn^{2+}

Krunal Modi et al.[75] reported fluorescent sensor which is functionalized from lower edge of thiacalix[4]arene having 8-Quinolinesulfonyl chloride as cationic binding with specially bind Co(II) particles. A novel Chemo sensor TCTQ8S (Thiacalix[4]arene Tetra quinoline-8-sulfonate) was synthesized and characterized which has 8QSC as an ionophore. TCTQ8S goes about as an effective BTurn-Off fluorescent chemo sensor for the specific and delicate acknowledgment of Co(II) metal particles among different cations, for example, Na(I), K(I), Ag(I) Fe(III), Cr(III), Cu(II), Hg(II), Ba(II), Co(II), Pb(II), Sr(II), Bi(II), Ca(II), Zn(II).

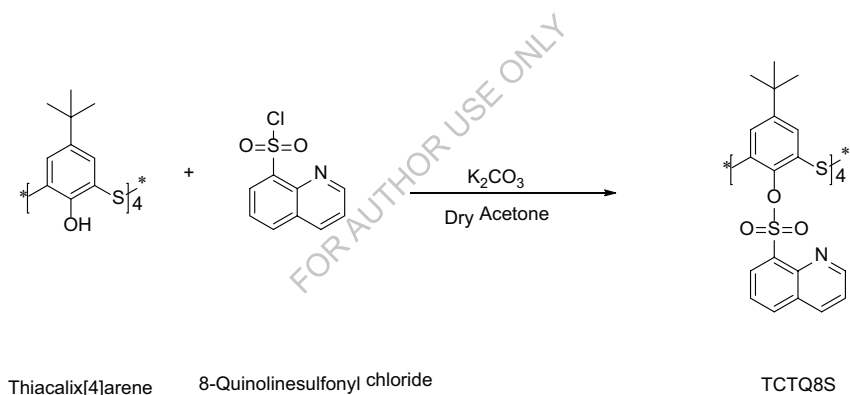
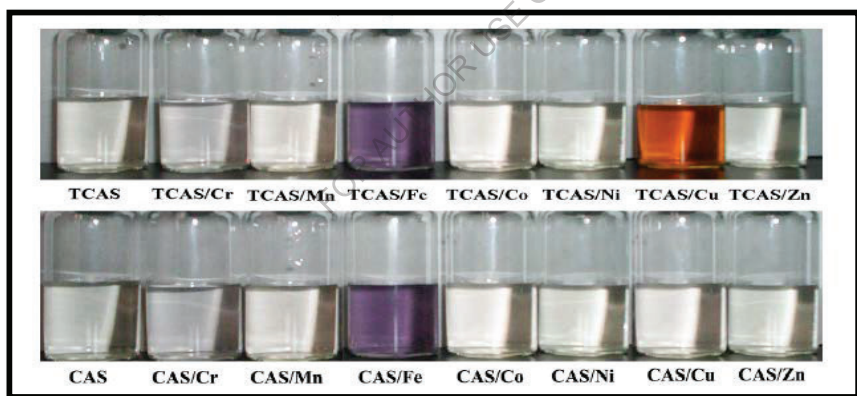


Figure-7 8-Quinolinesulfonyl chloride as cationic binding with Co (II)

Shufang Zhu et al. [76] reported that water-dissolvable thiacalix[4]arene tetrasulfonate (TCAS) showed specific chromogenic acknowledgment towards copper(II) particle over other progress metal particles.



Figure-8 Tetrasulfonate (TCAS) as cationic binding with Cu (II)



Savan M. Darjee et al. [77] reported fluorescent sensor which is functionalized from lower edge of thiacalix[4]arene having naphthoyl chloride as cationic binding with specially bind Zn^{+2} ions. The thiacalix[4]arene naphthalene 1-carboxylate (TCNC) species works a powerful receptor for

Zn^{2+} particles, in arrangement with a recognition breaking point of 1 nM to 740 nM. The consolidation of an extra TCNC ligand in the complex leads prompts a surprising increment of fluorescence, uncovering the interest of the TCNC atoms in the excitation and energy transfer measures. The mass and titration tests bolsters a solid official of the Zn^{2+} particles to TCNC indicating a slow disappearance of the free TCNC and its transformation to the TCNC: Zn^{2+} (1:1) complex.

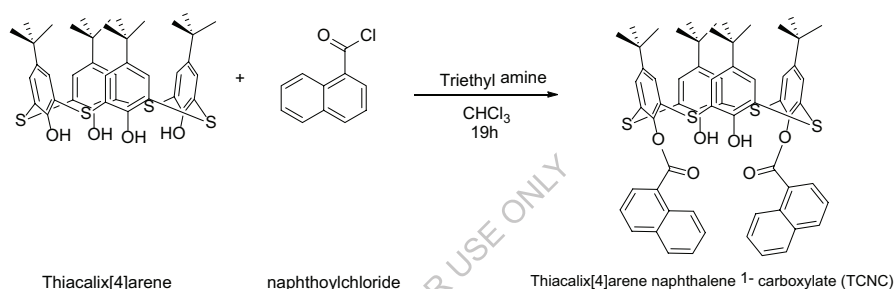


Figure-9 Naphthoyl Chloride as cationic binding with Zn^{+2}

Varma et al. [49] planned another thiactalix[4]arene subordinate in a 1,3-substitute conformation bearing four quinolinoloxo groups through propyl chains as a ligand, which displayed articulated Hg^{2+} -selective on-off-type fluoroionophoric properties among the agent transition and weighty metal particles, including Cu^{2+} . The location of turn-off for Hg^{2+} was discovered to be 2.0×10^{-6} M in the blended H_2O -THF framework. The receptor displayed just minor liking for Cr^{3+} and Ag^+ and no proclivity for the other change metal particles tried, including Cu^{2+} , in this way decreasing the chance of obstruction from these metal particles.

5.1.2 Anionic recognition

Keyur D. Bhatt et al. [78] synthesized the fluorescent chemosensor with two quinoline moieties which are based on thiacalix[4]arene armed for fluoride ions. They observed emission spectra of different anions like Cl^- , F^- , Br^- , H_2PO_4^- , I^- and CH_3COO^- in tetra butyl ammonium salt (TBA) with acetonitrile as solvent. Compound gives observed emission spectra at 408nm with addition of fluoride ions (F^-) it gives 470nm spectra which shown the red shift while another anions don't gives changed in adsorption spectra. This changed of spectra gives the information about interaction of electronegative fluoride (F^-) ions with given moiety due to hydrogen bonding.

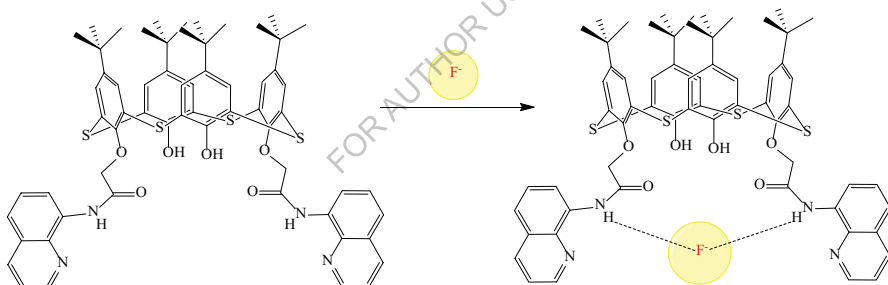


Figure-10 Proposed binding modes of compound with F^- ions

Kumar et al. [79] reported fluorescent chemosensor for fluoride ions with two naphthyl moiety of thiacalix[4]arene. Given moiety don't give emission spectra with given receptor but with the

addition of F^- (fluoride) ion into the moiety it gives emission spectra band. That results of spectra gives the information about the higher selectivity of fluoride ions with given receptor. The increase in emission spectra is motivated by the fluoride ions (F^-) as described by the intramolecular pi-pi interaction excimer formation among two naphthyl moiety. This intramolecular interaction is held due to intermolecular binding interaction of fluoride ions with -NH group of thiourea moieties

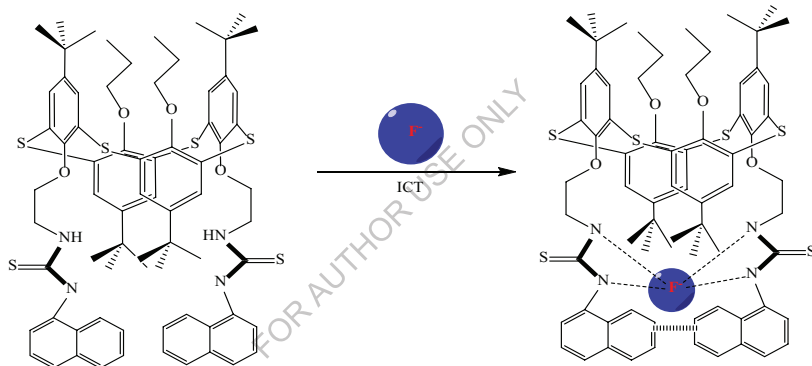


Figure-11 Proposed binding mode of compound with F^- Figure

Manoj Kumar et al. [80] synthesized fluorogenic chemo-sensors for fluoride ions and cyanide ions of thiacalix[4]arene in various modes. The nearness of fluoride particles initiates the fluorescence discharge to 'on state' and the nearness of cyanide particles results in 'ratiometric conduct. This pyrene based fluoride sensors gives intramolecular charge transfer mechanism

(ICT) and high selection to fluoride (F^-) with enhanced Monomer emissions and cyanide (CN^-) ion with ratiometric character.

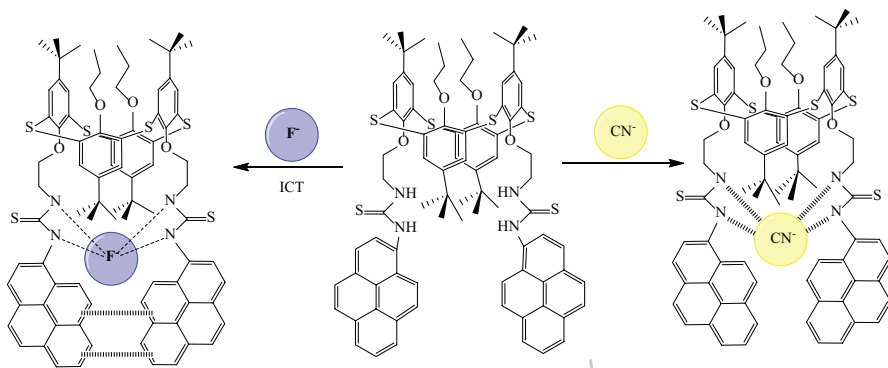


Figure-12 Fluorogenic sensors for fluoride and cyanide ions of TCA

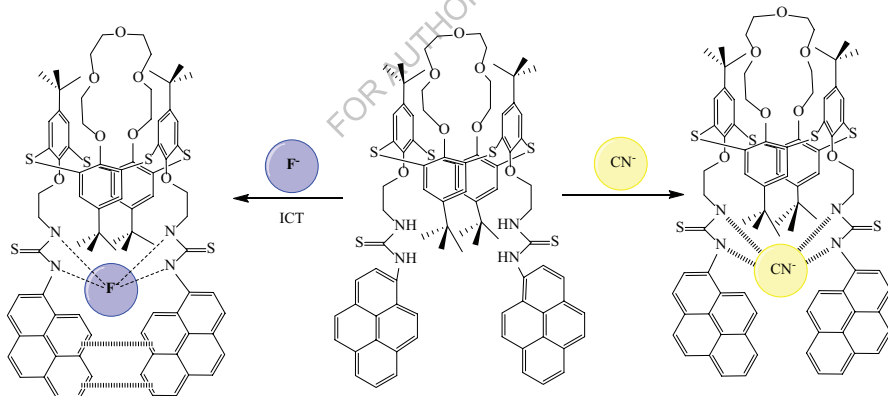
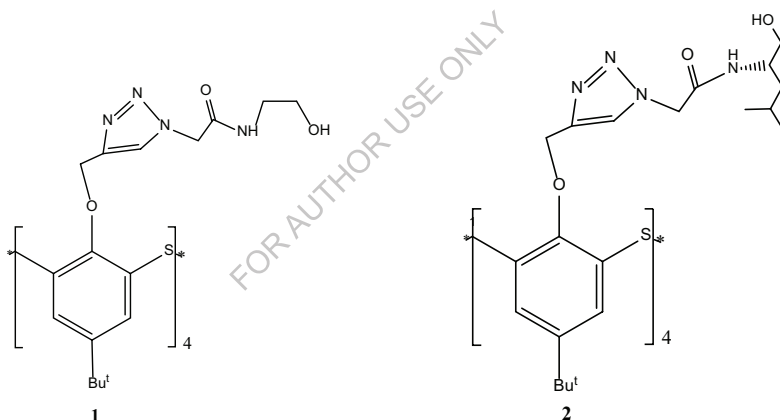


Figure-13 Fluorogenic sensors for fluoride and cyanide ions of TCA

Dye extraction agents

H.-Y. Guo, et al. [54] Synthesized alkynylthiacalix[4]arene and ethyl 2-azidoacetate followed by an ammonolysis with ethanolamine, leucinol and hydrazine hydrate, respectively, three novel thiacalix[4]arene derivatives 1, 2 and 3 with triazolyl groups and hydrogen bonding groups (NH and OH) were synthesized in high yields. They exhibited excellent extraction capability for six anionic and cationic dyes. The flexible cavity, π -triazole rings and hydrogen bonding groups all play crucial roles in dye complexation.



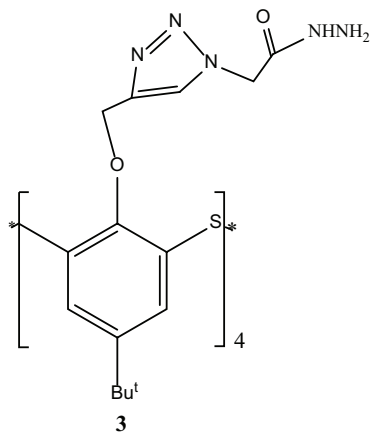


Figure-14 TCA as Dye extraction agents

Sensing Of Explosive

K.Modi et al. [81] synthesized the fluorescent chemosensor with reaction of thiacalix[4]arene with naphthalene sulfonyl chloride. The selectivity of fluoroionophore has been analyzed for 4-Nitrotoluene (4-NT) and 2,3-dinitrotoluene (2,3-DNT) among various nitro aromatic compounds (NACs) using the spectrofluorimetric technique.

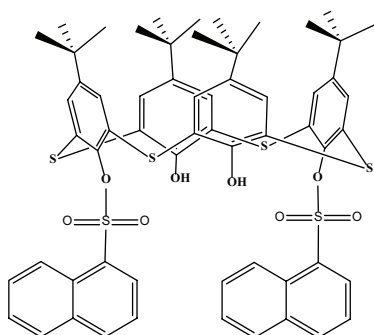
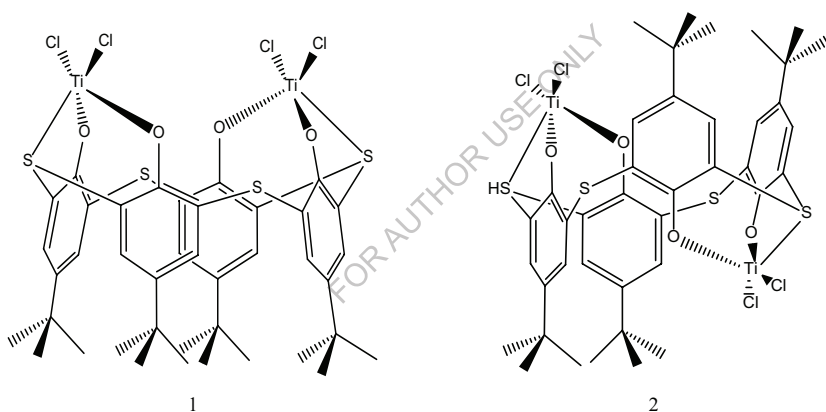


Figure-15 Fluorogenic sensors for 4-Nitrotoluene (4-NT) and 2,3-dinitrotoluene (2,3-DNT) of TCA

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Catalysts

Thiacalix[4]arenes have the ability to form mono-, di-, and polynuclear complexes with a wide range of metal ions due to the presence of O- and S-coordinating sites which could be used as efficient catalysts for various transformations. **Antonio Proto et al. [82]** synthesized thiacalix[4]arene based dinuclear titanium complexes were applied as catalysts for the [2+2+2] cycloaddition of terminal alkynes.



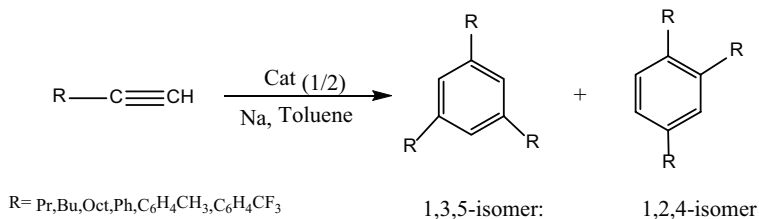
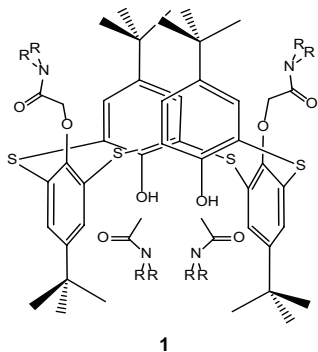


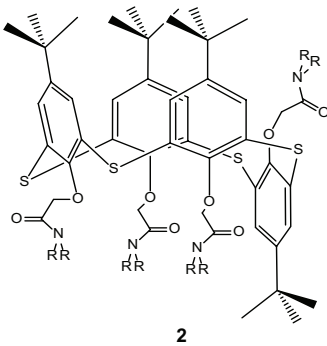
Figure-16 TCA as Catalysts

Biological Applications

Thiocalix[4]arene derivatives have also been employed for the detection of different biological analytes. **Evtugyn et al. [83]** developed a redox active matrix comprised of polycarboxylated thiocalix[4]arene embedded on the electro polymerized Neutral Red (NR) layer, which was immobilized by a DNA aptamer with NR as an amperometric aptasensor for the determination of thrombin. Poly carboxylated thiocalix[4]arenes in the partial cone 1, cone 2 and 1,3-alternate 3 conformations bearing NR were also employed for the label-free detection of thrombin. The 1,3-alternate conformer 3 showed better binding with thrombin as compared to the cone and partial cone conformers.



R = -CH₂COOH



R = -CH₂COOH

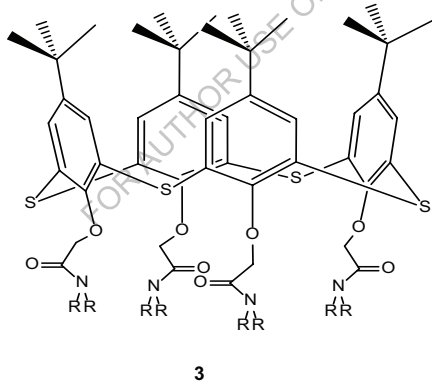


Figure-17 TCA as Biological Applications

Sensing of Metal Ions

The surprising complexation capacity of thiacalixarenes toward metal particles has been used for the detecting of them.

Lamartine et al and **J-Renault et al.** applied thiacalix[4]arene to a segment of thin films for electrolyte-separator semiconductor (EIS), ion-sensitive field effect transistor (ISFET), and gold microelectrodes, which permitted recognition of Cu^{2+} at a degree of as low as 10^{-7} M. [84-88] Needless to state, phenols are electroactive practical gatherings. In this manner, voltammetric acknowledgment of metal particles utilizing thiacalix[4]arene was examined. In pH 8 arrangement, voltammograms of thiacalix[4]arene drastically changed within the sight of progress metal particles, for example, Cd^{2+} , Co^{2+} , and Ni^{2+} , while alkali-metal particles also, alkali earth-metal particles caused just unimportant changes to that of thiacalix[4]arene even at high focuses. It was illustrated that the voltammetry was relevant to the investigation of Cd^{2+} particle [88]

Then again, adjusted thiacalix[4]arenes were to applied for detecting of metal particles. **Hamada et al.** adjusted the phenolic capacity of thiacalix[4]arene and its de-tert-butylated compounds with a Dansyl moiety to the relating sub-ordinates [fig-18], which were utilized as host atoms for the fluorescent detecting of metal particles in fluid arrangements.[59, 89]. It was discovered that the quantity of tert-butyl moieties altogether influenced the fluorescent power, expanding with diminishing number of tert-butyl gatherings.

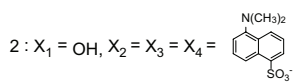
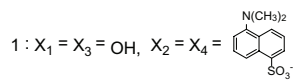
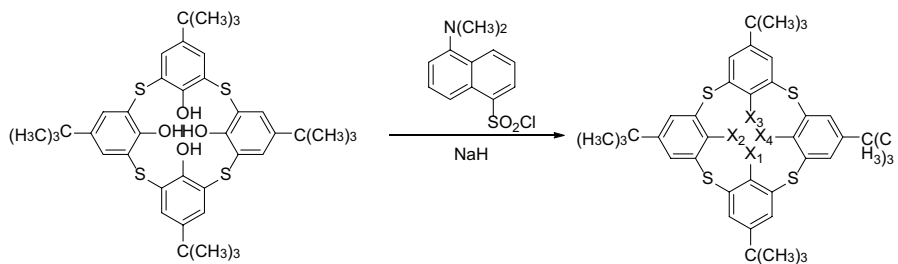


Figure-18 TCA as Detecting of Metal particles

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Aim and Scope

As Thiacalix[4]arene is versatile supramolecular receptor and find application as optical sensors, electrochemical sensors, HPLC supports, anion transporting agents, chelating polymer, optical chemosensors, host molecules components in liquid crystals, photo resists, selective membranes surface reforming agents, anions and cation extraction agents. Fluoroionophores find application as chemosensor for ionic and neutral analytes by complexation.

The aim is to synthesize two different platforms of thiacalixarenes and further functionalize them with the appropriate fluorophore to yield potential fluorescent sensors.

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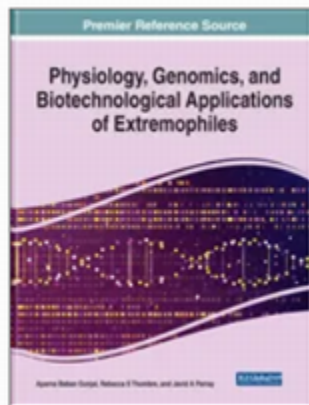
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Major Compatible Solutes and Structural Adaptation of Proteins in Extremophiles

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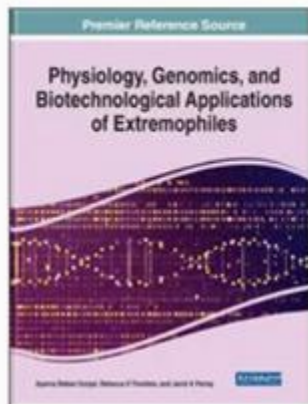
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Abstract

Extremophiles are the most ancient microbes on the Earth and also a center of attraction for the scientific community for research because of their ability to adapt to extreme habitats. Compatible solutes are among those factors which enable these microorganisms to thrive in such extreme habitats. Under osmotic stress, the majority of extremophiles accumulate specific organic solutes such as amino acids, sugars, polyols, and their derivatives. In addition, proteins in extremophiles are found to be evolved by changing their amino acid composition to alter the hydrophobicity of its core and surface charge to maintain activity. This chapter encompasses a comprehensive study about the role of various compatible solutes in the endurance of microorganisms under extremophilic conditions, synthesis of compatible solutes, nature of extremophilic proteins, and their applications. Furthermore, an attempt has been made to cover various strategies adopted by the scientific community while pursuing research on compatible solutes.



Thermophiles: Physiology, Metabolism, Enzymology, and Adaptation Mechanisms

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Abstract

Microorganisms are the diverse living things present on the Earth. India has numerous unique thermal habitats that comprise several diversity hotspots, such as hot springs, deep oceanic hydrothermal openings, anaerobic bioreactors. The existence of life at high temperatures is quite attractive. At both ends of the temperature range suited with life, only microorganisms can grow and survive. Thermophiles are a typical extremophilic microbes capable of existence in high temperature environments. At such high temperature, the ordinary cellular functions adversely affected for mesophiles. The thermophiles effectively manage instability of the plasma membrane, inactivation of enzymes instability of DNA, as well as other hostile physiological variations at such an elevated temperature. Heat shock proteins (Hsps) have established the most attention in thermophiles under stress condition, which is well described in this chapter. This chapter offers comprehensive information about thermophiles, physiology, metabolism, enzymes of metabolic pathways, and various adaptation mechanisms.



CHAPTER – 4
**DIFFERENTIAL QUADRATURE METHOD FOR SOLVING LINEAR AND NON-
LINEAR DIFFERENTIAL EQUATION**
BY
AMIT K PARIKH & JISHAN K SHAIKH

ABSTARCT: In this chapter, we have studied polynomial based differential quadrature method for solving linear and non-linear differential equations. We also studied use of uniform and non-uniform grid point in Polynomial based differential quadrature method. We obtained numerical solution of linear and non-linear differential equation by both the grid points and we compared solution between uniform and non-uniform grid points. We conclude that non-uniform grid point gives better accurate results compare to uniform grid points. We also observed that this method gives better approximate solution compare to some conventional methods like Finite difference method, Finite element method and many more. This method is required less number of grid points, less computer storage and also less time consuming.

Key words: Differential quadrature method, Polynomial based differential quadrature method, Linear and Non-linear differential equations, Uniform and Non-uniform grid points.

1. Introduction of Differential Quadrature Method:

There are many boundary value problems which involve partial differential equations. “Only a few of these equations can be solved by analytical methods. In most of cases, we depend on the numerical solution of such partial differential equations. There are many numerical methods available for solving linear and non-linear differential equations approximately. We are going to introduce differential quadrature method for solving linear and non-linear differential equation approximately. We are using some conventional methods like Finite difference method, Finite element method, Finite volume method and many more. Some of them methods are time consuming, more computer storage required and less accurate methods. It is difficult to obtain closed or exact solution of the differential equations. These methods are helpful to obtain numerical solution instead of exact solution. We are using different numerical techniques for obtaining numerical solution of the differential equations with the help of initial and boundary conditions. Most of engineering and real life problems mathematical models having linear or non-linear partial differential equations. There are two types of differential equations (1) Ordinary differential equations and (2) Partial differential equations. There are many methods available for solving both types’ differential equations. In this chapter, our main focus is solving linear and non-linear differential equations numerically. Many engineering problems and real life problems are governed by a set of partial differential equations. For examples, Elliptic equations, Laplace equations, Poisson’s equations, parabolic equations, Heat equation, hyperbolic equations, wave equation, Navier stokes equation and many more.”

R.E. Bellman and his associates “in early 1970’s were presented Differential Quadrature Method. Chang Shu has been also given remarkable work in this method with the different grid points [04]. He used different types of base functions also for obtaining numerical values of the weighting coefficients. This method is a numerical discretization procedure for the approximation of derivatives.” In this technique, “we approximate partial derivatives of some unknown functions at any grid point by using weighting coefficient methods [02]. For



weighting coefficients, we are assuming N grid points $y_1 < y_2 < y_3 < \dots < y_N$ on the real y -axis. Weighting coefficient of partial derivatives is also playing an important role in this method." So, in this method following points are very important for solving any linear or non-linear differential equation (1) Number of uniform or non-uniform grid points (2) Base function for obtaining the values of weighting coefficients (3) Weighting Coefficients of different order partial derivatives (4) Discretization of partial derivatives

2. Weighting Coefficient:

Here W_{lm}^1 and W_{lm}^2 are characterize weighting coefficients of first and second order partial derivatives respectively [01].

We will use following base functions to obtain the value of W_{lm}^1 and W_{lm}^2 .

$$h_k(y) = \frac{(y - y_1)(y - y_2)(y - y_3) \dots (y - y_N)}{(y - y_k)(y_k - y_1)(y_k - y_2)(y_k - y_3) \dots (y_k - y_N)}, \quad k = 1, 2, 3, \dots, N \quad (1)$$

$$S^{(l)}(y_l) = \prod_{k=1, k \neq l}^N (y_l - y_k), \quad l = 1, 2, 3, \dots, N \quad (2)$$

We will use (1) and (2), for obtaining W_{lm}^1 , which is given as follow

$$W_{lm}^1 = \frac{S^{(l)}(y_l)}{(y_l - y_m)S^{(l)}(y_m)}, \quad l \neq m, \quad l, m = 1, 2, 3, \dots, N \quad (3)$$

And
$$W_{lm}^1 = - \sum_{l=1}^N W_{lm}^1, \quad l = 1, 2, 3, \dots, N \quad (4)$$

We can obtain formula of W_{lm}^2 is given by

$$W_{lm}^2 = 2W_{lm}^1 \left[W_{ll}^1 - \frac{1}{y_l - y_m} \right], \quad \text{for } l \neq m, \quad l, m = 1, 2, 3, \dots, N \quad (5)$$

And
$$W_{ll}^2 = - \sum_{l=1, l \neq m}^N W_{lm}^2, \quad l = 1, 2, 3, \dots, N \quad (6)$$

Similarly we can obtain formula for n th order which is given by as follow

$$W_{lm}^n = 2W_{lm}^{n-1} \left[W_{ll}^{n-1} - \frac{1}{y_l - y_m} \right], \quad \text{for } l \neq m, \quad l, m = 1, 2, 3, \dots, N \quad (7)$$

And
$$W_{ll}^n = - \sum_{l=1, l \neq m}^N W_{lm}^n, \quad l = 1, 2, 3, \dots, N \quad (8)$$

3. Types of Grid Points:

In the approximation analysis, "we are using following grid points for obtaining numerical solution of the governing equation. (1) Uniform grid (2) Non-uniform (Chebyshev-Gauss-Lobatto grid) and (3) Roots of Chebyshev polynomial can be chose as grid points".[05]



(a) **Uniform grid:** Uniform grid points can be defined as follow [05].

$$y_i = y_1 + ih, \quad i = 1, 2, 3, \dots, N$$

i.e. where $y_1 = a$ and $h = \frac{b-a}{N}$ (9)

(b) **Non-uniform grid:** We will define non-uniform grid points as follow. These types of grid points known as Chebyshev-Gauss-Lobatto Grid points [05].

$$y_i = A + (0.5) * \left(1 - \cos \left(\frac{(i-1) * \pi}{N-1} \right) \right) (C - B), \quad i = 1, 2, 3, \dots, N \quad (10)$$

Generally we are using uniform or non-uniform (Chebyshev-Gauss-Lobatto) grids points for the numerical analysis.

4. Runge Kutta Method:

We are using 4th order Runge-Kutta Method to discretize time derivatives in the resulting system of algebraic equations. Runge-Kutta Method is a one-step method for solving initial value problems [07].

For example

We are using Runge Kutta method for solving following differential equation

$$\frac{dy}{dx} = F(x, y), \quad \text{with } x(0) = a \text{ and } y(0) = b \quad (11)$$

For using 4th order Runge-Kutta method first of all we have to rewrite our differential equation in this form

$$y_{n+1} = y_n + \frac{h}{6} [K_1 + 2K_2 + 2K_3 + K_4] \quad (12)$$

Where

$$K_1 = f(x_n, y_n) \quad (13)$$

$$K_2 = f\left(x_n + \frac{h}{2}, y_n + \frac{h}{2}K_1\right) \quad (14)$$

$$K_3 = f\left(x_n + \frac{h}{2}, y_n + \frac{h}{2}K_2\right) \quad (15)$$

$$K_4 = f(x_n + h, y_n + hK_3) \quad (16)$$

Above method we are using for explicit dependence on independent variable types differential equations.

5. Pike and Roe four stage RK4 method:

Pike and Roe presented “the following four-stage RK4 scheme for the problem that function having no explicit dependence on independent variables”. [05]

Consider the ordinary differential equation

$$\frac{dy}{dx} = F(y), \quad \text{with } y(0) \text{ given} \quad (17)$$

$$\begin{cases} y = y^n \\ g = f(y) \end{cases} \quad (18)$$



$$\begin{cases} y = y^n + \frac{h}{4} * g \\ g = f(y) \end{cases} \quad (19)$$

$$\begin{cases} y = y^n + \frac{h}{3} * g \\ g = f(y) \end{cases} \quad (20)$$

$$\begin{cases} y = y^n + \frac{h}{2} * g \\ g = f(y) \end{cases} \quad (21)$$

$$y^{n+1} = y + h * g \quad (22)$$

“Where the superscripts denote the independent variable level at which the term is evaluated. The RK4 scheme requires two levels of storage. All the Runge-Kutta schemes of a given order have the same stability properties”. The stability regions for this class of schemes expand as the order increases [05].

Examples

(1) Let we consider Burger’s equation as follows [11]

$$\frac{\partial c}{\partial T} + c \frac{\partial c}{\partial X} = M \frac{\partial^2 c}{\partial X^2}; 0 \leq X \leq 1, T > 0 \quad (23)$$

Where $M = \frac{M_L}{L}$ is dimensionless variable [11].

The initial condition has been chosen as a negative exponential function of space variable-x, which is according to the physical behavior of the longitudinal dispersion phenomenon. The concentration of the contaminated water or saline water reduces as it moves on along x-direction. The appropriate boundary conditions are taken as [11]

$$\begin{aligned} c(X, 0) &= \frac{e^{-X}}{4}, & 0 \leq X \leq 1 \\ c(0, T) &= c_0 = 1, & T \geq 0 \\ c(1, T) &= c_1 = 0.001, & T \geq 0 \end{aligned} \quad (24)$$

The non-linear partial differential equation (23) has been discretized by using Polynomial based differential quadrature scheme as follows [03]

$$\frac{\partial c}{\partial T} = \frac{dc_l}{dT}, \quad l = 1, 2, 3, \dots, N, \quad \text{Where } c_l = c(x_l) \quad (25)$$

$$\frac{\partial^2 c}{\partial X^2} = \sum_{m=1}^N W_{lm}^2 c_m, \quad l = 1, 2, 3, \dots, N \quad (26)$$

$$\frac{\partial c}{\partial X} = \sum_{m=1}^N W_{lm}^1 c_m, \quad l = 1, 2, 3, \dots, N, \quad \text{where } c_m = c(x_m), \quad (27)$$

We have to calculate weighting coefficient of first and second order partial derivatives using equation number (3), (4), (5) and (6) for uniform and non-uniform grid points.



The weighting coefficients W_{lm}^1 and W_{lm}^2 for uniform grid points $N=5$ [08].

$$\begin{aligned} W_{11}^1 &= -8.33333, W_{12}^1 = -16, W_{13}^1 = 12, W_{14}^1 = -5.33333, W_{15}^1 = 1 \\ W_{21}^1 &= 1, W_{22}^1 = -3.33333, W_{23}^1 = -6, W_{24}^1 = 2, W_{25}^1 = -0.33333 \\ W_{31}^1 &= -0.33333, W_{32}^1 = 2.66667, W_{33}^1 = 0, W_{34}^1 = -2.66667, W_{35}^1 = 0.33333 \\ W_{41}^1 &= 0.33333, W_{42}^1 = -2, W_{43}^1 = 6, W_{44}^1 = 3.33333, W_{45}^1 = -1 \\ W_{51}^1 &= -1, W_{52}^1 = 5.33333, W_{53}^1 = -12, W_{54}^1 = 16, W_{55}^1 = 8.33333 \end{aligned}$$

Similarly,

$$\begin{aligned} W_{11}^2 &= 46.66667, W_{12}^2 = 138.6667, W_{13}^2 = -152, W_{14}^2 = 74.66667, W_{15}^2 = -14.66667 \\ W_{21}^2 &= -14.66667, W_{22}^2 = -26.66667, W_{23}^2 = -8, W_{24}^2 = -5.33333, W_{25}^2 = 1.33333 \\ W_{31}^2 &= 1.33333, W_{32}^2 = -21.33333, W_{33}^2 = -40, W_{34}^2 = -21.33333, W_{35}^2 = 1.33333 \\ W_{41}^2 &= 1.33333, W_{42}^2 = -5.33333, W_{43}^2 = -8, W_{44}^2 = -26.6667, W_{45}^2 = -14.6667 \\ W_{51}^2 &= -14.66667, W_{52}^2 = 74.66667, W_{53}^2 = -152, W_{54}^2 = 138.6667, W_{55}^2 = 46.66667 \end{aligned}$$

Similarly let we obtain weighting coefficients W_{lm}^1 and W_{lm}^2 for non-uniform grid points $N=5$ [08].

$$\begin{aligned} W_{11}^1 &= -11.0000, W_{12}^1 = 13.6568, W_{13}^1 = -3.9999, W_{14}^1 = 2.3434, W_{15}^1 = -0.9999 \\ W_{21}^1 &= -3.4142, W_{22}^1 = 1.4142, W_{23}^1 = 2.8284, W_{24}^1 = -1.4142, W_{25}^1 = 0.5857 \\ W_{31}^1 &= 1.0000, W_{32}^1 = -2.8284, W_{33}^1 = 0, W_{34}^1 = 2.8284, W_{35}^1 = -1 \\ W_{41}^1 &= -0.5857, W_{42}^1 = 1.4142, W_{43}^1 = -2.8284, W_{44}^1 = -1.4142, W_{45}^1 = -1.4142 \\ W_{51}^1 &= 1, W_{52}^1 = -2.3431, W_{53}^1 = 4, W_{54}^1 = -13.6568, W_{55}^1 = 11 \end{aligned}$$

Similarly,

$$\begin{aligned} W_{11}^2 &= 68, W_{12}^2 = -113.9411, W_{13}^2 = 72, W_{14}^2 = -46.05887, W_{15}^2 = 20 \\ W_{21}^2 &= 36.9705, W_{22}^2 = 55.9999, W_{23}^2 = 23.9999, W_{24}^2 = -7.9999, W_{25}^2 = 3.0294 \\ W_{31}^2 &= -3.9999, W_{32}^2 = 16, W_{33}^2 = -24, W_{34}^2 = 16, W_{35}^2 = -4 \\ W_{41}^2 &= 3.0294, W_{42}^2 = -8, W_{43}^2 = 24, W_{44}^2 = 55.9999, W_{45}^2 = 36.9705 \\ W_{51}^2 &= 20, W_{52}^2 = -46.0588, W_{53}^2 = 72, W_{54}^2 = -113.9411, W_{55}^2 = 68 \end{aligned}$$

Now we substituting equation (25), (26) and (27) in equation (23)

$$\frac{dc_l}{dT} = M \sum_{m=1}^N W_{lm}^2 c_m - c_l \sum_{m=1}^N W_{lm}^1 c_m \quad (28)$$

Above equation is a set of ordinary differential equations [07].



Let we solve above equation by using RK4 method with uniform and non-uniform grid points for different time level.

Table-1: Concentration $c(X, T)$ for uniform grid points $N = 5$

X	0	0.25	0.5	0.75	1
T					
0	0.795422	0.764992	0.729996	0.690242	0.652142
0.1	0.710122	0.674612	0.635311	0.601246	0.558952
0.2	0.643224	0.594124	0.541203	0.500124	0.460943
0.3	0.564252	0.505699	0.461201	0.414332	0.370635
0.4	0.508514	0.456340	0.396122	0.351992	0.307834
0.5	0.461255	0.399744	0.330192	0.289837	0.248958
0.6	0.422313	0.348819	0.279452	0.230454	0.182468
0.7	0.381132	0.308487	0.237680	0.181952	0.127046
0.8	0.335261	0.267110	0.199422	0.140135	0.081176
0.9	0.296838	0.232821	0.167800	0.104618	0.041242
1	0.254051	0.189352	0.123478	0.080962	0.017421

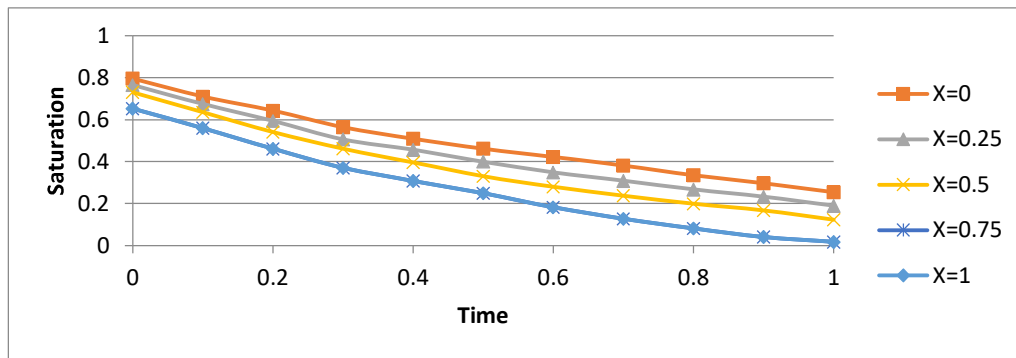


Figure-1: Concentration Vs Time

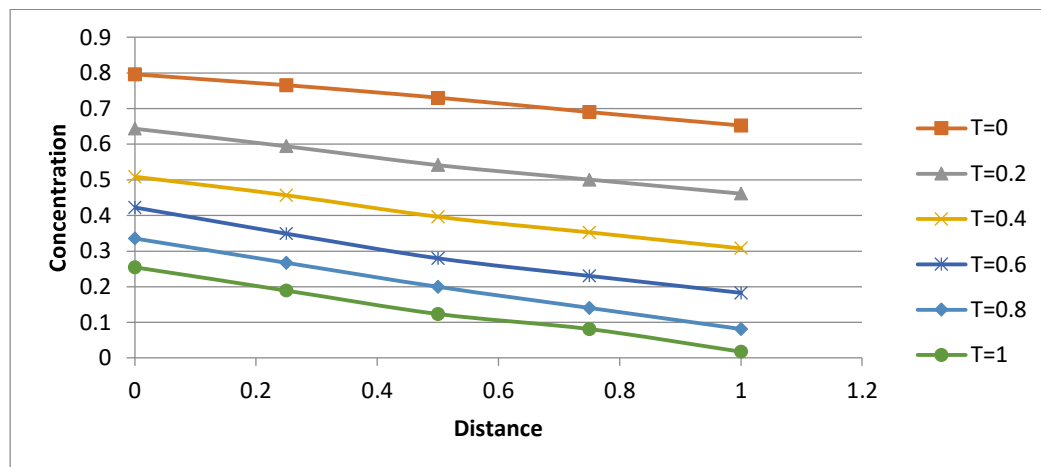


Figure-2: Concentration Vs Distance

Table-2: Concentration $c(X, T)$ for non-uniform grid points $N = 5$



X	0	0.308382	0.499602	0.83	0.999999
T					
0	0.8260474	0.8070885	0.7857240	0.771201	0.755856
0.1	0.7182382	0.7092745	0.6803108	0.661234	0.642719
0.2	0.6031246	0.5846934	0.5762622	0.558950	0.530943
0.3	0.5367522	0.512612	0.4947260	0.464332	0.420635
0.4	0.4538350	0.4200253	0.3961225	0.361992	0.327834
0.5	0.4109011	0.370546	0.3419216	0.289837	0.248958
0.6	0.3646932	0.327073	0.2794528	0.230454	0.182468
0.7	0.3366484	0.2921645	0.2376806	0.181952	0.127046
0.8	0.3066483	0.2580355	0.1994227	0.140135	0.081176
0.9	0.2738261	0.2308135	0.1678009	0.104618	0.041240
1	0.2505274	0.207003	0.1434786	0.080960	0.017421

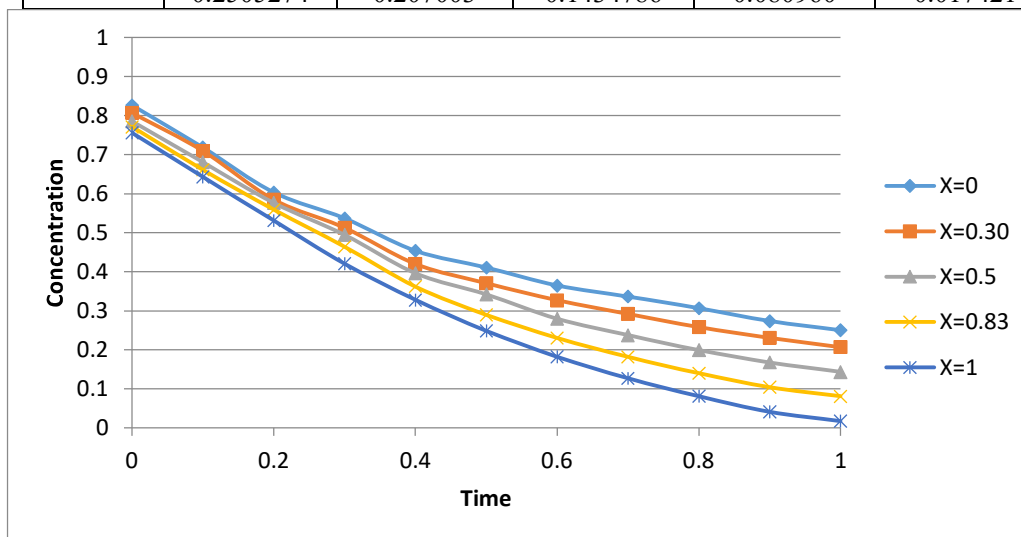


Figure-3: Concentration Vs Time

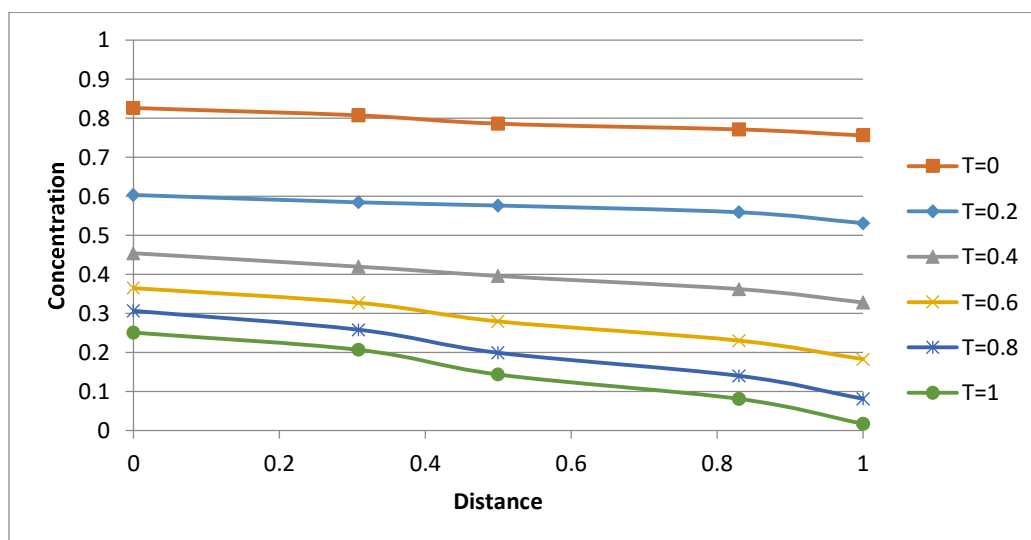


Figure-4: Concentration Vs Distance



(2) Let we solve following equation by using uniform and non-uniform grid points. This is a governing equation of the Counter-current imbibition phenomenon in a Homogeneous porous medium [09, 10].

$$\frac{\partial S}{\partial T} = \left(\frac{\partial S}{\partial X} \right)^2 + S \left(\frac{\partial^2 S}{\partial X^2} \right) \quad (29)$$

Discretize equation (29) by applying the equation (30) to (32)

$$\frac{\partial S}{\partial T} = \frac{dS(x_i)}{dT}, \quad i = 1, 2, 3, \dots, N \quad (30)$$

$$\frac{\partial S}{\partial X} = \sum_{j=1}^N a_{ij} S(x_j), \quad i = 1, 2, 3, \dots, N \quad (31)$$

$$\frac{\partial^2 S}{\partial X^2} = \sum_{j=1}^N b_{ij} S(x_j), \quad i = 1, 2, 3, \dots, N \quad (32)$$

Substitute equation (30), (31) and (32) in equation (29) [08]

$$\frac{dS(x_i)}{dT} = \left(\sum_{j=1}^N a_{ij} S(x_j) \right)^2 + S(x_i) \left(\sum_{j=1}^N b_{ij} S(x_j) \right), \quad i = 1, 2, 3, \dots, N \quad (33)$$

Initial condition selected as follow [08]

$$S(X, 0) = 1 - X^2, \quad 0 < X < 1 \quad (34)$$

Boundary Conditions as follow

$$S(0, T) = 1, \quad X = 0, T > 0$$

$$S(1, T) = 0, \quad T > 0 \quad (35)$$

To solve equation number (33), we are applying equation number (3), (4), (5), (6), (34) and (35) respectively. We also used RK-4 method for solving above system of first order differential equation [08].

Table: (1) Numerical results applying Chebyshev-Gauss-Lobatto grid points N=5 [12].

Distance(X)	0	0.308382	0.499602	0.83	0.999999
Time(T)					
0	0.746441	0.719054	0.682082	0.630201	0.552612
0.1	0.65541	0.612397	0.573225	0.526024	0.460542
0.2	0.580619	0.536022	0.496552	0.444243	0.370513
0.3	0.51296	0.458069	0.418251	0.366112	0.29761
0.4	0.457663	0.400617	0.361291	0.301022	0.228762
0.5	0.403545	0.34807	0.306732	0.239153	0.162224
0.6	0.35399	0.287775	0.250265	0.187281	0.107012
0.7	0.303552	0.251341	0.210265	0.149223	0.061056
0.8	0.264477	0.210856	0.170238	0.107601	0.03044
0.9	0.229433	0.171875	0.130227	0.090179	0.012221
1	0.197943	0.144444	0.106261	0.072068	0.009268

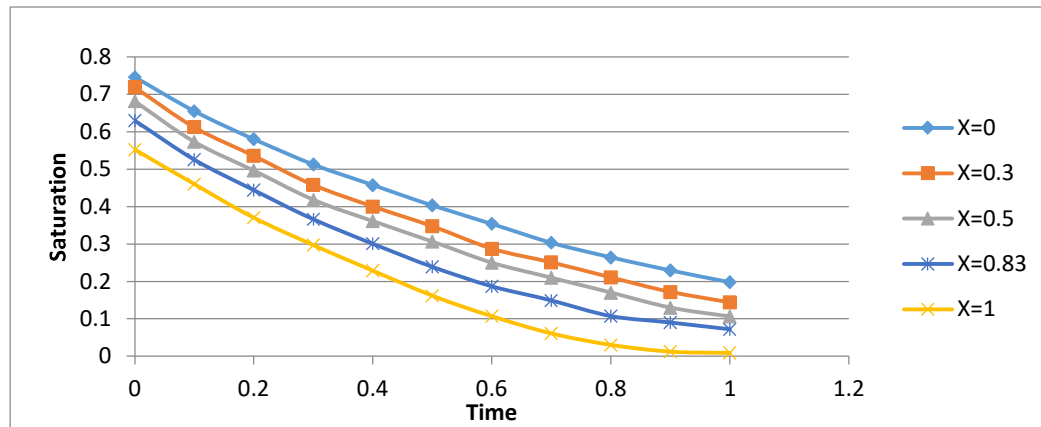


Figure-1: Saturation Vs Time

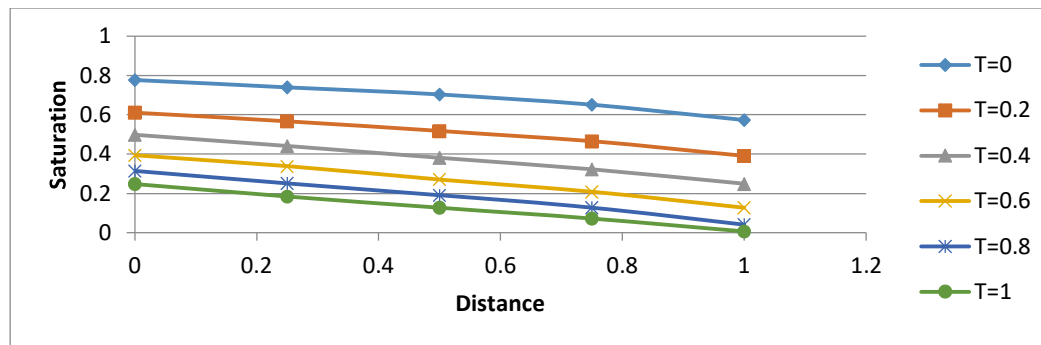


Figure-2: Saturation Vs Distance

Table: (2) Numerical results applying uniform grid points N=5 [08].

Distance X/ TIME T	0	0.25	0.5	0.75	1
0	0.776441	0.739154	0.702382	0.650311	0.572719
0.1	0.68541	0.632797	0.593125	0.546262	0.480943
0.2	0.610619	0.566622	0.516752	0.464727	0.390635
0.3	0.55296	0.498069	0.43835	0.386123	0.317834
0.4	0.497663	0.440617	0.38109	0.321922	0.248958
0.5	0.443545	0.385807	0.326932	0.259453	0.182468
0.6	0.39399	0.337775	0.270665	0.207681	0.127046
0.7	0.353552	0.291341	0.230665	0.169423	0.081176
0.8	0.314477	0.250856	0.190738	0.127801	0.04124
0.9	0.279433	0.211875	0.150527	0.103479	0.017421
1	0.247943	0.184444	0.12676	0.072168	0.005868

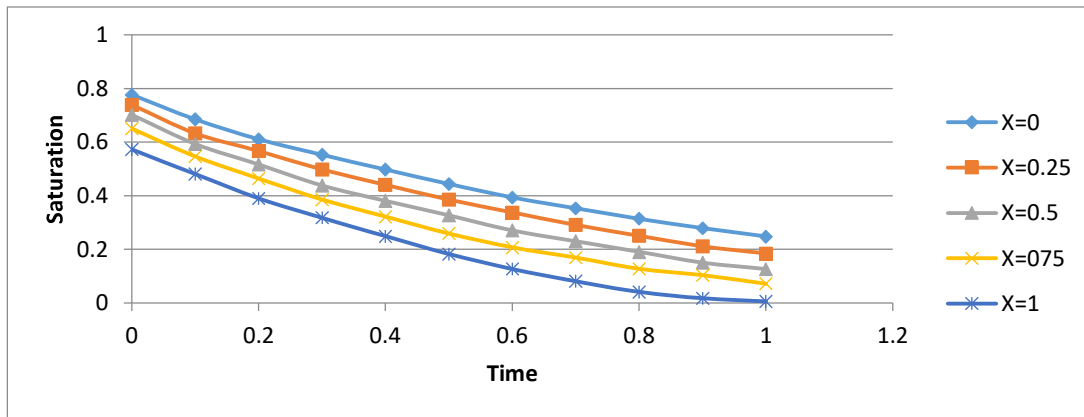


Figure-3: Saturation Vs Time

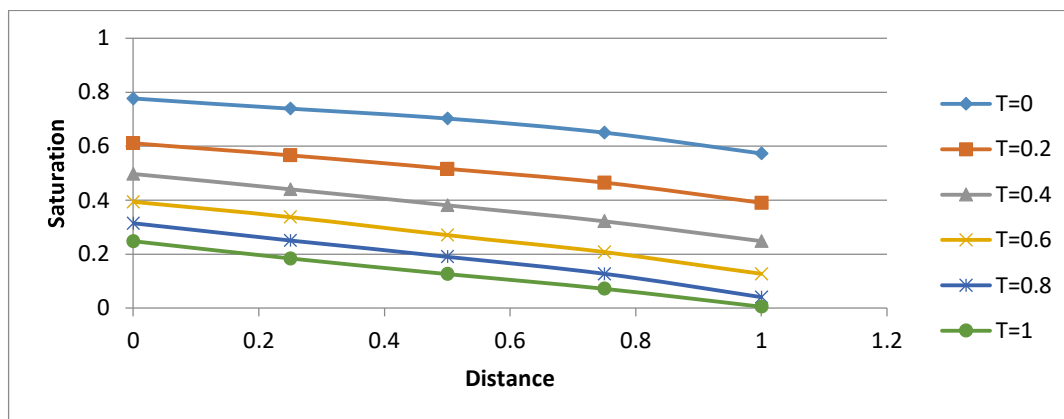


Figure-4: Saturation Vs Distance

Scope of the method and Problems:

The DQM will yield extremely correct solutions with comparatively little machine effort and storage necessities and, thus, are very suitable for recently in style personal computers. Moreover, the mathematical techniques concerned within the methodology aren't refined. So, the DQM is well learned and used. The theoretical analysis and numerical experiments conjointly show that the DQM is particularly economical for highly nonlinear issues. The numerical study shows that the right test functions are essential for the machine potency and responsibility of the DQM. It conjointly shows that the DQM provides similar results however with relatively quicker calculation speed, less nodes and memory usage. Compared with the opposite existing approaches, this approach shows easy use, smart stability, wide relevancy and high accuracy. Engineers in several fields have endeavored to be told the mechanics of drain and to use to issues of water system, land reclamation and stabilization of foundations and conjointly to the fields of rock oil production and agriculture [13].

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Broad spectrum application of nanotechnology for wastewater treatment

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34.1 Introduction

34.1.1 Water a basic but a limited renewable resource

Human civilization needs one of the most important valuable source, and a basic human necessity. It is an important solvent of life, which is being used by humans in daily life. For example, the average need of water per person is 40 L per day in India. [1] Various reservoirs present on the earth such as oceans and seas contain high amounts of salt in it comprising about 97.5% of total water available. The remaining 2.5% portion is of freshwater reservoirs such as ground water, freshwater lakes, rivers, glaciers and permanent snow cover. A total of 68.9% of this portion is unavailable as it is stored in permanent snow covers and glaciers. [2] Further details of distribution of water are shown in Fig. 34.1. Because of such limited resources of freshwater the problem of water supply could be more severe in developing countries, least developed countries, and heavily indebted poor countries.

34.1.2 Importance and problem of limiting water

Water is important and essential constituent of life whose demand is increasing day by day with the increase in population, industrialization, and advances in agriculture to feed the millions mouths. However, we are far from meeting the global demands; this problem will only increase with time [3]. The demand is increasing due to population growth, global climate change, and water-quality deterioration [3]. India being a developing country, with a rapid population growth, meeting demand of potable water to millions of people is very tedious job. Only 2.5% of the world's oceans and seas harness freshwater. However, 70%

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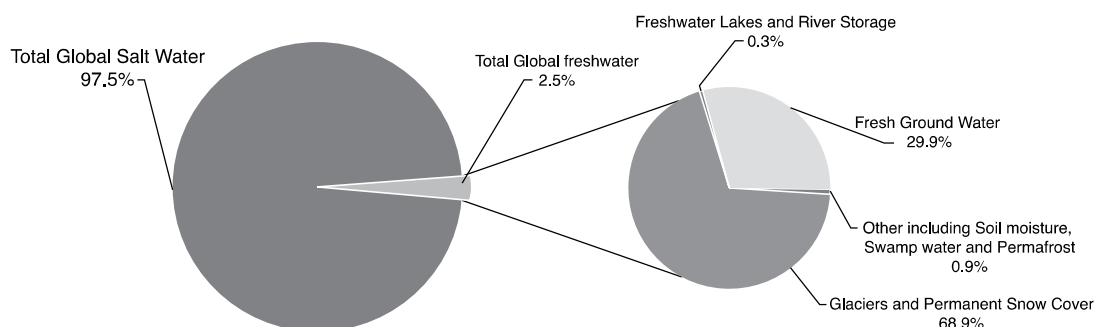


fig001

Fig. 34.1: Distribution of water on the earth (Source data: Shiklomanov and Rodda [2]).

of freshwater is frozen as ice. Only <1% of freshwater can be used for drinking. Globally, >700 million people do not have access to potable water. This problem is severe in developing nations [4].

para003

Waterborne diseases are serious issue in our country as reported by Ministry of Drinking Water and Sanitation. The department has reported a very alarming situation of 37.7 million Indians being contracted with pathogenic water-transmitted disease especially children with diarrhea [5]. Water is a precious resource, which has to be made accessible to all humans as a basic human necessity, which is a challenge in the current supply scenario.

para004

According to the WHO, globally still 780 million people are short of improved potable water [4]. However, the condition is still troublesome because of the poor quality of water, which is the root cause of all problems. The major concern is the microbiological contamination where fecal matter contamination mix with potable water due to poor sanitation management and deprived water storage capabilities. All these problems are genuine concerns of developing country like India, and have to be given attention at an urgent priority basis [6].

para005

As per report by the WHO in 2019, Eight of 10 people living in rural areas are still lacking even basic services. Same scenario is true for nearly half of the least developed countries. According to report by the UNICEF and WHO in 2019, 3 of 10 people were not able to use safely managed drinking water services in 2017. Providing sufficient amounts of water for drinking and domestic purposes to the huge population of many countries like India is a very challenging task. In addition, the industrial sector also has a high demand for water for many purposes. The management of water supply with limited sources requires micro-level planning at each and every step distribution. The disposal of industrial and domestic wastewater is another issue that should be considered as critical.

para006

In some cases, if water is plentifully available, contamination of ground water and other water bodies with a variety of xenobiotic compounds and microbial population is also a serious concern. Treatment of wastewater and purification of contaminated water can solve many problems related to water supply and consumption at various levels. The major problems of

developing countries are nonexistent water and wastewater treatment infrastructure. Human activities and anthropogenic pollution are contributing to the ever-increasing scarcity of water by contaminating it with dangerous pollutants. All these conditions have led to stringent water controlling standards with new scrutinization principles to the already available water treatment and circulation systems practiced in developed countries. Also, natural water resources are very unevenly distributed, which destabilize the uniform water supply [7]. The global climate change and increasing population demand have forced the system to use unconventional sources of water such as seawater, polluted brackish water, and contaminated fresh running water are currently being treated and used in water-deficient regions such as developing Asian countries and sub-Saharan nations.

para0007 [AU3] Only 2.5% of the world's oceans and seas harness freshwater, FW (salts concentration of <1 g/L). However, 70% of freshwater is frozen as eternal ice [7].

cesecititle0006 **34.1.3 Varieties of pollutant in water**

para0008 Varieties of pollutants can be found in wastewater and water from various bodies depending on its origin (Fig. 34.2). Such contaminants may be organic, inorganic, or biological that may also have deleterious effects on living organisms as well as the environment. Concentration of many of these pollutants is in parts per billion (ppb) or even parts per trillion (ppt) which is extremely low for efficient treatment but high enough to trigger health issues [9]. Removal of such pollutants from water is necessary before either making it potable or dischargeable because such water is hazardous to consumers and environment, respectively [10].

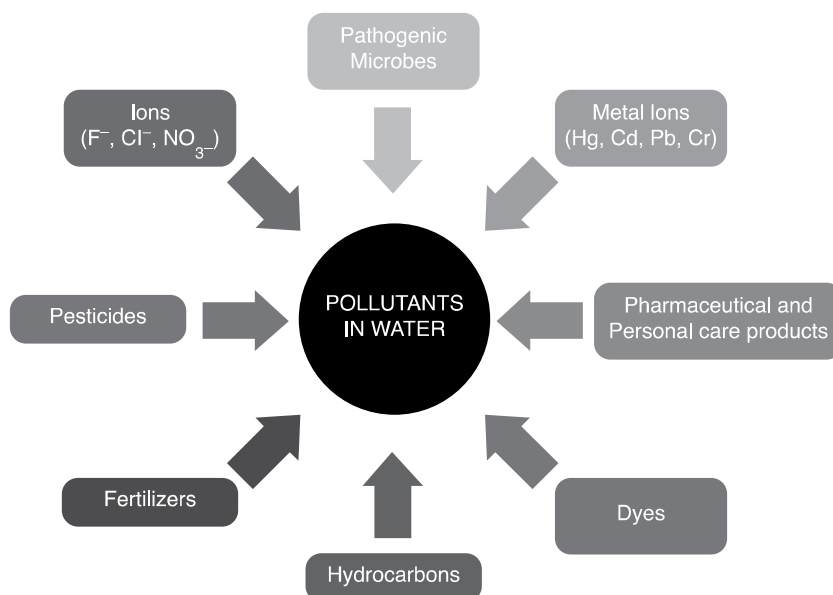


fig0002 **Fig. 34.2: Varieties of pollutants found in water.**

4 Chapter 34

cesecitle0007

34.1.3.1 Heavy metals

para009

Leaching of various toxic metals into ground water and other drinking water supplies occurs due to geological composition of aquifers. Their contrasting behavior under different redox conditions makes it difficult to degrade these metals [11]. Organic as well as inorganic form of arsenic is well known for causing cancerous and noncancerous health effects. Physiological activities of various cation, enzymes, and various steps of transcription are also affected due to arsenic [12]. Chromium (VI) is carcinogenic in nature, while intake of molybdenum in excess causes a physiological copper deficiency [13]. Other examples of metals with global concern include mercury, lead, cadmium, etc. [13].

cesecitle0008

34.1.3.2 Azo dyes

para010

Azo dyes are produced using aromatic amines and account for more than 50% of dyes produced annually worldwide. Synthetic azo dyes such as amido black, orange-G, methyl red, orange-II are used widely in textile industries and hence cause a severe contamination of various water sources nearby [14]. It has been estimated that during dyeing process, about 10% of the dyestuff do not bind to fibers and hence released in to environment. The conventional methods cannot readily remove these dyes from wastewater [10]. Because of the azo reduction, azo dyes form various cleaved products such as benzidine that is reported carcinogenic for humans causing tumors of the lung, stomach, rectum, and prostate [15]. Such azo reduction is reported to be carried out by degradation of azo dyes by human skin bacteria that express azo reductase activity. *p*-Phenylenediamine, a component of synthetic azo dye that is used as a hair dye component and in engineering composites and polymers, is a contact allergen [10].

cesecitle0009

34.1.3.3 Inorganic ions

para011

Varieties of inorganic ions are present in water especially due to industrial and agricultural practices. The presence of such ions does not cause any organoleptic changes in drinking water, increasing the possibility of not being detected. Nitrate ions present in water are reduced to nitrite in human gastrointestinal tract and causes methemoglobinemia. Nitrite and nitrate both can form carcinogenic N-nitroso compounds, while phosphate is directly connected with the formation of toxic cyanobacterial blooms in water. The administration of high concentrations of sulfate is responsible for causing dehydration, catharsis, and gastrointestinal irritation [17]. Fluorides are present as fluoride ion (F⁻) in natural water reservoirs. Fluoride levels of more than 1mg/L are responsible for dental and skeletal fluorosis. In addition, it may also cause lesions in liver and endocrine glands [18].

cesecitle0010

34.1.3.4 Hydrocarbons

para012

Most common hydrocarbons of environmental and human health concern are polycyclic aromatic hydrocarbons (PAHs) that can be released from either natural or anthropogenic sources

and found throughout the environment. The anthropogenic sources include incomplete burning of fuels, coal, oil, gas, plant materials, and other organic substances. Few PAHs are also used in medicines and to make dyes, plastics, and pesticides [19]. Although the solubility of PAHs in water is very low, various PAHs have been found in water, for example, anthracene, benzopyrene, chrysene, fluoranthene, and phenanthrene. Key factor determining the concentration of PAHs in surface waters is organic loading of aqueous systems as it directly affects solubility of PAHs [20]. PAHs can accumulate in any of the internal organs especially those rich in adipose tissue [21]. The exposure to PAHs for longer periods of time results in lethal effects on skin, brain, liver, kidneys, reproductive system, and immune system of animals [13]. Short-term effects of PAH exposure include nausea, vomiting, irritation, and diarrhea. In addition, experimental studies in animals had revealed teratogenic ability of PAHs. The human studies showed that exposure to benzo[a]pyrene, a PAH compound, is associated with various neurological issues such as lower IQ, childhood asthma, and increased behavioral problems [20].

cesectitle0011 **34.1.3.5 Pesticides**

para0013 Most pesticides are organochlorine compounds that are highly effective against insects in agriculture. Due to their effectiveness and lower cost, pesticides are also applied extensively to protect agricultural land, flower gardens, stored grains, and for sanitization purposes. Agriculture farms discharge large quantities of agrochemicals including pesticides into environment. Pesticides such as DDT, PCBs, and lindane are degraded very slowly [9,22] Many pesticides are found to be exhibiting fatal health effects. Lindane can cause CNS intoxication [23], while occupational exposure to DDT can increase psychiatric and neuropsychological symptoms [23].

cesectitle0012 **34.1.3.6 Pharmaceutical and personal care products (PPCP)**

para0014 Pharmaceutical and personal care products (PPCPs) are emerging contaminants and are originated from hospital and household waters. They are present in concentrations from nanogram per liter to microgram per liter in water. Due to such low concentrations of PPCPs, the conventional methods used for water treatment may give unsatisfactory results. Usually, PPCPs are resistant to natural means of biodegradation. The examples include various drugs and their products and additives to detergents [25]. The presence of PPCPs in even nano-level concentrations in natural bodies poses eco-toxicological risks [24].

cesectitle0013 **34.1.3.7 Microbes**

para0015 Pathogenic microbes present in water are responsible for causing several waterborne diseases and is major reason for more than 2 million deaths worldwide annually among which most are children of less than 5 years of age [11].

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cesectitle0014

34.1.3.8 Nanoplastics

para0016

Huge amount of plastic material is disposed throughout the world and is a serious concern for environment. Even, the worldwide demand of plastic materials is increasing day by day. In marine environment, the persistence of microplastics has been studied and their presence as a major constituent of anthropogenic marine debris is uncovered [18]. Fibers closely resembling acrylic and polyester fibers used in clothing were detected at costal sediments where the sewage is discharged [26]. However, clear confirmation regarding the occurrence of nanoplastics in aquatic environments and biota is not thorough enough because of a lack of proper methods for the reliable detection of plastic nanoparticles (NPs) in samples [27]. A study of effects of microplastics on living organisms showed that it can be taken up by the digestive cells which in turn results in induction of distinct adverse effects [28].

cesectitle0015

34.1.4 Different types of problem associated with water contamination

para0017

Water contaminates with organic, inorganic, and biological agents. Some contaminants are toxic and carcinogenic and have deleterious effects on humans and ecosystems [2]. Some heavy metals are notorious water pollutants with high toxicity. Arsenic is one of the deadliest elements, well known since ancient times. Other heavy metals water pollutants with high toxicity are cadmium, chromium, mercury, lead, zinc, nickel, copper, and so on; they have serious toxicities [2]. Nitrates, sulfates, phosphates, fluorides, chlorides, selenides, chromates, and oxalates show hazardous effects at high concentrations; these ions also change the characteristic of water.

para0018

For example, a high level of fluoride in water causes fluorosis. Organic pollutants such as pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, and greases are associated with toxicities [29]. Emerging contaminants include pharmaceuticals and personal care products [5]. PPCPs are usually resistant against natural biodeterioration.

para0019

The general origin of such compounds is household and hospital water, which contains metabolized and nonmetabolized, that is, drugs, drugs products, additives to detergents, and packaging. Therefore, water treatment must be implemented in these affected places. Available technologies for water treatment are reaching their limits in providing sufficient quality to meet human and environmental needs [29].

para0020

Aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes, labeled as BTEX, are the most predominant components in water treatment unit among other volatile contaminants. These volatile organic compounds can easily evaporate when water is exposed to the atmosphere. BTEX chemicals are toxic and have carcinogenic persistent contaminants. The current maximum contaminant levels ($\mu\text{g/L} = \text{ppb}$) for BTEXs is benzene 5; toluene 1000; ethylbenzene 700; xylenes (total) 10000. As customary procedures of water purification (filtration, flocculation, and sedimentation) do not remove organic compounds at low

concentrations, eliminating BTEX pollutants is challenging. Hence, recycling and reuse of water is an essential requirement of the current times. Therefore, reuse, recycle, and repurpose are the “needs of the day.” Hence, the conventional water treatment provides unsatisfactory results, because treatment facilities are not equipped to remove stable low-concentrated pollutants. Effluent water containing hydrocarbons necessitates measures that are fast and simple. Moreover, current treatment expertise and infrastructure are bounded for providing sufficient water superiority to meet individuals and ecological needs [29]. The objective for the present water scenario is reuse, recycle the water, by achieving these targets we can fulfill the needs and demands of the current situation. Working expenses depend on various factors, but nanotechnology is getting highly advanced day by day and hence can be the key arm of mankind by developing the next-generation systems for solution of problems related to treatment of water.

cesectitle0016

34.1.5 Implications of contaminant water on human health

para0021

With the recent advances in industrialization and technology advancement, there arises new water-associated pathogens. These emerging waterborne pathogens are new serotypes of the conventional harmful organisms like *Vibrio cholera* O139 and enterohemorrhagic *Escherichia coli* (*E. coli* O157:H7). One of the conventional methods of water treatment is excessive chlorination, which has resulted in upcoming of chlorine-resistant strains of cryptosporidium. Many other new protozoa and viruses such as *Microsporidia*, *Cystoisospora belli*, adenoviruses, and parvoviruses are also becoming potential threats to human health. The exploited use of antibiotics has led to the emergent of multidrug-resistant *Pseudomonas aeruginosa*. Together all these infectious and harmful rising pathogens are becoming a health concern [30]. These organisms cause fatal and serious diseases such as gastroenteritis, cholera, urinary tract infection, kidney failure, hemorrhagic fever, and dysentery. All these organisms minimum infectious dose vary to cause severe infection in healthy or immunocompromised patients [31].

para0022

The negative impact of using unsafe, contaminated, and polluted water can be seen on every sphere of life and economy. Human use of hazardous water causes health issues sometimes, which may be fatal leading to massive economic losses. A report submitted by the World Health Organization (WHO) has estimated that two million people die every year due to waterborne diarrheal diseases, where most of the mortalities occur due to drinking harmful inadequate water [32].

para0023

[AU4]

The economic burden to cure and treat these diseases is causing serious impact on the developing and underdeveloped countries. The monetary losses to treat these infectious diseases are estimated to be approximately \$3.8 billion. The costliest and advanced hospitalization systems required for the treatment of *Campylobacteriosis*, *Cryptosporidiosis* which is almost \$1,783, \$2,035, \$1,709. All these losses to economy will have deleterious effect on the prosperity of country's development [33].

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cesecitile0017

34.1.6 Traditional techniques for treatment of water with their limitations

para0024

With the increasing population, it is estimated that by 2020, the global population would be around 7.9 billion, so it is necessary that we save the world from the severe water scarcity. With the limited supply of water, we have to utilize it maximally, so that all the contaminated sources can be made pollutant free to have healthy life [34].

para0025

The traditional techniques for treatment of drinking water follows a train of treatment process chain where chlorination is carried out along with filtration. Filtration is aided with other processes such as coagulation (by adding chemicals such as alum, ferric chloride, and ferric sulfate), flocculation (physical process involving gentle stirring of water to increase inter-particle collisions), and sedimentation (a physical process based on gravitational settling of suspended particles) [35].

para0026

Wastewater can be from different sources that are primarily defined as domestic and industrial sources. The treatment of domestic wastewater is more complex compared to the treatment of drinking water. It involves the process in various stages. The primary treatment includes the separation of large solids from the stream of wastewater by using filtration and sedimentation techniques. In the secondary treatment, the suspended solids are allowed to decompose by microorganisms which in turn results in the reduction of overall pathogens. Finally, in the tertiary treatment physicochemical processes are undertaken to achieve further reduction of turbidity, organics, phosphorus, nitrogen, metals, and pathogens [35]. Industrial wastewater has different compositions depending on its origin and discharge timings [36]. All the chemical methods utilized for the treatment of water have their own disadvantages such as use of inorganic coagulants requires more time to settle as they form smaller and lighter flocs, which, in turn, reduces its efficiency. One more disadvantage of inorganic coagulants is pH sensitivity because of which they work in a narrow pH range [37]. Other problems faced by using chemical methods are cost of operation and materials, requirement of regeneration due to rapid clogging of the reactors, the elimination of adsorbents, etc. [38]. Biological methods used for the treatment also have limitations. In this case, an optimally favorable environment is necessary to be created to support biological reactions and maintain microorganisms required for it. Other issues faced in biological methods are related to kinetics, low degradability of certain molecules, poor decolorization, sludge bulking and foaming, etc. [38]. Application of nanotechnology can provide promising solutions to many problems associated to the traditional processes used for treatment of water.

para0027

All the methods described earlier are used since ages but all are not efficient or sufficient for removing all types of pollutants. Thus for a better prospective, the methods are combined according to the contaminants and intensity of pollution [39]. Also, the cost associated with these technologies also limits their uses on a large scale. The continuous use of these water treatment strategies also leads to the decrease in the efficiency of these plants [40]. In recent

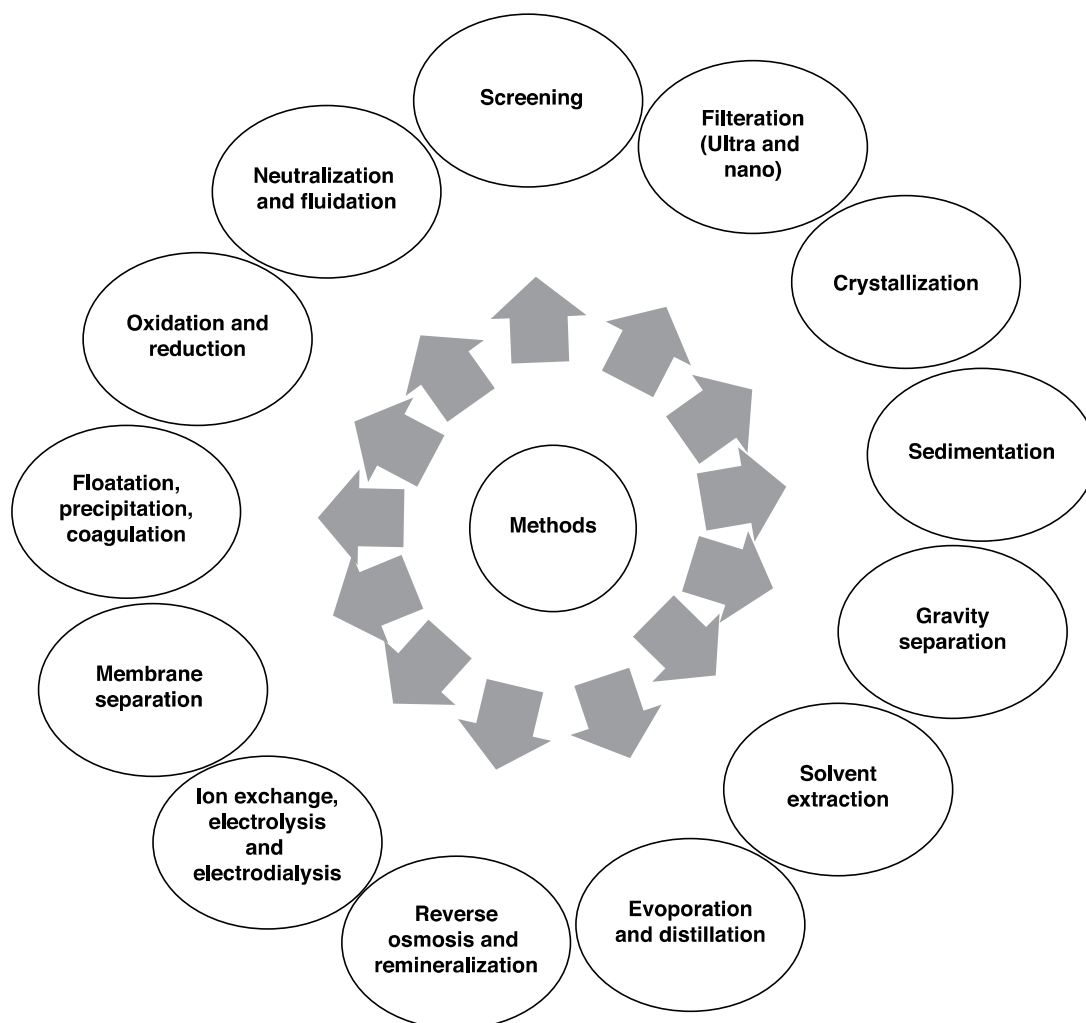


fig0003 [AUS]

Fig. 34.3: Different methods currently employed for water filtration (Ali [3]).

years, we have observed a tremendous increase in nondegradable, novel anthropogenic pollutants that are very difficult to remove by the use of the traditional treatment strategies. The following figure shows the conventional methods used for the treatment of water to obtain potability but also the limitations that are linked with each of the techniques [23]. With the disadvantages posed by the conventional method, the necessity arises to search for new technologies that are cost effective, efficient, easy to maintain, and less energy consuming.

para0028

The current methodologies, such as chlorination, ozonization, and use of chloramines compounds, applied for disinfection process are efficient to treat the virulent organisms. However, the recent research has exposed the fact that these disinfection procedures can form

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disinfection byproducts (DBP) that are harmful or may be carcinogenic and using disinfection methods for them is surrounded by dilemma [41]. Some of the carcinogenic byproducts cited in the literature are nitrosamines, bromated, halogenated DBPs [42]. Some of the alternative methods employed are UV-disinfection that causes lesser DBPs, but the disadvantage of this procedure is they are required in very high dose to kill the viruses. Hence their arise a strong urge to find the best alternative method that is efficient, safe, robust, and free from the disadvantage posed by the traditional disinfectants discussed earlier [41].

para0029

Some of the common properties that an ideal disinfectant should possess are as follows [43]:

celistitem0001

1. Broad spectrum nature to disinfect maximum of microorganisms at ambient temperature

celistitem0002

2. No harmful and deleterious byproducts

celistitem0003

3. No problems to human health

celistitem0004

4. Cheap and easily available

celistitem0005

5. Easy to maintain and store

celistitem0006

6. Highly water-soluble and noncorrosive

celistitem0007

7. Disposal should not cause any environment hazards

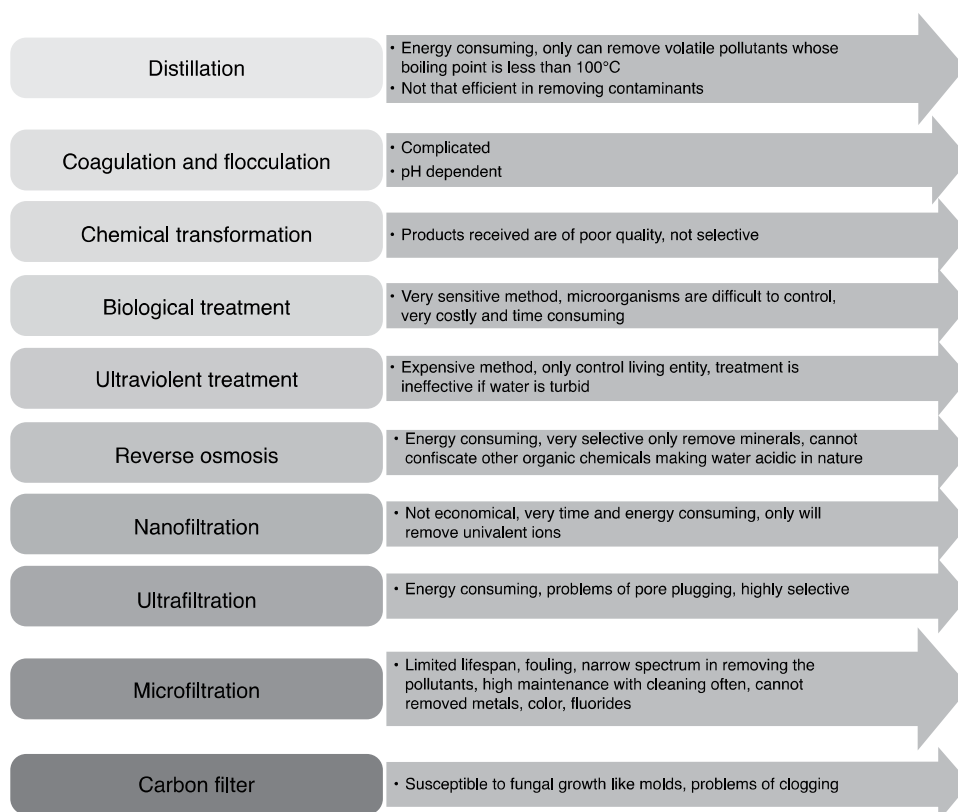


fig0004

Fig. 34.4: Uses of currently available different treatments of water.

cesectitle0018

34.2 Why need advance approach: Nanotechnology for treatment of water

para0037

Various conventional methods are used to process effluent treatment of water. In distillation, most contaminants remain behind and require high amounts of energy and water.

para0038

Pollutants with boiling point $>100^{\circ}\text{C}$ are difficult to remove. Chemical method is not a highly selective method, because this method needs excess reagents. Product may be a low-quality mixture and cannot be released into environment. Inactive in harsh conditions. The third approach, coagulation and flocculation, is a complex and less-efficient method and requires alkaline additives to achieve the optimum pH for the treatment of effluent.

para0039

In biological treatment approach, microorganisms are sensitive to environmental factors and difficult to control. Intermediates damage the microbial cells. This is not cost-effective and time-consuming process. Ultraviolet treatment is an expensive method and inactivated by water cloudiness and turbidity. It is ineffective for heavy metals and other nonliving contaminants removal. Reverse osmosis method removes unhealthy minerals from water, and the treated water will be acidic. This method cannot remove volatile organics, chemicals, chlorine, chloramines, and pharmaceuticals. It requires high energy for the treatment of effluent system.

para0040

Nanofiltration technique requires high energy and pretreatment. The is limited retention for salts and univalent ions. Membrane fouling will occur with limited lifetime and expensive method and ultrafiltration will not remove dissolved inorganics. This method requires high energy, is susceptible to particulate plugging, and is difficult to clean filter.

para0041

Microfiltration cannot remove nitrates, fluoride, metals, sodium, volatile organics, color, and so on. This technique also requires regular cleaning. Membrane fouling will occur. It is less sensitive to microbes, especially virus. Carbon filter cannot remove nitrates, fluoride, metals, sodium, and so on. Clogging occurs with undissolved solids. It is susceptible to mold and requires frequent changing of filters in system. The unconventional methods are a challenging task for the effluent treatment of water.

para0042

Wastewater treatment processes by nanotechnology show great innovation in laboratory studies. Before scale up of advance techniques; some of these technologies are marketed, and others require significant research. Their commercialization is challenging; we need to overcome many technical hurdles to make them cost effective and safe. Research is needed before a full-scale operation of nanotechnology for treating natural and wastewaters.

para0043

Studies should be conducted under realistic conditions to assess the efficiency of available nanotechnology to validate the nanomaterial-enabled sensing. Another research need is to measure the long-term efficiency of available technologies, which are conducted on a laboratory scale. The commercialization of these technologies is possible only by their long-term performance in the treatment of wastewater. Also, the adoption of an innovative technology

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strongly depends on the cost effectiveness and potential risks involved. At the moment, the cost of nanomaterials is very high, with few exceptions, such as nano-TiO₂, nano-scale iron oxide, and polymeric nanofibers. Cost effectiveness can be achieved by the regeneration and reuse of these nanomaterials [44]. As these materials are nano-scale, risk assessment and management is a challenge. Researchers should understand the potential hazards of these materials in the treatment of wastewater.

cesecite0019

34.3 Importance of nanotechnology in water treatment

para0044

India being a developing nation, our current water storage and distribution systems are mostly dependent on conveyance, centralized system has mostly failed to sustain the pressure of current targets. Recently, science has reached sky limits and has started using nanotechnology that provides ample opportunities to develop the next-generation supply systems that are efficient, multitasking, and very efficient. The nanotechnology tools are affordable, which are envisaged to be sustainable solutions to the current water treatment strategies that one time was thought of only relying on large infrastructure stuffs [45]. These technologies utilizing nanotechnology approaches have the capacity to overcome all the technical hurdles faced by the present water treatment methodologies.

para0045

These nanotechnology-based strategies provide novel capabilities that allow best reuse, repurpose utilization of our unconventional water resources to solve our deficit water supply problems [46].

para0046

The last decade has gained much attention in the utilization of nano-based materials, which has been considered to be the best probable way to kill harmful waterborne pathogens in real time [47]. Numerous nano-based devices such as catalysts, nanomembranes, and different metal-based NPs (MNPs) are offering great advantage due to nano-scale sizes, which immensely increase the surface areas. These nanomaterials are having promising outcomes because they have implausible physical and chemical properties. The nanomaterials in routine use are: alum silicate, MNPs such as zinc oxide (ZnO), carbon mixed with NPs, dendrimers, etc.

para0047

These nano-based particles are biocompatible and biosafe, which have different mechanisms, such as ZnO, to obtain bactericidal activity and have natural water filtration ability [49]. These nano-based metal particles are capable of generating free radicals of oxygen, which interfere with the lipid molecules of bacteria and destroy the cell membrane eventually causing death of the pathogenic organisms [48,50,51]. Other NPs used are broad spectrum silver NPs [49] that give bactericidal properties by interacting with the protein thiol group of cell membrane, which causes damage in the cell membrane and blocks the replication of DNA in prokaryotic bacterial cells [49]. Today silver NPs are used in the real time to disinfect the water by adding these particles in the water disinfecting units [52]. Another interesting NP

currently being used is copper oxide (CuO) that has antibacterial mechanisms by blocking the majority of the vital process of microorganism [53]. Beside these NPs, other nanodevices used are carbon nanotubes (CNTs), graphenes, fullerenes that are coated on the filter membrane and are recognized as best adsorbing agents for the removal of all types of bacteria, viruses, and other polluting agents [54].

34.4 Strategies and properties of nanotechnology in treatment of water

Nanotechnology provided innovative solutions for effluent treatment of wastewater. Nanomaterials are fabricated with features, such as high aspect ratio, reactivity, and, hydrophilic, and hydrophobic interactions, which are useful in adsorption, catalysis, sensing [54]. Nanotechnology-enabled processes are highly efficient, multifunctional in nature, provide high performance, and wastewater treatment solution. Materials consisting of nano-objects are durable and instantiated by high specific surface area. In other words, a huge surface-to-volume ratio controls the interaction with pollutants. Nanotechnology-enabled processes for the water treatment constitute major challenges to the existing methods. Nanotechnology can also be extended to the purification and utilization of unconventional water sources in an economic way.

Treating industrial wastewater with nanomaterials is also important and widespread. The remediation technologies available now are effective, but they are costly and time consuming.

Nanotechnologies are advantageous in treating wastewater, as they eliminate contaminants and help in the recycling process to obtain treated water. This leads to the reduction in labor, time, and expenditure to industry solving various environmental issues [56].

It should be noted that nanomaterials for the treatment of water must be environment-friendly and nontoxic. Unsafe particles can cause severe injury to vital organs upon contact with the human body. Due to dimensional features, nano-objects may translocate to various organs, which aggravates the danger of biological damage.

34.5 Utilization of innovative nanomaterial and nanodevice in treatment process

The traditional methodologies used for the purification of water are based on two important processes: First the removal of toxic chemicals, which is called decontamination and second the removal of harmful parasites and pathogenic organisms called as disinfection. The different process that help in achieving these goals are used to remove chemical, biological, or disinfecting the water [57].

All these process, that is, adsorption, chelation, coagulation, ion exchange, boiling, UV treatment, filtration, and ozonation have advantages, but they are also associated with

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drawbacks. Many of this process can only be used with small-scale set up, as it is not at all economical to scale up this process as it will cause more secondary pollution. Some of the disinfecting process used can only kill the vegetative living cells living behind the resistant forms of cysts and spores that will continue to be present in the water even after the treatment. These resistant structures will overcome the harsh treatment of chemicals or biological approaches and will persist until it has found a host where it will show its virulent behavior. Some of the chemical process produces secondary pollutants such as trihalomethanes that may be carcinogenic [58].

para0054 Nanotechnology is a wing of science concerned with analysis, functions, and molding of material at nanoscale. The term “Nano” is originated from the Greek for “dwarf” [59]. Nanomaterials can be defined as materials with at least one dimension smaller than 100 nm [54]. Manufactured nanomaterials were also entitled “Well-known chemicals in a new dress” by Liu et al. [54] as these materials completely change their behavior and fate in such a physical state. Dr. Horst Störmer, a Nobel laureate and discoverer of fractional quantum Hall effect, mentioned nanoscale as more interesting compared to the atomic scale because nanoscale is the first point where one can start assembling something. Innovations in nanotechnology had brought great transformation to many scientific and industrial areas such as food, agriculture, medicine, engineering, etc. Briefly, it is almost impossible to find a field where nanotechnology had not made any advances. Because of its smaller scale with promising solutions, it can also be considered as a “small solution to big problems.”

para0055 Nanomaterials are having a wide variety of application in field of chemistry, physics, optics, biomedical sciences, electronics and mechanical devices [60], drug delivery [58], and bioencapsulation [60].

para0056 A characteristic of these nanomaterials is their large surface area that increases their rate of reaction. Nanomaterial provides high surface area to volume ratio in comparison to their normal form; there advanced application in recent time includes TiO₂ in cosmetics, advanced self-cleaning windows and sunscreen, nanocomposites and nanocoatings in automobiles and bicycles [61].

para0057 The preparation of nanomaterials by development of processes having less cost effect and high turnover is an impressively big challenge since the beginning of nanoscience.

cesectitle0022 **34.5.1 Different type of approaches**

para0058 A different type of top-down and bottom-up approaches is being applied up till now, for the economic production of nanomaterial [62]. The top-down approach includes carving of small size creation from big raw molecules with different procedures and bottom-down way of processing includes assembly from small-sized material into nanomaterial [63].

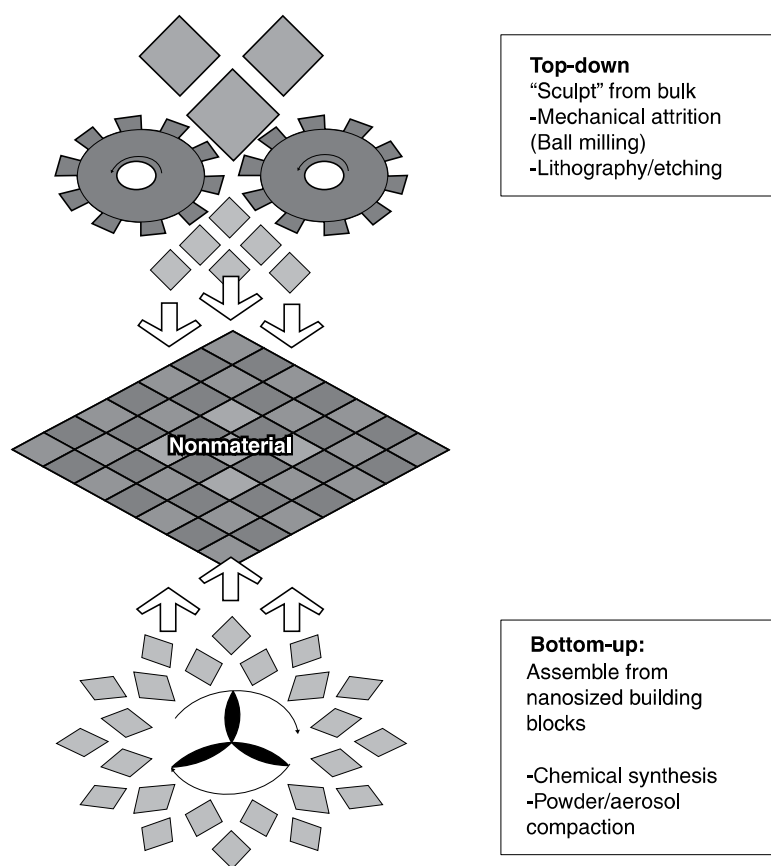


fig005

Fig. 34.5: Schematic diagram of top-down and bottom-up processes (Data Source: Sobolev and Gutiérrez [82]).

para0059

Top-down approach is widely used for the preparation of carbon nanodots (CDs) and graphene quantum dots (GQDs) using CNT, graphene, suspended carbon powders, graphite column, and such compounds by physical cutting that is, top-down methods. The majority of cutting-down processes for the formation of CDs includes electrochemistry, laser irradiation, and chemical oxidation [65]. The work of John Benjamin [85] and his co-workers has shown the successful production of fine and uniformly dispersed particles of Al_2O_3 , Y_2O_3 , ThO_2 and in addition to this some other reactive components such as Ti. This process of synthesis of material at high temperature is known as ball minning [66]. This top-down method can be used to make metal compounds, composites, and new materials with some special properties [67].

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para0060 One can also synthesize copper-doped TiO₂ having size in nanometer, with the help of this mechanical alloying technique [68].

para0061 In mechanical milling method, an appropriate powder is placed in a high energy mill in mixture with appropriate milling medium. The reduction in the particle size and blending of particles in new forms is the main objective of this technique. A variety of ball milling can be used to synthesize the nanomaterials [69]. A variety of ball milling can be used to synthesize the nanomaterials [88]. Mechanical millings economical processes are used for the large-scale nano-sized material production [70].

para0062 In electrochemistry method, ideal material for electrode is a CNT and graphite, and they are widely used as a carbon sources for nanodots; various methods are being developed for the conversion of nanodots from multiwalled CNTs [69]. The benefit of this method is economically feasibility and ease to manipulate [70].

para0063 Another approach of the chemical oxidation is an easy and impactful approach for the bulk production; using oxidative reagents chemical oxidation of substrate can be carried out [68].

para0064 Laser irradiation method synthesis occurs via high heat and high pressure produced by laser. The original synthesis using this method consisted few strict reaction and complex steps, which involved employment of laser for irradiation of graphite powder suspended in organic solvent [71].

para0065 Another bottom type of approach exactly opposite to the top-down technique is bottom-up technique, where small building blocks assemble to form a complex structure; small molecules assemble due to their specific binding site known as “Molecular recognition properties” by which they arrange themselves properly in a correct way. Self-assembly is the key feature in the bottom-up approaches, pairing of antigen-antibody and DNA double strands are examples of this mechanism [72]. Material synthesized using bottom-up approach harbors some advantages against other molecules in context of chemical variety and an amazing modification of position and orientation to obtain vast surface area and chemical scale [73]. Commonly used methods in bottom-up approaches are: microwave-assisted synthesis, thermal decomposition, ultrasonic synthesis.

para0066 Another innovative nanotechnology approach based on adsorption techniques can be defined as capability of all solid substances to attract molecules, ions, or atoms from liquid, dissolved solids, or gas. The solid material used for adhesion is referred as an adsorbent, while the adsorbed molecules are called an adsorbate. Adsorption may results in the formation of a monomolecular layer of adsorbate on adsorbent. The invariable physicochemical properties of adsorbent, such as chemical composition, ultimately determine the degree at which adsorption will occur [74]. Other factors that can affect adsorption are surface area, selectivity, and adsorption kinetics. Due to small size, extremely high specific area can be achieved in case

of nanoadsorbents. The utilization of nanomaterial can be advantageous as it minimizes the adsorbent material required. In addition, a superior adsorption efficiency makes it easier to design compact devices with smaller footprints for the treatment of water and wastewater especially for decentralized applications.

para0067

Metal-based nanomaterial in which nanomaterials utilized some metals and their oxides had received attraction of many researchers. Depending on metals and their oxides, various advantages can be achieved by metal-based nanomaterials. Metals such as silver, gold, iron, copper, palladium, and zinc have been reported to be used for synthesis of NPs [75]. Synthesis of such NPs can be done via chemical, physical, or biological means with the help of either top-down or bottom-up approaches. Methods utilized for the synthesis of NPs may involve chemical reduction, irradiation reduction, electrochemical reduction, photocatalytic or photoinduced reduction, ultrasonic-assisted synthesis, microwave-assisted synthesis, template method, and microemulsion method [76]. Biogenic synthesis of NPs has been categorized in to bottom-up approach. Biogenic synthesis includes synthesis of NPs using bacteria [77], fungi, and plant sources.

para0068

Zero-valent silver NPs (AgNPs) are highly toxic for many microbial species. Hence, it can exert antibacterial, antifungal, and antiviral effect. The antimicrobial property of AgNPs is due to the release of Ag^+ ions, because of which they can be effectively used for disinfection of water. Deposition of AgNPs on carrier materials such as blotting sheet made up of cellulose can be a cheap and efficient point-of-use method for purification of drinking water. These AgNP sheets achieved good log reduction values against *E. coli* and *Enterococcus faecalis* on percolation of water through it, indicating inactivation of bacteria. Similarly, polyether sulfonate membranes prepared using a phase-inversion technique incorporating AgNPs by the chemical reduction were observed to inhibit *Pseudomonas fluorescens*. In a study about assessing the potential of zero-valent AgNPs to revert adverse effects of cadmium (Cd) and lead (Pb) on a plant *Moringa oleifera*, the AgNPs were found to reduce mobility of Cd and Pb by adsorption thereby attenuating the oxidative stress induced by them. Such AgNPs can also be beneficial treatment of water containing both these heavy metals. Biogenically synthesized iron NPs–calcium alginate hydrogel composite membrane was tested to carry out the removal of chromium from wastewater containing 1mg/L Cr (VI). It was found able to remove 99.5% of Cr (VI) from wastewater. It is proposed that the membrane itself acted as a carrier for biosynthesized iron NPs, while the removal of Cr (VI) occurs through adsorption on calcium alginate membrane as well as on immobilized iron NPs giving a synergistic effect. The calcium alginate hydrogel may also protect the iron NPs from oxidation.

para0069

Zero-valent iron NPs (ZVINS) have multiple applications in water treatment. ZVINS were found to be able to completely inactivate *Bacillus subtilis var. niger* and *P. fluorescens* on treatment with 10 mg/mL ZVINS aerobically under vigorous shaking. Iron sulfide NPs synthesized by *Shewanella oneidensis* MR-1 (ATCC700550) have been tested for the removal of

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Cr (VI) from water with competitive efficiency. In addition to all these applications, ZVINS were also testified to successfully carry out decolorization of dyes with 95% efficiency within just 6 h.

para0070 Biogenically synthesized Pb-based NPs had captured attention of researchers due to their eco-friendly nature and antimicrobial ability.

para0071 In the metal oxide NPs, metal oxides such as titanium dioxide, silver oxide, copper oxide, iron oxide, stannic oxide, and alumina are effective and economically feasible adsorbents for many of the heavy metals and radionuclides. Copper is well known for its ability to kill microbes. Similarly, NPs synthesized using Cu_2O were effective against Gram-positive bacteria such as *B. subtilis* (MTCC 869), *Staphylococcus aureus*, and Gram-negative bacteria such as *E. coli*, *P. aeruginosa*. Hence, can be efficiently utilized for disinfection purpose of water.

para0072 Titanium dioxide (TiO_2) has been of huge importance in variety of applications including the complete removal of dyes such as congo red from water [95], In addition, it is also helpful in case of wastewater treatment. TiO_2 NPs show aggregating behavior when it interacts with humic acid and metal ions such as Pb^{2+} . It can greatly improve the removal of such things from wastewater. The reason behind such behavior was reported to be complexation between Pb^{2+} and humic acid [81].

para0073 In a study by Yue et al. [63], TiO_2 NPs were loaded on to surface of oxidized chitin NPs. These NPs exhibited the removal of methyl orange by synergistic action adsorption as well as photocatalytic degradation. Within 150 min, 8.5% adsorption of methyl orange was observed while 97.3% photocatalytic degradation was recorded after 90-min exposure to UV rays. In terms of reusability, these NPs performed very well by maintaining 96% methyl orange removal efficiency after 10 reuse cycles.

para0074 Carbon-based nanomaterial was first reported by Ijima [64], CNTs are outstanding in terms of unique chemical, physical, and mechanical properties and most commonly applied in the removal of heavy metals and dyes from wastewater. Depending on the manufacturing process, they can be categorized into two categories: single-walled nanotubes and double-walled nanotubes.

para0075 The important properties of CNTs include high specific surface area, adjustable surface chemistry, and highly reckonable adsorption sites. Due to hydrophobic surface, CNTs, should be stabilized in aqueous suspensions to avoid aggregation, which, in turn, may reduce its active surface. Adsorption data of a hybrid structure containing CNT/ ZnCo_2O_4 based on the Langmuir isotherm and the pseudo-second-order kinetics highlighted CNT-based material ideal for the adsorption of eosin Y dye. The reusability study indicated its strength to be used for at least five times. Similarly, the adsorption of other dyes such as indigo carmine, methylene blue, and acid orange 7 [92] with CNT-based materials is also reported that can be useful for treatment of water.

para0076

A nanocomposite made up of nickel zinc ferrite with CNT can be used for adsorption of arsenic (V) from wastewater by surface complexation as a dominant mechanism of adsorption. The elimination of other metal ions such as zinc (II), lead, chromium (VI) is possible using CNT-based nanomaterials. Nearly 100% removal of other pollutants belonging to category PAHs such as naphthalene, phenanthrene, acenaphthene, pyrene, fluorene, fluoranthene, and benzo[a]pyrene from well, rain, and agriculture water is successful using β -cyclodextrin–CNT composite. As we discussed earlier, PPCPs are one of the major concerns in wastewater. CNT-based nanomaterial Zn^0 -CNTs- Fe_3O_4 can be used for adsorption-oxidative removal of an antibiotic oxytetracycline. Wastewater treatment to remove two more antibiotics, sulfamethoxazole and ketoprofen, had also been reported using CNTs.

para0077

Photocatalytic degradation involves attractive means of application of light rays along with the nanomaterials for the removal of various pollutants from water. Various toxic organic compounds such as *p*-nitro phenol and coumarin along with Cr (VI) can be photoreduced using CNT-based nanocomposite material.

para0078

Graphene is typically made up of carbon atoms arranged in one or more atomic layers forming a unique two-dimensional structure with reliable thermal, mechanical and electrical properties. Many new approaches are attempted to utilize the potential of grapheme. In one of the attempts, a biphasic paper containing grapheme oxide and chitosan was prepared and used for treatment of wastewater. It was found beneficial for the adsorption of cationic as well as anionic dyes such as methylene blue and methyl orange. In addition to adsorbing dyes, this paper was also found to bear antimicrobial property against *E. coli* and *S. aureus*. Antimicrobial activity against these both microbes has also been reported by using graphene-based ultrafiltration membrane with antifouling property against bovine serum albumin. The antifouling property and superior permeability of the ultrafiltration membrane might be attributed to a guanidyl-functionalized graphene/polysulfone mixed matrix [94]. Graphene-based nanomaterials have also been deployed for treatment of water with a special purpose of removal of heavy metals. Beneficial results for adsorption of uranium (VI) from mine-drainage contaminated water using phosphate-functionalized graphene oxide nanosheets have been observed. Treatment of lead-contaminated water using various strategies including graphene oxide as a support material with bentonite and ZVINs had exhibited a satisfactory removal of lead by adsorption.

para0079

[AU7] Polymeric nanoadsorbents such as dendrimers had gained attraction of researchers because of the excellent adsorption capacity and thermal stability at various pH due to its hyperbranched polymeric nature. Polymeric adsorbents can be used either as a template or a bed to develop nanomaterials or as a system to insert in organic nano-sized material. Its properties can be controlled by the addition of various terminal groups.

para0080

Dendrimers based on poly (4-vinyl pyridine) beads can be used to stabilize silver, gold, and palladium NPs. These dendrimer-stabilized NPs have been utilized as catalysts for the

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reduction of trypan blue. The nanomaterials based on polymer can also have recyclable nature. Using poly (amidoamine) (PAMAM) dendrimers to support magnetic NPs can create NPs with such nature. These nanomaterials were reported as successful sorbents for the removal of naphthalene from aqueous solutions.

cesc0023

34.6. Conclusion

para0081

Currently and in years to come, the scarcity of clean pure water is a burning issue that is having a deep effect on human lives. A rapid increase in population, industrial, and domestic population, fast consumption, and droughts are some of the factors responsible for this situation [96]. There are many types of processes and methods that have been designed, and the use of nanomaterial is one of them. Nanomaterial are serving as an effective solution in many aspects of wastewater treatment such as (1) water filtration and separation, (2) separation oil from water for treatment of oil-containing wastewater, (3) the removal of toxic heavy metals, (4) arsenic removal from water, (5) dye removal, and (6) antimicrobial activity.

cesc0024

Uncited References

[AU8]

para0082

[8,16,55,78–80,83,84,86,87,89–91,93]

cesc0025

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Non-Print Items

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Abstract

Providing a clean and affordable technology for treatment of water is one of the modern times challenges. The world's growing population causes water scarcity, and pollutants contaminate whatever water sources are left. Nanotechnology has provided innovative solutions for water purification. Due to the exceptional characteristics that resulted from nano-scale size, such as improved catalysis and adsorption properties as well as high reactivity, nanomaterials have been the subject of active research and development worldwide in recent years. Numerous studies have shown that nanomaterial can effectively remove various pollutants in water and thus have been successfully applied in wastewater treatment. In this chapter, the most extensively studied nanomaterial: zero-valent metal nanoparticles (NPs), metal oxide NPs (TiO_2 , ZnO , and iron oxides), carbon nanotubes, and nanocomposites are discussed and highlighted in detail. Besides, future aspects of nanomaterials in wastewater treatment are discussed.

cesectitle0002

key0001

[AU19]

Key Words

Aerobic and anaerobic mechanism; Mixed culture; Nanomaterial; TiO_2 ; Water contamination

Structural and electrical properties of BaTiO₃:YFeO₃ composites at room temperature

Cite as: AIP Conference Proceedings 2265, 030659 (2020); <https://doi.org/10.1063/5.0016686>

Published Online: 05 November 2020

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Structural and Electrical Properties of BaTiO₃:YFeO₃ Composites at Room Temperature

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Abstract: The polycrystalline composite of BaTiO₃ (BTO) and YFeO₃ (YFO) has been prepared by solid state reaction method using high purity carbonates, oxides and ferrites. The structure of prepared samples has been analyzed by X ray diffraction which indicates that structure of BTO is a single phase tetragonal while structure of YFO doped material is orthorhombic and having the existence of doublet. The dielectric property has been investigated by impedance gain phase analyzer at room temperature which shows that at lower frequency the dielectric constant is maximum and reduces as move towards the higher frequency which shows the good property of any dielectric material. Similarly loss of the material is also minimum which directly supports the requirements of low loss energy storage device.

Keywords: Polycrystalline, composite, XRD, Orthorhombic, dielectric.

INTRODUCTION

The single phase materials used in several electric and magnetic applications may possess some limitations to use it at high frequency applications due to their high losses and inflexibility of properties associated with them. Therefore, there is a need of smart material which possesses the properties of ferroelectricity and ferromagnetism. This new era of the material is a multiferroic material. In this category there is an existence of the perovskite material i.e. BaTiO₃, BiFeO₃, BiMnO₃, YMnO₃, YFeO₃ etc. [1-7]. Among them property of ferroelectricity is found in BaTiO₃ by A Von Hippel in 1945[8]. Here, it is found that this material possess the effect of spontaneous polarization which is main factor responsible for generation of ferroelectricity. YFeO₃ is the another ABO₃ type largely studied perovskite structure. It also shows ferroelectric and ferromagnetic property at room temperature and at high temperature there is existence of antiferromagnetic property [6, 9-10]. The properties of centrosymmetric and ferroelectricity are opposite to each other. In this paper a composite system comprising of $x(\text{BaTiO}_3) + (1-x)(\text{YFeO}_3)$, with $x = 0, 0.25, 0.50, 0.75$ & 1 is prepared using solid state reaction method. We then studied XRD and dielectric properties of the prepared composites.

EXPERIMENTAL DETAILS

The Polycrystalline fine powder of $x\text{BTO} + (1-x)\text{YFO}$ were prepared by mixing and grinding of high purity oxides (99.9%), carbonates (99.9%) and ferrites (99%) as per the stoichiometry using solid state reaction method. The oxides/carbonates of constitute elements were mixed using agate mortar pestle for 8 hours (mixing, grinding). Pressure of 1 ton was applied in order to form the pellets using hydraulic press. The diameter of the made

pellets were 8 mm. The prepared pellets have undergone the process of calcination and sintering at 1100°C and annealing at 900°C. In this way series of YFO, 0.25BTO+0.75YFO, 0.5BTO+0.5YFO, 0.75BTO+0.25YFO, BTO is prepared for $x=0, 0.25, 0.50, 0.75, 1$ respectively. The XRD measurements of prepared pellets were done with the help of Bruker D8 Advance X-ray diffractometer. The structural refinements were carried out using the Match 3 software. For dielectric analysis the made pellets were silver painted in order to make good electrical contact. The dielectric properties were examined by impedance gain phase analyzer at room temperature for wide range of frequencies.

RESULTS AND DISCUSSION

1.1. Phase and Structural Identification of Prepared $x\text{BTO} + (1-x)\text{YFO}$ Ceramics

Crystallographic phase identification of $x(\text{BaTiO}_3) + (1-x)(\text{YFeO}_3)$ system was done with the help of powder X-ray diffraction (XRD) analysis using $\text{CuK}\alpha$ radiation with a monochromatic source. Figure 1(a), 1(b), 1(c), 1(d) & 1(e) illustrates XRD patterns of $x\text{BTO} + (1-x)\text{YFO}$ with $x=1, 0, 0.25, 0.5, 0.75$ i.e. BTO, YFO, 0.25BTO+0.75YFO, 0.5BTO+0.5YFO, 0.75BTO+0.25YFO respectively. From the X-ray analysis we can conclude that structure of BaTiO_3 is a single phase tetragonal structure having the value of lattice parameters are $a=4.000324\text{\AA}$, $b=4.000324\text{\AA}$, $c=3.978404\text{\AA}$. The sharp peak exists at $2\theta = 31.705^\circ$ with $hkl=101$ which is exactly similar to that obtained from standard data [4]. YFO possess the orthorhombic structure. The intermediate composite also possesses the orthorhombic structure. For all the three intermediate compounds it is found that there is an existence of the doublet which indicates that it is due to the presence of both the type of unit cells (BTO and YFO). From the figures we can say that for the intermediate composition both the phases (BTO and YFO) coexist simultaneously without much distortion in the parent phase. It reveals that YFO and BTO unit cell matrix separately exist in the compounds and have not merged in to each other. Further by comparing all four XRD patterns it has been observed those peaks related to BTO are dominating in the XRD patterns of 0.25BTO+0.75YFO, 0.5BTO+0.50YFO and 0.75BTO+0.25YFO.

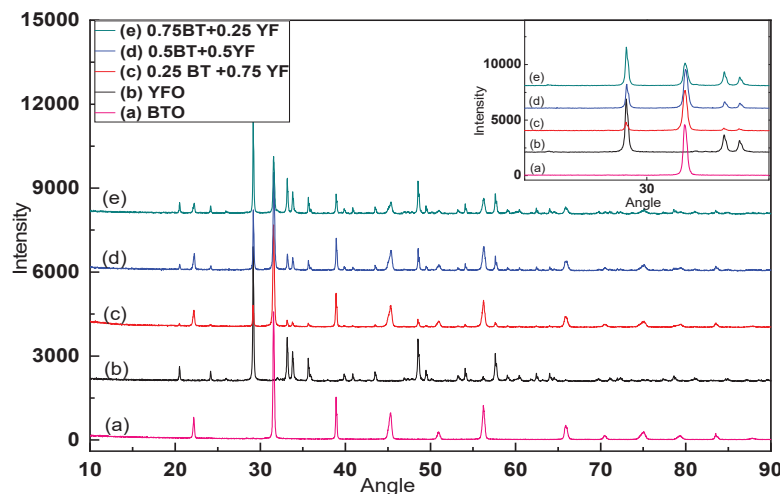


Fig.1 XRD Pattern of (a) BTO, (b) YFO, (c) 0.25 BTO+0.75 YFO (d) 0.5 BTO+0.5 YFO (e) 0.75 BTO+0.25 YFO systems

1.2 Dielectric Analysis

The dielectric properties of the prepared samples $x\text{BTO} + (1-x)\text{YFO}$ i.e. (BTO, YFO, 0.25BTO+0.75YFO, 0.5BTO+0.5 YFO, 0.7 BTO+0.25YFO, YFO) were evaluated by impedance gain phase analyser at room temperature ($\sim 25^\circ\text{C}$) for wide range of frequencies (1Hz to 2MHz). The variation of real part of permittivity

ϵ' (dielectric constant) is shown in fig 2. The inset figure shows the logarithmic variation of the same. The samples exhibit high dielectric constant at low frequency and decreases with increase in frequency for all samples. It is also observed that the values of dielectric constant increases with concentration of BTO. The high dielectric constant for BTO rich samples arises from the very strong local internal electric field of TiO_2 , which is caused by the external applied electric field, which in turn responsible for generation of strong electronic polarization and ionic polarization. The observed very high values of dielectric constant at lower frequencies are not due to the electronic and ionic contribution but due to the space charge contribution [11]. It is observed from the inset figure that ϵ' decreases with increasing the frequency and goes to the negative in some case which indicates that electric flux density will be opposite to the direction of applied electric field.

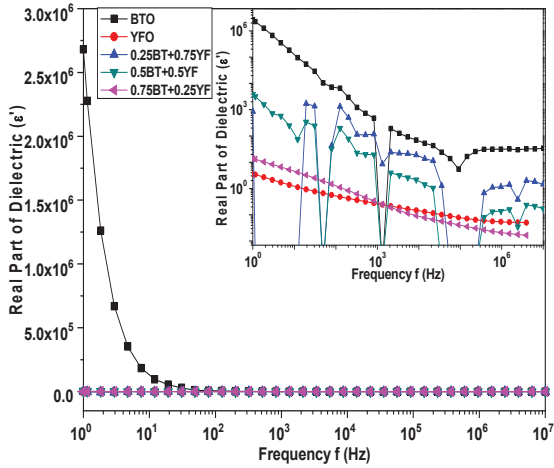


Fig 2. Real part of Dielectric constant (ϵ') \rightarrow frequency (f)

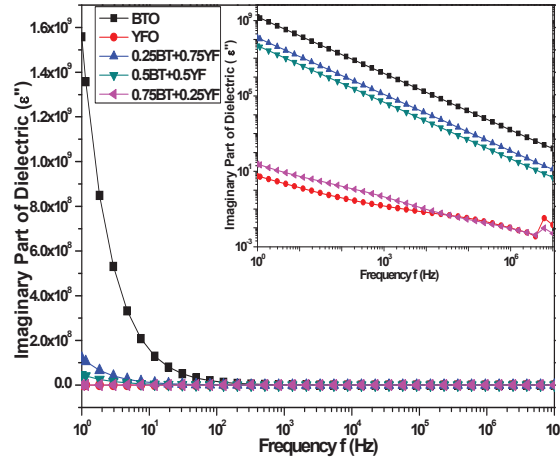


Fig 3. Imaginary part of dielectric constant (ϵ'') \rightarrow frequency (f)

Fig 3. represents the frequency response of imaginary part of permittivity ϵ'' at room temperature for $x\text{BTO} + (1-x)\text{YFO}$ (BTO, YFO, 0.25BTO+0.75YFO, 0.5BTO+0.5YFO, 0.75BTO+0.25YFO). The nature of the fig 3 is nearly same as that of obtained for real part. From the theory of dielectric dispersion, it is related to the Maxwell-Wagner type of interfacial polarization which is in accordance with Koop's theory [12-14]. From the Koop's phenomenological theory it is further concluded that conductivity contributes more in this range [14]. The observed variation in dielectric constant is due to interfacial polarization.

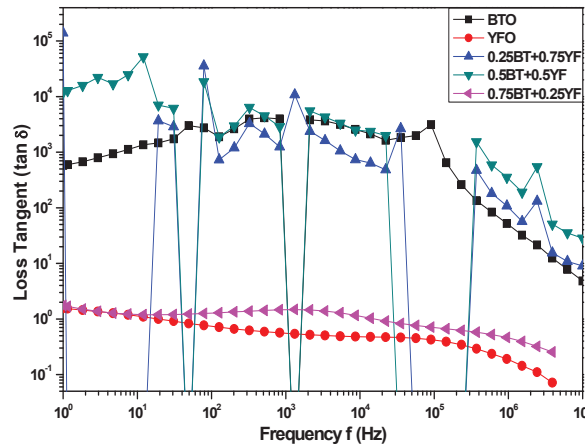


Fig.4 loss tangent ($\tan \delta$) \rightarrow frequency (f):

Fig4. Represents the dielectric loss of the materials at room temperature which is denoted by $\tan\delta = \frac{\epsilon''}{\epsilon'}$. At lower frequencies of applied ac voltage dipoles are able to keep in phase with changes in electric field and power losses are low. As the frequency is increased, space charge, orientation and ionic polarization become inoperative and dipoles becomes out of phase. When several polarizations such as ionic, orientation, space charge etc. occurs in a material, it follows that the dielectric loss decreases with increasing frequency. The loss of the material shows the conventional nature of the samples. As shown in graph it can be concluded that dielectric loss is decreased with frequency and it becomes minimum or negligible as move towards the higher frequencies. This type of behavior may have huge impact on low loss energy storage devices.

CONCLUSION

Multiferroic composites of xBTO + (1-x) YFO (x=1, 0, 0.25, 0.50, 0.75) and its intermediate compounds are prepared by solid state reaction method. The XRD patterns BTO is a single phase tetragonal structure while the structure of YFO and the doped structure indicate the orthorhombic structure. The dielectric constant of all the three doped samples and pure samples decreases exponentially with operating frequency. At higher frequencies both dielectric constant and dielectric loss remains almost constant (relaxation behavior). This variation of dielectric constant at lower frequencies is not due to the electronic and ionic contribution but due to the space charge contribution. The loss of the material shows the conventional nature of the samples. This type of behavior may have huge impact on low loss energy storage device.

ACKNOWLEDGEMENTS

The authors are thankful to Pandit Dindayal Petroleum University (PDPU), Gandhinagar, Gujarat; and UGC-DAE CSR centre, Indore for providing the experimental facility.

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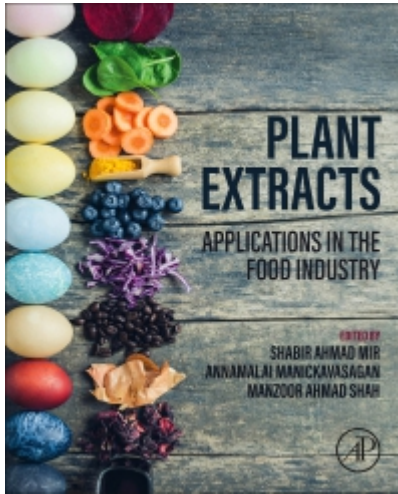
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