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Metallic and organic nanomaterials and their use in pollution control: A Review

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ABSTRACT

A number of chemical contaminants have endangered the quality of drinking water. Realizing the molecular nature of contamination in drinking water, significant progress has beenmade to utilize the chemistry of nanomaterials for water purification. This article summarizes recent efforts in the area of metallic and organic nanoparticle synthesis and the origin of their reactivity at the nanoscale. The application of metallic and organic nanomaterials based chemistry for waste water treatment is summarized for three major types of contaminants: halogenated organics including pesticides, heavy metals and dyes. Besides the above efforts for the removal, as well as ultra low concentration detection of such species, using metal nanoparticles and organic nanomaterial are summarized. Important challenges during the commercialization of nano-based products are highlighted through a case study of pesticide removal using metalallic and organic nanoparticles. Recent efforts in drinking water purification using other forms of nanomaterials are also summarized. The article concludes with recent investigations on
the issue of nano size metallic and organic material and its applications for the pollution control.

Keywords: Metallic and organic nanomaterial, Pollution control, Water purification.

INTRODUCTION

Environmental pollution is a serious day-to-day problem faced by the developing and the developed nations in the world. Air, water and solid waste (plastics) pollution due to the anthropogenic sources contribute a major share to the overall imbalance of the ecosystem.

According to the Color Index (C.I.), which is managed by the Society of Dyers and Colorists and the American Association of Textile Chemists and Colorists, currently more than 10,000 various types of dyes are synthesized and available in theworld. Although no recent data is available on worldwide dye production, annual production of over 700,000 tonnes has been often reported in the literature [1–3]. Dyes are organic compounds consisting of two main groups of compounds, chromophores (responsible for color of the dye) and auxochromes (responsible for intensity of the color) [4]. Dyes are classified according to the chemical structure and type of application. Based on chromophores, 20–30 different groups of dyes can be discerned, with azo, anthraquinone, phthalocyanine and triarylmethane accounting for the most important groups. Azo (around 70%) and anthraquinone (around 15%) compose the largest classes of dyes.

The common pollutants include toxic organic compounds like chlorinated and non chlorinated aliphatic and aromatic compounds, dyes, detergents and surfactants, agro wastes like insecticides, pesticides and herbicides, disinfection byproducts, volatile organic compounds, plastics, inorganic compounds like heavy metals, noxious gases like NO_x, SO_x, CO and NH_3, and pathogens like bacteria, fungi and viruses. Hence, strict environmental legislations on the use of these recalcitrant pollutants and their safe disposal drives the research community to develop clean and green processes to degrade the pollutants before they are admitted into the atmosphere and water bodies.Some of heavy metals like copper, cobalt are necessary for human life, while some heavy metals like lead, cadmium are problematic for human. Main sources of heavy metals in the environmental samples are industrial facilities and traffic [5,6].Accurate and sensitive determinations of them are the important part of analytical chemistry studies. Due to its cheap cost simplicity, atomic absorption spectrometry is the main instrument for the determination of heavy metals in many laboratories. However, the determination of metals at gm/Ltr level by especially flame atomic absorption spectrometry is impossible due to their lower levels and interferic effects of 1A and 2A group elements in the determinations [7–9]. In order to solve these problems in flame atomic absorption spectrometric determinations, separation-enrichment procedures including cloud point extraction, membrane filtration, liquid–liquid extraction, coprecipitation, solid phase extraction have been used 10–15]. Among these preconcentration techniques, solid phase extraction is preferred a lots of researchers due to its advantages including as simple and fast extractor system, easily adaptable to the preconcentration and to the determination of trace metal ions by flow injection analysis technique. Solid phase extraction has a relatively high concentration factor and the ability of treating large volume samples free from contamination [16,17]. Solid phase extraction technique has been widely used in the preconcentration/ separation of trace and ultra trace amounts of inorganic and organic species, in order to enhance sensitivity and to separate analytical matrix.

The objective of this review article is to provide a consolidated view of the research efforts accomplished so far, in the area of metal and organic nanoparticles for drinking water purification. The article begins with a review of challenges in drinking water purification. Thereafter, metal nanoparticle based chemistry is discussed in detail: Thereafter, a few of the other nanomaterial based approaches for drinking water purification are also summarized.

1]. Drinking water purification

With the evolution of human civilization, our understanding of pure drinking water underwent dramatic changes. In early civilizations,the commonly practiced measure for purity was the taste of the water. Water was recognized as a symbol for the origin of life and for its medicinal value; it was not designated as a carrier of diseases. In the 17th century, Anton van Leeuwenhoek's discovery of the microscope started to change the perception of purity: We were empowered to see beyond the suspended particles e.g., the tiny material particles to the micro-organisms. Following the discoveries of Louis Pasteur (study of micro-organism based diseases) and John Snow (linking of cholera spread in London with the quality of water),our understanding of pure drinking water was changed [17].Interestingly, the first governmental act was passed in 1852 and was titled, Metropolis Water Act of 1852. Access to pure water was being recognized as a right to every human being.

Over 150 years, our understanding of water quality, its effects on health and methods for water purification has undergone a sea-change. A number of important events had happened prior to this period which significantly influenced the course of the last 150 years. The historical records suggest that the importance of purewaterwas emphasized even during ancient civilizations. Early Sanskrit writings outlined several methods for purifying water such as crude sand and charcoal filters (Sushruta Samhita). The first recorded use of ion-exchange appears in the Old Testament of the Holy Bible [18]. The second part of the problem arises as an effect of brisk industrialization accomplished globally. Economic growth has led to significant improvement in the economic status of human life; however it has also been coupled with many environmental issues which have largely been ignored, primarily due to unavailability of economic solutions.

Many bodies such as USEPA, WHO, and EU (see list of acronyms and their definitions at the end of the article) have played a key role in developing regulations for many toxic species found in drinkingwater. Looking at some of the information provided by such bodies (Fig. 1), a few conclusions can be drawn.

- Most of the regulated chemicals fall in the organohalogen group
- Organochlorine pesticides and halogenated organics continue to remain on the USEPA radar for future regulative activity
- The other major contributors to the list are metals, inorganic salts and micro-organisms
- Regulatory coverage of the USEPA for safe drinking water has increased over four times since its inception (in 1974), with revisions in maximum limits for many contaminants

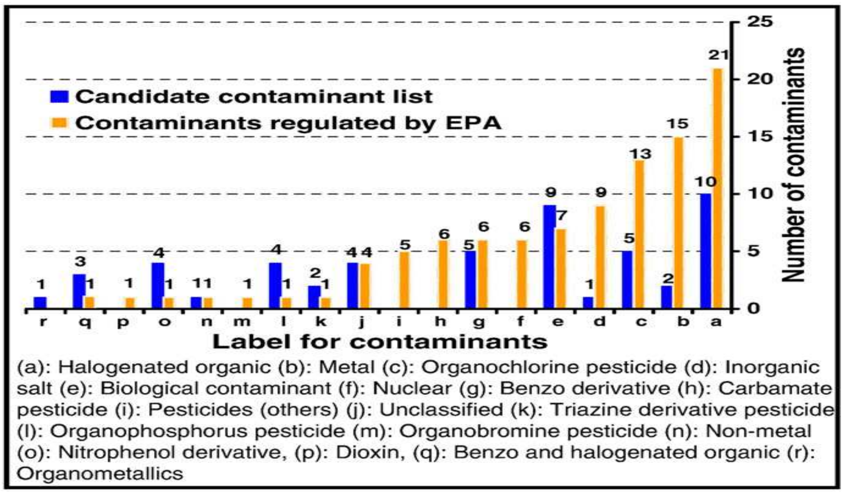

Fig. 1. Category-wise distribution of contaminants regulated by USEPA and futurecontaminants (USEPA CCL 2005) [19]

As a result, the technology to remove these contaminants must also reach molecular limits. There must be highly efficient molecular capturing agents which would grab them during single encounter events. The other equally important requirements of such a solution are: minimum electricity, economical feasibility and environmental friendliness.Importantly, the chemistry should be effective even at parts per billion concentrations. Inmost chemical processes we see around us, the concentrations involved are sufficiently large such that the encounters between the reacting partners are numerous. On the contrary, at a dilution of 109, the encounters also get reduced proportionately. Traditional approaches for the removal of such trace contaminants lead to further ecological damage in terms of waste generated; e.g., adsorption capacity of fluoride with conventional sorbents such as activated alumina is usually in the range of b10 mg/g [20]. Thus, a minimumof 6.5 kg of activated alumina is required for the design of a domestic purifier unit (with a capacity to purify 6500 l of water) catering to complete removal of 10 ppm fluoride. All of these pose numerous requirements, difficult to meet entirely.

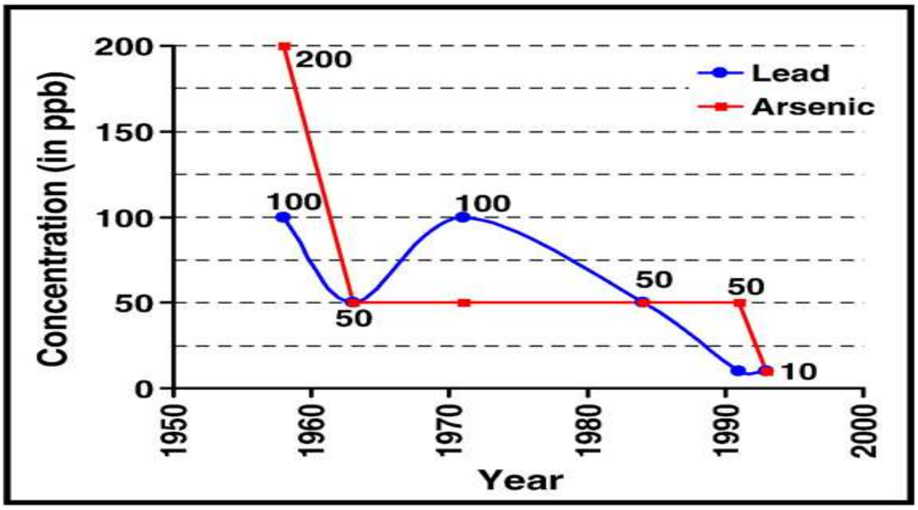

Fig. 2: Changes in maximum allowable concentration for lead and arsenic in drinking water, based on WHO advisory

It is vital to summarize a few of the advantages of nanomaterial chemistry with respect to conventional technologies The surface-to-volume ratio increases drastically with the reduction of the size of the adsorbent particle from bulk to nano dimensions. It leads to the availability of higher numbers of atoms/molecules on the surface for adsorption of contaminants. Accordingly the surface energy available with each adsorbent particle also increases significantly. This provides many advantages to drinking water purification:

- Effective contaminant removal even at low concentrations
- Less waste generation post-treatment as less quantity of

Nanomaterial will be required vis-à-vis its bulk form. This happens since more adsorbent atoms/molecules are present per unit mass of the adsorbent and thus are actively utilized for adsorption.

2]. Synthesis protocols

The seminal work of Faraday and Turkevich on metal nanoparticle synthesis and the mechanism behind the growth kinetics of nanoparticles, stimulated research on various synthetic protocols. It is appropriate to say that ongoing nano-research has largely been enabled due to the large number of synthetic protocols. As a result of this, many interesting size and shape dependent properties of nanomaterials have been discovered.

Excellent review articles and books are available describing a multitude of synthetic protocols [21,22–39]. However, novel as well as improved methods are continuously being developed and it would be difficult to cover the entire spectrum of valuable activity in metal nanoparticle synthesis. Thus, here only selected contributions in the area of chemical synthesis of noble metal nanoparticles are discussed. The usual method followed for metal nanoparticle synthesis is reduction of metal salts (precursors). During the reduction process, the growth kinetic parameters are controlled by a combination of low precursor concentration (increasing the diffusion distance), nature of solvent (higher solvent viscosity), slow acting reducing agent (reduced electrochemical gradient) and appropriate protection of the growth surface with a stabilizing agent (controlling surface reactivity). This enables the hindered diffusion of growth species from the solution to the nuclei and consequent formation of monodisperse nanoparticles.Organic nanomaterial like chitosan are also important adsorbant for removal of organics present in waste water and can be synthesise by ionic gelation of chitosan with tripolyphosphate anions (TPP). [40], the inherent nature of the stabilizing agent renders the nanoparticle system soluble in an organic solvent.

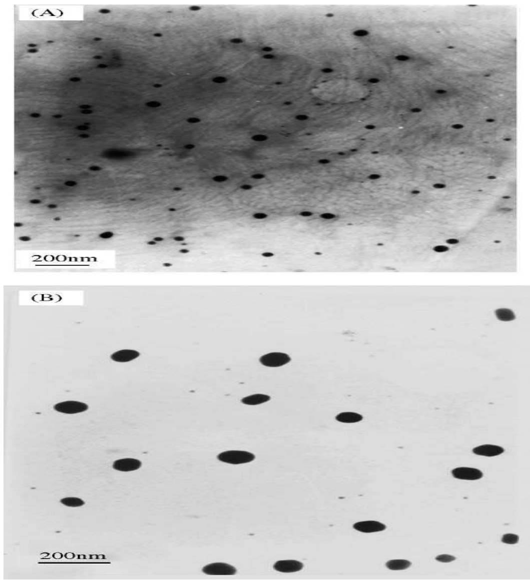

Fig. 3. TEM of chitosan-TPP nanoparticles [40]

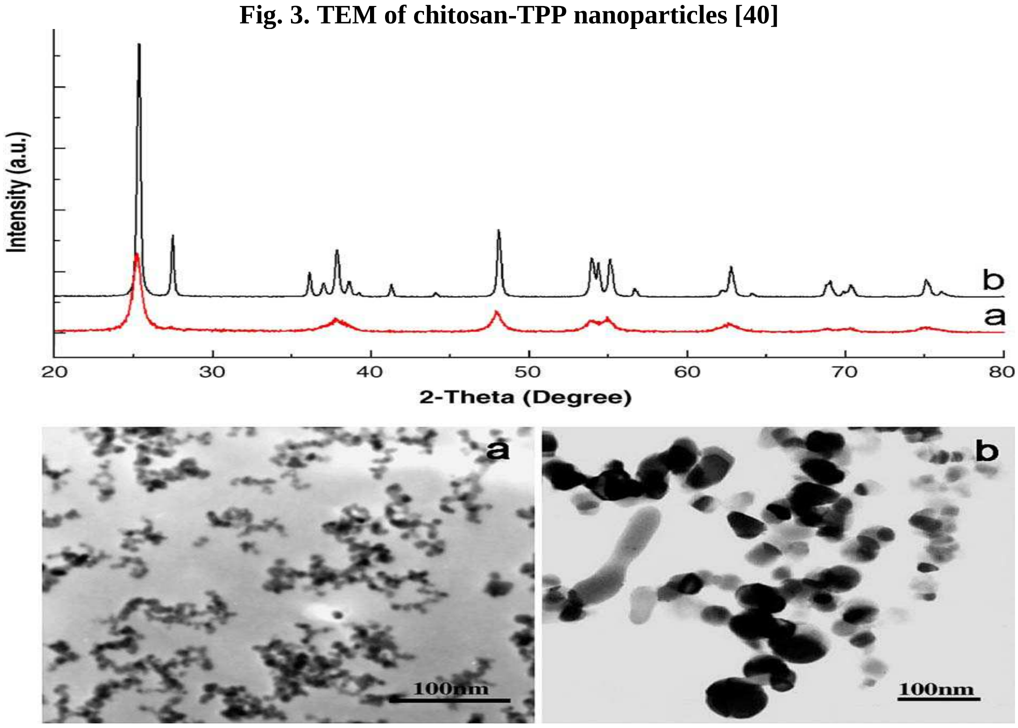

Fig. 4. XRD and TEM images of the TiO_2 nanoparticles[48]

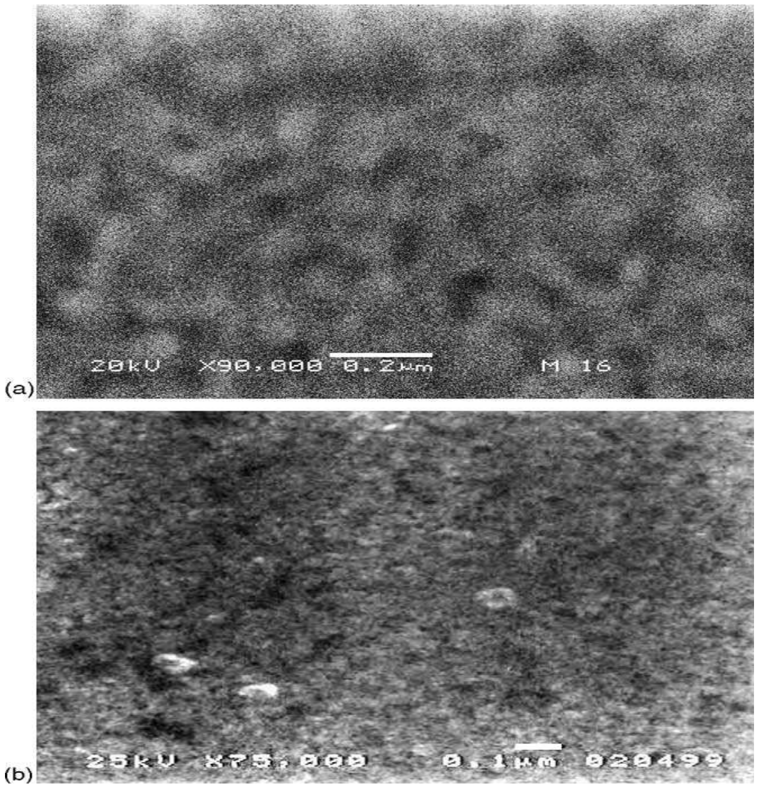

Fig 5.SEM micrograph from a TiO_2 thin film [49]

Similar approaches for functionalization of noble metal nanoparticles have been developed using various other organic molecules (aliphatic and aromatic) containing a wide variety of functional groups;e.g., cyano (–CN), mercapto (–SH), carboxylic acid(–COOH) and amino (–NH_2) are known to have a high affinity for gold and thus are useful as surface protective functional groups [41–47]. Metallic nanomaterial like TiO_2 and their thin film can be synthesise by different methods and their charecterisation was done by SEM and XRD these nanomaterial is use as photocatalyst for degradation of dyes and removal of metal [48,49].

3]. Heterogeneous catalysis

Methods for nanoparticle deposition on supports contaminants such as pesticides are removed through homogeneous or heterogeneous chemistry. In the homogeneous process, the molecules of relevance are degraded by the nanoparticles dispersed in the solution phase. This methodology is attractive because it utilizes all the available surface area offered by nanoparticles.However, amajor issue of concern is the possible presence of nanoparticles contaminating the purified water. This is important as the dispersed nanoparticles cannot be easily separated. Heterogeneous chemistry utilizes supported nanoparticles. Here, highly dispersed nanoparticles on supports such as oxides, polymers, fibers, etc. are used and water is passed through such media. The binding between the particle and the support must be strong enough to avoid leaching of the particles intowater. Additionally, with decrease in size, metal particles gradually become unstable without protecting agents, due to increasing surface energy [50]. Consequently, immobilization of metal nanoparticles on a suitable highsurface- area solid helps in avoiding agglomeration, even though it leads to changes in the properties and behavior of the isolated particles [51]It is also important to highlight that chemical reactivity of nanoparticles (especially in the lower size regime) can be significantly altered by the nature of the support. A remarkable example is the catalytic oxidation of CO with supported gold nanoparticles [52]. It has been shown that gold nanoparticles around 3 nm in diameter on supports such as TiO_2, Fe_2O_3 and Co_2O_3 are very active for CO oxidation, while particles on more conventional supports like SiO_2 and Al_2O_3 are practically inactive. In another procedure, nanoparticles can be supported on the support through direct impregnation. In a generalist representation of the method, noble metal nanoparticles prepared separately can be impregnated with metal oxide supports such as Al_2O_3 or organic supports such as activated carbon [53–55,56].

3.1] Photocatalytic degradation:

Many studies have been devoted to the photocatalytic degradation of chlorinated aromatic compounds like chlorophenols and chlorobenzenes, chlorinated pesticides like DDT,59 hexachlorobenzene, atrazine and parathion, surfactants like sodium dodecyl benzene sulfonate59 and trimethyl phosphate, aliphatic and olefinic compounds, dyes, nitrogeneous compounds like nitrophenols and nitrobenzenes, carboxylic acids, alcohols and heteroatom compounds. A compendium of the different studies on the Epling and Lin67 have studied the degradation of 15 dyes belonging to different class by functionality in presence of visible light. The order of degradation among the different dyes followed the order: indigo ≈ phenanthrene > triphenyl methane > azo ≈ quinoline > xanthenes≈thiazine > anthraquinone. The order of degradation of the dyes in the presence of different light sources followed: natural sunlight _ 90 W halogen flood light > 150 W spotlight. The presence of electron withdrawing groups was found to retard the degradation rate of the dye. They have attributed the degradation of the dye to both photosensitized oxidation and reduction mechanisms.

4]. Drinking water purification: novel reactions at the nanoscale:

Here, we discuss noble metal nanoparticle-based chemistry for the detection and removal of two sets of organic compounds – pesticides and halogenated organics – from drinking water. Removal of pesticides with noble metal nanoparticles The earliest study of interaction between halogenated organics and transition metals began with the discovery of zero-valent iron catalyzed degradation of halogenated aliphatics [57–59]. It was reported that carbon tetrachloride induces corrosion in the metals, in a way similar to air and water [57 59]. The concepts of corrosion held true: metal surface is oxidized to metal chloride, the degree of corrosion differs with metals as protective layers are formed on some metal surfaces and reactivity is dependent on the reduction potential [57–59]. The reaction product was found to be metal chloride and partially dehalogenated organic compound. This was subsequently followed by the study of other organics with iron metal [30] and then iron nanoparticles for enhanced degradation of pesticides became popular. Several review articles are available on the subject [60–64]. From the elucidation of the reaction mechanism, it became increasinglyclear that zerovalent iron (ZVI) acts as a good reducing agent, In a similar approach, the use of other reactive metals such as magnesium, tin and zinc was attempted to study the degradation of halocarbons [65].

5.Environmental applications of nanomaterials as Adsorbents:

Removal of heavy metal ions and micropollutants from aqueous streams using nanomaterials continues to be extensively researched. The focus is primarily on modifications to improve the removal efficiency and in some cases, the nanoparticle stability. Comprehensive reviews on related topics include nano-adsorbents targeting removal of metal ions from water / wastewater[66], advances in functionalization of CNTs for various adsorption and catalytic applications[67] Further to the application of nano sized zero-valent iron (ZVI), combinations of metals have been examined. For example, nano-sized bimetallic mixtures (Pd/Fe, Cu/Fe and Pd/Cu) enhanced the reduction of Cr(VI) compared to using ZVI alone[68]. The improvement was attributed to the reasoning that cementation of a noble metal acts as a reaction catalyst and also protects the metallic surface from inactivation. In addition to its application as an adsorbent, nano-sized ZVI can also be used as an electron donor. This has been verified in the degradation of trichloroethylene in groundwater by the microbial species Dehalococcoides spp. in the presence of nano ZVI[69]. This is an interesting example integrating nanotechnology and biotechnology for environmental remediation. In another application targeted at in situ subsurface environment remediation, chitosan was used as a stabilizer to prepare ZVI chitosan nanoparticles for Cr(VI) removal by adsorption followed by reduction to Cr(III) [70]. Due to its high efficiency in chelating the Fe(III) ions, chitosan prevents the precipitation of Fe(III)–Cr(III).The Cr(VI) to Cr(III) reduction follows pseudo first order kinetics and is dependant upon parameters like temperature, iron loading, initial Cr(VI) concentration, pH. Chitosan nanoparticles alone have also been used as adsorbents for dye removal [71] Nanoparticles As important as it is to develop novel materials for removal of toxic pesticides from drinking water, it is also imperative to realize that such compounds have become extremely important analytes for ultra low concentration sensing. The large-scale use of different pesticides across the world has contaminated a number of water sources, and thus it is a necessity that rapid, sensitive and selective detection protocols be developed for such molecules [72,73].

Over the past 25 years, many methods have been developed for ultra-low concentration detection of pesticides [74,75]. A number of widelypracticed methods such as chromatography, mass spectromety, and biosensors, offer high sensitivity and selectivity.However, the aspect of rapid measurement is now being improved by use of nanomaterial chemistry [76]. An important work on the utilization of nanomaterials for biomolecular detection was the use of oligonucleotidemodified gold nanoparticles for colorimetric low-concentration detection of polynucleotide [77]. It is important to realize that while in the case of contaminant removal, a higher surface area of the adsorbent is a pre-requisite whereas in the case of contaminant detection, change in the surface with adsorbate interaction and a consequent manifestation in reliable spectroscopic signatures is a necessity. The selectivity of molecular detection is an important dimension to contaminant detection which can be ensured through the use of appropriate nanomaterials and the choice of an appropriate ligand immobilization on the surface of nanoparticles; e.g., selective detection of cysteine and glutathione at micromolar concentrations using gold nanorods [77].

6]. Other nanomaterial based approaches for water purification:

Iron-based nanoparticles: One of the most important nanomaterials studied for water purification is zero-valent iron (ZVI). Amongst the nano-absorbents popular today, ZVI is the most utilized, primarily because it covers the broadest range of environmental contaminants [60,61]: halogenated organics, pesticides, arsenic, nitrate and heavy metals. The mechanism of reactivity for ZVI is similar to the mechanism of corrosion [50].

CONCLUSION

The unavailability of quality drinking water is a critical problem a cross the world. A number of hazardous species are introduced in large concentrations in drinking water. Examples include pesticides, heavy metals,dyes by textile and printing industries, etc. especially around industrial locations.in order to provide a sustainable enviorment for aquatic life wastewater treatment becomes highly essential . The discovery of pesticides and other synthetic organic compounds is a representative example.Hence, it becomes clear that without disturbing the path of scientific discovery for novel materials and their commercialization, we need to focus our attention on developing preventive technologies for inhibiting their impact on the environment. While traditional synthetic protocols have helped in controlling the spread of toxic species, the finest method has been practiced by Nature for ages. Although we have just started to understand and implement the chemistry of biological degradation of organic compounds, it is certain that

Nature's path will remain by-far the most desired method for detoxification of the environment. However nanotechnology has been highly efficient for degradation of organics like dyes,metals and pesticides by the use of metallic and organic nanomaterial

Thus one thing becomes clear to us. To do things in the most efficient fashion -whether chemical synthesis, energy transfer or water filtration – novel materials are likely to play a critical role. The unique properties of novel materials are likely to help in finding newer applications as well as solving the old problems, partially solved by conventional technologies. metals are historically known to be extremely non-reactive.

This is understood from a number of facts: unusually high reduction potential, high ionization energy, high melting point, relativistic contraction, etc. A number of such properties have a dependence on the size of the particle, Research conducted over the past few years has descover numerous methods for size controlled synthesis of metallic and organic nano particles, . A number of new properties have been found which originate at the nanoscale. Thus nanomaterials are effective for removal of metals,dyes and pestisides from industrial wastewater and hence control the water pollution caused by textile and printing industries.

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