

SIGNIFICANT MANIPULATIONS OF NANOTECHNOLOGY IN WATER PURIFICATION

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ABSTRACT

In recent days Nanotechnology is a multidisciplinary field in the area of water purification as it offers the possibility of an efficient remover of pollutant and germs from the drinking water. A number of chemical and biological contaminants have endangered the quality of drinking water. Nanoparticles, nanomaterials and nanopowder used for detection and removal of chemical and biological substances include metals (eg. Cadmium, copper, lead, mercury, zinc) Nutrients (eg: phosphate, ammonia, nitrate and nitrite). In this paper, recent effort puts in the area of application of noble metals nanoparticle chemistry in water purification are reviewed. Three major types of contaminants: halogenated organics including pesticides, heavy metals, and microorganisms are discussed in this paper. The use of nanomaterials such as zero valent iron-Nzvi, carbon nanotubes (CNT) in environmental cleanup like ground water remediation for drinking and reuse. Basically four classes of nanoscale materials that are being evaluated as functional material for water purification

Keywords: Nanoparticles, carbon nanotubes, nanomaterials, zeolites, dendrimers, noble metal nanoparticles, photocatalytic nanoparticles

Introduction

Today most of the countries facing drinking water problem and the conditions are very severe especially in developing countries. The world is facing formidable challenges in meeting rising demand of clean water as the available supplies of fresh water depleting due to –

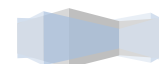
- (i) extended droughts
- (ii) population growth
- (iii) more stringent health based regulations
- (iv) competing demands from variety of users clean water i.e. water free from toxic chemicals and pathogens.

A number of techniques are used for the treatment of water physical and chemical agents i.e. chlorine and its derivatives UV light, boiling, ultra sonic radiations, distillation, reverse osmosis, water sediments filters (fiber and ceramic) activated carbon. Biological (bacteria to decompose waste, oxidation of chemicals). Recent application of nanoparticulate 20 ppm silver colloidal suspension in purified water has 100% cure rate of malaria. Titanium dioxide (TiO₂) especially as nanoparticulate anatase, is also an interesting antibacterial, with notable photocatalytic behavior. Iron oxides and TiO₂ are good sorbents of metal contaminants. The increased production of hydroxyl free radical is responsible for enhanced viral inactivation by (nAg/TiO₂) in drinking water.

Nanoparticles used in water treatment

Four classes of nanoscale material that are being evaluated as functional materials for water purification-

- (i) dendrimers
- (ii) metal-containing nanoparticles
- (iii) Zeolites
- (iv) Carbonaceous nanomaterials.

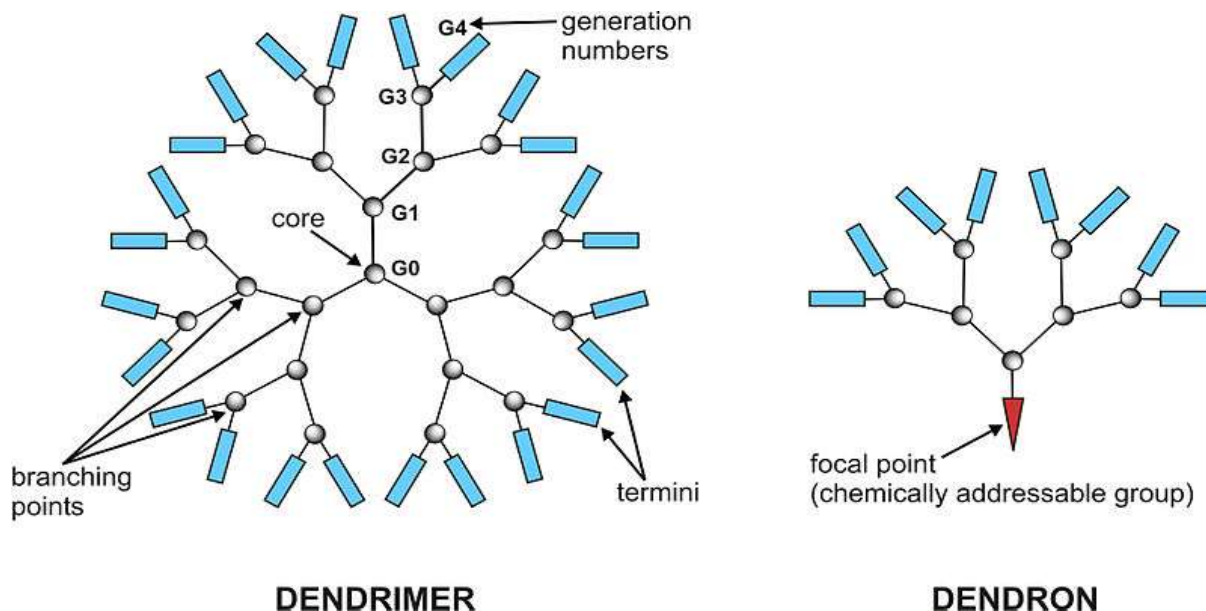


Dendrimers

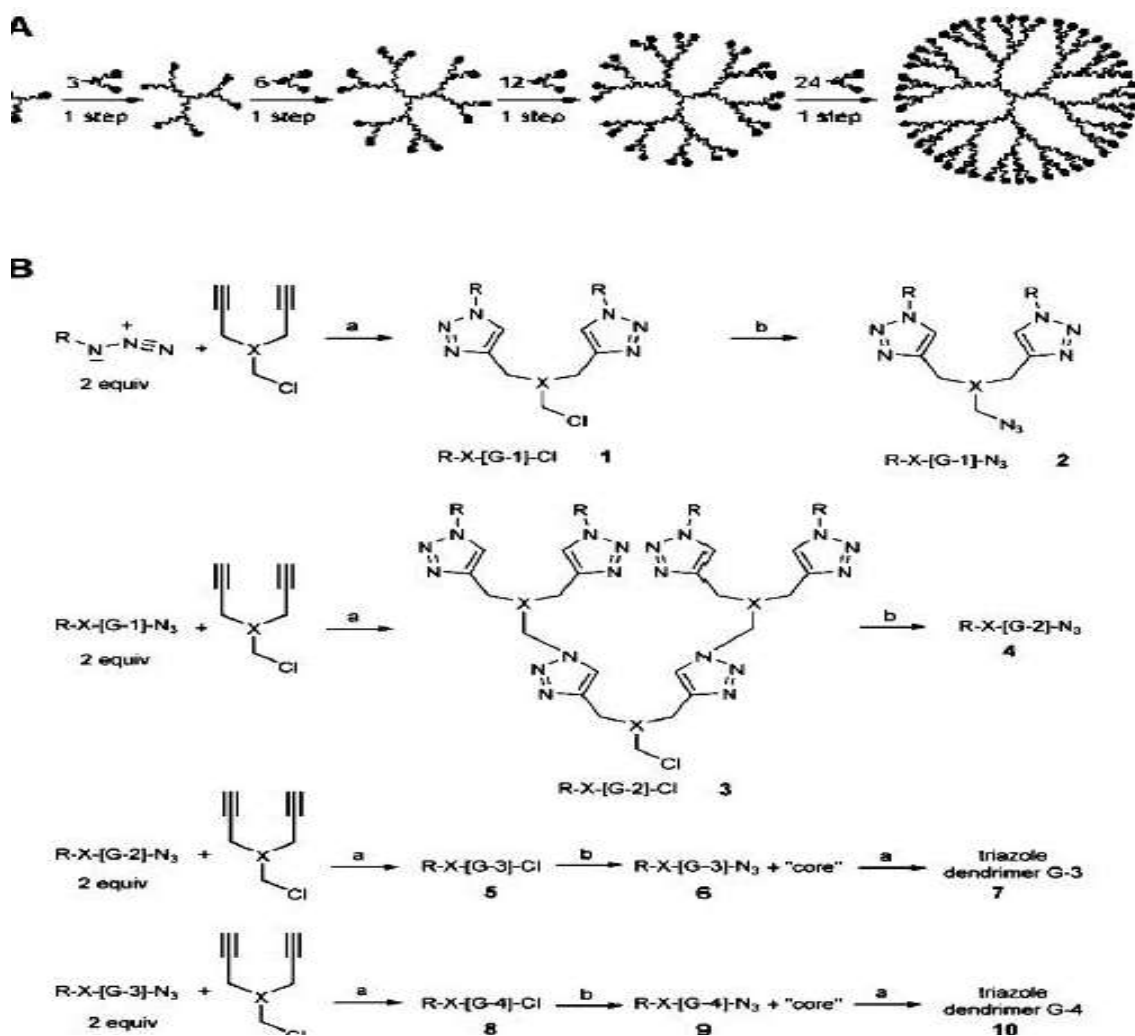
Reverse osmosis (RO) have pore size 0.1-1.0 nm and thus are very effective and retaining dissolved inorganic and organic solutes with molar mass below 100 Da. Nanofilter membrane (NF) removing hardness and organic solutes with molar mass 1000-3000 Da. However high pressure is required for both RO and NF membranes. Ultrafine membrane (UF) requires low pressure (200-700 kpa). Invention of dendritic polymer providing unprecedented opportunities to develop effective UF process for purification of water contaminated by toxic metal ions, radionuclides, inorganic and organic solutes bacteria and viruses. Dendrite polymers which include random hyperbranched polymer, dendrigraft polymers, dendrons, and dendrimers are relatively monodispersed and highly branched macromolecules with control composition and consisting of three components: a core, interior branch cell, terminal branch cell and tissue silver level with 10% silver. Dendrimers formed a well defined surface. Their interior may be similar or may be different from the surface of the molecule. Chemical and physical properties such as reactivity, complex or salt formation and hydrophilicity so forth can be varied and optimized. As a proof of the feasibility of Dendron enhanced ultra filtration (DEUF) and poly (amido amine) (PAMAM) Dendrimers with ethylene di amine (EDA) core and terminal NH₂ group to recover Cu(II) ions from the solution. On the mass basis PAMAM dendrimers are much larger and more sensitive to solution pH.

To obtain a dendrimer structure several dendrons are reacted with multifunctional core to yield a dendrimer using two key synthetic strategies. The first strategy utilizes highly functionalized cores and branched monomers to create phosphorus dendrimers. The second approach is based on click chemistry i.e. the near perfect reliability of Cu I catalyzed synthesis of 1,2,3- triazoles from azides and alkynes to produce dendrimers with various surface groups in high purity and excellent yield. PAMAM synthesized by a divergent method involving a two step reaction sequence concentric shells of branch cell (generation) around a central initiator core. This PAMAM core shell architecture grows linearly in diameter as a function of added generation, while the surface group amplifies exponentially at each generation. Poly (amido amines) PAMAM dendrimers are obtained by iterative branching of L-alanine repeating units. Dendritic polymer can also be used as

- (i) Recyclable unimolecular micelles for recovering organic solutes from water.
- (ii) Scaffolds and templates for the preparation of redox and catalytically active nanoparticles.



Dendritic polymers have also been successfully used as delivery vehicles or scaffolds for anti microbial agents such as Ag (I) and quaternary ammonium chloride poly (amide amine) PAMAM based silver complexes and nanocomposites proved to be effective anti microbial agents. Macroscopically silver remained conjugated to the dendrimer in the form of ions, stable silver metallic silver cluster and silver compounds. Because the dendrimer host is soluble it is able to delivered the immobilized silver in agar medium by diffusion .The silver clusters remains active due to their large surface area. Reaction with sulphur and chlorides ions neither blocks the diffusion of the silver nor the activity against *S. aureus*, *Ps aeruginosa* and *E. coli*. The protected silver and silver compounds displayed highly antimicrobial activity, without the loss of solubility. However the diffusion of dendrimers is totally prevented if common cellulose membranes are used.



(A) Divergent approach using click chemistry towards highly functionalized phosphorous dendrimers.

(B) Convergent approach towards triazole dendrimers using click chemistry American chemical society.



ZEOLITES

Zeolites are effective sorbents and effective ion exchange media for metal ions. NAPI zeolites $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$ have a high density of Na ion exchange sites. They can be inexpensively synthesized by hydrothermal activation of fly ash with low Si/Al ratio at 150 C IN 1.0-2.0 M NaOH solution. Zeolites have been evaluated as ion exchange media for the removal of heavy metals from acid mine waste water Alvarez- Ayuso et. al reported the successful use of synthetic NAPI zeolites to remove Cr(III), Ni (II), Zn (II), Cu (II), Cd(II) from metal electroplating wastewater. Nonporous ceramic oxides with very large surface area ($1000 \text{ m}^2 \text{ g}^{-1}$) and high density of sorption sites that can be functionalized to increased their selectivity towards target pollutants. Zeolite nanoparticles are prepared by laser-induced fragmentation of zeolite LTA microparticles using a pulsed laser. Zeolite nanoparticles formation is attributed to absorption of the laser at impurities or defects within the zeolite microcrystals generating thermoelastic stress that mechanically fracture the microparticles into small nanoparticles.

CARBONACEOUS NANOPARTICLES

Carbonaceous nanoparticle can serve as high capacity and selective sorbents for organic solute in aqueous solution. A number of polymer that exhibit antibacterial properties were developed for this purpose including soluble and insoluble pyridinium-type polymer which are involved in surface coatings azidated poly(vinyl chloride) which can be used to prevent bacterial adhesion of medical devices PEG polymer that can be modified on polyurethane surface and also prevent initial adhesion bacteria to the biomaterial surfaces and polyethyleneimine (PEI) that exhibit high antibacterial and antifungal activity. High activity of polycationic agents is related to absorption of positive charged nanostructure on to negative by charged cell surface of the bacteria. Crosslinked polycations prepared as nanoparticles. These are formed from PEI crosslinking and alkylation followed by methylation in order to increased degree of amino group substitution. Because of its positive charged and hydrophobicity, PEI nanoparticles are attracted as possible antimicrobial agents. The antibacterial activity is evaluated against Streptococcus mutants cariogenic bacteria. Various PI nanoparticles from 100 nm to 1micron in diameter are prepared having different degree of cross linking, particle size, zeta potential, that are achieved by alkylation with a bromo alkane followed by methylation. PEI nanoparticles having long chain alkyls demonstrated high antibacterial effect against streptococcus mutants for more than four weeks.

METAL CONTAINING NANOPARTICLES (I)

Nanoparticles having two key properties make them particularly attractive absorbents. On the mass basis they have a much larger surface area than bulk particles. Nanoparticles can also be functionalized with various chemical groups to increased their affinity towards target compounds. It has been found that the unique properties of nanoparticles to developed high capacity and selective sorbents for metal ions and anions. Characterization of the interaction of the nanoparticles with the bacteria by atomic force microscopy (AFM), Transmission electron microscopy (TEM) and laser co focal microscopy showed considerable changes in the integrity of the cell membrane, resulting in the death of the bacteria. Photolytic nanomaterials allowed ultra violet light also used to destroy pesticides industrial solvents and germs. Ag (I) and silver compounds have been used as antimicrobial compounds for coliform found in waste water. Silver nanoparticles nanodots or nanopowder are spherical or flake surface area metal particles having high antibacterial activity are used in wounds. Application of silver nanocrystals include as an antimicrobial, anti-biotic and anti-fungal agents when incorporated with coatings, nanofibers, textiles, plastics and soaps in treatment of certain viruses, in self cleaning fabrics as conductive fillers and in nanowires and certain catalysts applications. Ag nanoparticles were active biocides against gram positive gram negative bacteria including Escherichia coli, streptococcus aureus, klebsiella pneumonia and pseudomonas aeruginosa. Stable Ag nanoparticles of narrow size which have various monometallic particles Au, Ag, Pt, Pd can be synthesized in the laboratory. Zinc oxide used to remove arsenic from water.

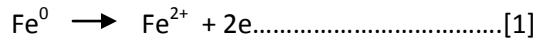
GROUND WATER REMEDIATION

Nanoremediation methods involved application of reactive material for detoxification and transformation of pollutants. These materials initiate both chemical reduction and catalysis of the pollutants of concern. Many different nanomaterials have been evaluated for used in nanoremediation. They include nanoscale zeolites, metal oxides, carbon nanotubes, noble metals and titanium dioxide. Nanoscale zero-valent iron is currently widely used in groundwater remediation.



A. NANOSCALE IRON NANOPARTICLE (NZVI)

The practical ability of nano zero valent iron(Fe0) particles lies in the fact to get oxidized in to +2 and +3 oxidation state there by reducing organic and inorganic impurities. Metallic iron (Fe0) serves electron donor.



Chlorinated hydrocarbon accepts the electrons and undergoes reductive dechlorination.

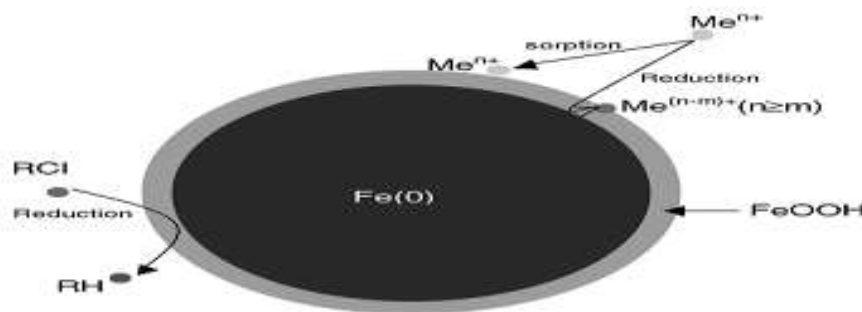
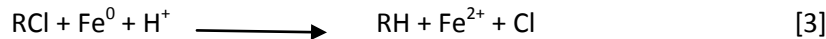


Figure 1: Schematic diagram of zero valent iron

From a thermodynamic perspective the coupling of rxn [1] and [2] is highly favorable



The standard reduction potential of (E=) of ZVI (Fe2+/Fe) is -0.44 V, Which is lower than many organic compounds like chlorinated hydrocarbons and metals such as Pb, Cd ,Ni, and Cr hence these organic compounds and metals prone to reduction by ZVI nanoparticles Nano ZVI extensively used in degradation of toxic and hazardous organic pollutants lindane andAstrazine ,Pentachlorophenol ,4 4'- dinitrostilbene 2 2'- disulphonic acid e.t. zero valent iron can also be modified based on the contaminant present. It could be modified to include catalysts like palladium coatings such as polyelectrolyte or triblock polymer .For the treatment of trichloroethane (TCE) a hazardous organic contaminant present in water the surface of the zero valent iron particle I modified to contain an oil-liquid membrane. This oil-liquid membrane which is generally composed of food grain surfactant and biodegradable oil and water is hydrophobic form an emulsion with ZVI termed as EZVI.

B. CARBON NANOTUBES

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure .CNTs are nanomaterial that are rolled in to a tube and are classified as single walled carbon nanotubes (SWCT) and multi layered carbon nanotubes (MLCT) according to the carbon atom layers in the walls of the nanotube. The hexagonal area of carbon atoms in graphite sheet of CNTs surface has a strong interaction with other molecule or atom which makes CNTs a promising adsorbent material. They are utilized for removing of heavy metals like Cr3+ and Pb 2+ and Zn2+ , metalloids such as arsenic compounds, organic biological impurities, and removing many kind of organic and inorganic pollutants such as dioxin and volatile organic compounds.



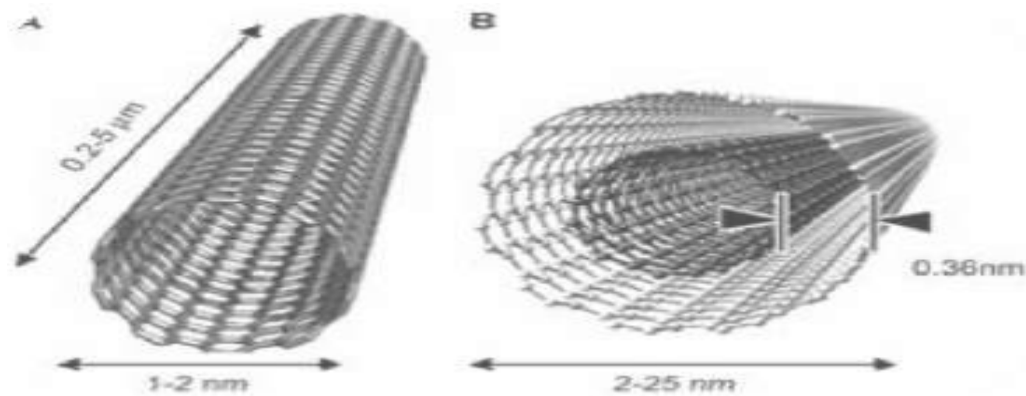


Fig.2 A schematic diagram of carbon nanotube and a multi walled carbon nanotube

Any increase in the discharge of heavy metals in to aquatic environment is toxic as they can accumulated in living tissues. These are removed from the water by multi walled carbon nanotubes (MWCT). To increased the absorption capacity of (MWCTs,) it is oxidized with nitric acid resulting to which a higher level of Adsorption was achieved. The sorption of Pb (II), Cu (II) and Cd (II) on to MWCTs were 3-4 times larger than those of powdered activated carbon and granular activated carbon which are the two conventionally used sorbents in water purification.

C. TITANIUM DIOXIDE PHOTOCATALYST

Photo catalytic silver doped titanium di oxide nanoparticle ($n\text{Ag}/\text{TiO}_2$) were used for water treatment(18). It is resistant to corrosion and non-toxic when ingested. The basic mechanism of photo activity of TiO_2 is reactive oxygen species(ROS) generation. Metal doping has been used to enhance TiO_2 photo catalysis by trapping excited electrons to prevent charge recombination. Electron trapping can occur if a dopant has a lower Fermi level than the excited electrons. Several metals including Fe, Ru, Mo, Os, Re, V, Rh, Au, Pt and Ag have been shown to enhance TiO_2 performance. Silver in particular has been shown to enhance the photocatalytic efficiency of TiO_2 for both organic contaminant degradation and bacteria. Silver doping TiO_2 enhance the photocatalytic inactivation of viruses by increasing hydroxyl ion (OH^-) production in addition to slightly increasing.

CONCLUSION

The aim of this review is to give an overall perspective of the use of nanoparticles (dendrimers, zeolites, metal containing nanoparticles, carbonaceous particles) zero valent iron Nzvi , CNT(carbon nanotubes) and Ag doped TiO_2 to solve the potential water issues and treatment of contaminated water and ground water remediation and reuse more effectively from conventional water treatment methods. Metal nanoparticles such as Ag, Zn, gold, silver shows promising results for water purification. The success of the technique in field conditions is a factor of interdisciplinary work that is involved. The collaboration of chemistry, material science and geology is one of the key challenges of this research.

BIOGRAPHY

Tanu Mittal is an M-Phil Scholar in chemistry department, Amity University, Noida. She received her M.Sc. degree in Chemistry from Punjab University, Chandigarh. Her area of interests includes environmental chemistry, nanotechnology in chemistry, organic compounds etc.

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