Use of nanomaterials for purification of drinking water: A review

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***Abstract*-Water is required for all life forms. Being a natural resource, it is the right of every individual to get safe, clean and disinfected water for their use in adequate quantity. Due to increase in urbanization, industrialization, population, global warming etc., exploitation of natural resources has increased extensively. Other than the depletion of quantity of safe drinking water, human interference has also degraded the quality of water by the insertion of industrial waste, domestic waste, agricultural waste, bio-medical waste etc. These substances have abruptly altered the natural composition of water. For the decontamination of water, several techniques have been identified and are in practice. Out of these, nanotechnology has been reported to demonstrate highly active against water decontamination and proved to be one of the most advanced and effective techniques. Owing to their nano size, high rate of reaction, chemical stability and high surface area, nanomaterials are better agents against water remediation as compared to their bulky particles. This review paper mainly focuses on the use of various types of nanomaterials like metal nanoparticles, nano metal oxides, carbon-based nanomaterials, dendrimers, zeolites and nanocomposites for the purification of drinking water. Use of these nanomaterials as catalysts, sorbent, membrane etc. has also been identified. Besides, a few drawbacks associated with nanotechnology along with their remediation have also been discussed in this paper.**

***Keywords*–Nanomaterials, nanocomposites, catalysts, decontamination**

1. INTRODUCTION

Water is the vital source of energy and required in many biological, physical, chemical and environmental processes. Although the earth is called as blue planet, only 2-3% of water is present in the form of fresh water [1], rest is in the oceans or seas. Out of the available freshwater resources, now-a-days it has become a challenging task to supply safe and pure drinking water for human activities. Due to increasing industrialization and human population worldwide, there is over exploitation of ground water sources leading to increase in pollutants and scarcity of fresh water. Increasing pollutants and toxicity effect severely the health of human beings, even may cause death due to use of contaminated and infected water. Discharge of various micro pollutants, pharmaceuticals, surfactants and chemicals cannot be even treated by conventional treatment methods. There is a strong need of treatment of polluted water and make it available for drinking purpose. Biological methods used for waste water treatment cannot remove all types of pollutants and these remain in effluent. Coagulation and lime soda method are not effective against medicines, drugs and pharmaceutical wastes. Method of disinfection such as chlorination and ozonation are also not perfectly suitable due to development of unpleasant odour and taste of chlorine and costing respectively. Even, UV and ion exchange methods are not effective against microcontaminants. Although RO techniques are recognized to be the best among the membrane filtration methods but yet its energy consumption is much higher. These all observations have drawn the attention of many researchers, private and government organizations to improve the quality of water by modifying existing water purification techniques.

Nanotechnology has emerged out as the best method for water purification both for its non-toxic approach and resource utilization [2]. It proves to be optimum for the removal of microcontaminants, pharmaceuticals, heavy metals etc [3]. Nanotechnology can be used in various facets such as nanomembranes, nanocatalysts, carbon compounds, metallic oxides, zero valent metals, nanosorbents, dendrimers, zeolites etc. Nanomaterials are the particles with nano size (1-100 nm) [4]. Owing to their nano size, they differ from macroparticles in terms of many properties like electrical, optical, mechanical and magnetic etc. Because of the size, these particles exhibit the properties of adsorption, catalysis etc [5]. Nanomaterials are in extensive use since many times in the field of chemical reactions, catalytic reactions, medicinal & pharmaceuticals chemistry and biology. Many researchers have reported the removal of pollutants, toxic metals, microbes and impurities of water by the use of various types of nanomaterials as their nano size and large surface area make them highly reactive and catalytic in nature. In present time, the most widely used and identified nanomaterials are zerovalent metal particles, metal oxides, mixed compounds (composites), dendrimers and carbon nanotubes, graphenes etc as depicted in Figure1.

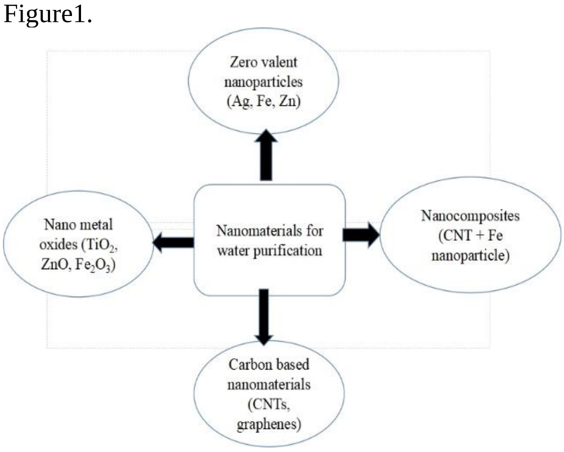

Figure 1: Various types of nanomaterials for water purification

2. NANOMATERIALS FOR WATER PURIFICATION

The significant properties of nanomaterials like high reactivity, adsorption and dissolution depend on the high surface area which is because of their nano size. These characteristics make the nanomaterials suitable for the treatment of drinking and wastewater in the form of membrane, catalyst, adsorbent, surface and reagents. This paper discusses about the use of following nanomaterials which are extensively used for water purification.

Adsorption: It is a surface phenomenon. Due to large surface area, nanomaterials have proved to be better adsorbent as compared to conventional activated charcoal. Besides organic pollutants, these materials are also used significantly for the adsorption of inorganic, heavy metal and micro pollutants as well. Following type of nanomaterials have been identified as nanoadsorbents:

2.1 Zero Valent Metal nanoparticles

The most commonly used and studied metals under this category are Fe, Zn and Ag nanoparticles. The most remarkable feature of AgNPs is that it can work on all types of microbial impurities of water. It is an effective germicide. The action of AgNPs has been suggested that either these damage the bacterial cell wall and penetrate inside the cell [6] or form free radicals which are responsible for killing of micro-organisms [7]. AgNPs are mixed with PES (polyethyl sulfone) membranes, which are studied to be very effective against bacterial impurities [8]. Ag ions release in the water for disinfection purpose and after a certain period of time the silver coating need to be changed. Zero Valent iron nanoparticles are also found to be induldged in various decontamination reactions. Due to high surface area, cheap in cost, absorption capability and participation in redox reaction, these are proved to be effective against water contamination. In acidic and nuetral media, FeO forms Fe^{2+} and in alkaline media Fe^{2+} combines with pollutants to form Fe^{3+} which is finally converted to $Fe(OH)_3$ that shows remarkable activity against microbial impurities. In the presence of D.O., an electron transfer reaction occurs between FeO and D.O. to form H_2O_2 and FeO gets converted in the form of Fe^{2+}. Both Fe^{2+} and H_2O recombine together to form hydroxy free radicals which effectively degrade the organic impurities of water [9].

$$FeO + O_2 + 2H^+ \text{-----------------} Fe^{2+} + H_2O$$

$$Fe^{2+} + H_2O_2 \text{------------------} Fe^{3+} + OH + OH$$

$$2H_2O_2 \text{------------------} H_2O + OH + OOH$$

Now-a-days Zn nanoparticles have also drawn the attention of several researchers because of their higher reducing ability as compared to FeO. Especially against halogen based organic pollutants [10], Zn particles have exhibited significant action in water.

2.2 Metal Oxide nanoparticles

Nanosized metal oxide particles provide high surface area and high compressibility without dimension change. Nano iron hydroxides are abrasion resistant and exhibit adsorption capacity towards arsenic from water. Nano metal oxides and nano metals are converted in the form of porous particles and used for decontamination. Further, nano TiO_2 particles are also in use for the purpose of removal of organic and inorganic pollutants. Titanium di oxide is a photocatalyst which effectively degrades the microbial impurities of water. But it requires UV lamp for the purpose of activation that makes it more energy consuming.

In this section TiO_2, ZnO, Fe_2O_3 and Fe_3O_4 are mainly studied for water decontamination.

Owing to high stability, photo catalytic activity, TiO_2 has been found as the most commonly used nanomaterial. In photocatalytic degradation process, TiO_2 convert reducing contaminates of water in the form of inorganic ions and CO_2. TiO_2 nanoparticles, in the presence of U.V. radiation produce OH, which readily degrade the microbial impurities of water. TiO_2 NPs are not only effective against compounds like fertilizers, pesticides, toxic materials, dyes etc. [11], but also against all strains of bacteria, viruses, fungi etc [12].

The band gap of TiO_2 is 3.2 eV which corresponds to U.V. region. After the absorption in radiation in the U.V. region, electron-hole pairs are produced. Electrons jump into the conduction band and holes are developed in the valence band. As the result of continuous charge separation, e^--h^+ reach at the surficial site, where H_2O reacts with h^+ to produce.

OH and on the other hand, O_2 absorbs the e^- to generate O^{2-}. The reactive species formed owing to above changes are OH and O^{2-} effectively degrade the organic pollutants.

After TiO_2, ZnO nanoparticles are also used for water decontamination, because their properties are very much similar to each other like band gap energy around 3.2 eV in near U.V. region, photocatalytic in nature and capability to oxidize impurities etc [13]. In order to increase the activities of ZnO nanoparticles, these are either doped with certain cations, anions and rare earth elements or with semiconductors such as cerium oxide, cadmium oxide, grapheme oxide and many more [14].

For the removal of impurities of heavy metal, iron oxide nanoparticles have found their applications, also because of their availability and usability. Various forms of iron oxide used are nonmagnetic hematite, magnetic magnetite and meghemite. These are used in the form of nanoabsorbents and used especially for the removal of heavy metals. Some ligands like EDTA, DMSA etc. [15] may also be inserted with iron-oxide nanomaterials to increase their adsorbtion capacity. Some iron-based nanomaterials have also been synthesized that show remarkable activity against hydrocarbons especially in oily water [16].

2.3 Carbon based nanomaterials

Because of the high absorption tendency, unique structure, higher surface area and reaction rates, various forms of carbon nanomaterials like CNTs, fibres, graphenes etc. have been identified and tested for water decontamination. Among the various, carbon-based nanomaterials, carbon nano tubes have found applications mainly for the removal of impurities from water. Carbon nanotubes are nanomaterials with cylindrical structure. These are the allotrope of carbon materials with single walled and multi walled structure [17]. CNTs provide high surface areas for the adsorption of pollutants especially metal ions are adsorbed due to electrostatic force. CNTs are also considered antimicrobial in nature as they destroy the bacterial cell wall via oxidation and while disinfection. Unlike chlorination, no harmful by-products have been formed. Besides, it’s quite simple to regenerate it by minor change in pH conditions. Yan and his co-workers [18] developed an ultra long CNT system which was two times more effective than the conventional system. These systems have the properties of disinfection, desalination and filtration. A sponge made up of CNT with boron has also been fabricated which was capable in absorption of oil from water [19]. The use of CNT for large scale water purification was not found suitable owing to high cost instead this can be used for the removal of antibiotics and pharmaceuticals [20]. CNTs have been found to show significant absorbtion tendency for metal ions, organic and inorganic chemicals and fabric dyes. CNTs can be also used in the form of composites by combining it with our nanometals and suppot.

Graphene is a planar carbon based, most widely used for filtration purpose as the membrane. The graphene layer has pore size of 1-15 nm, which is selectively perameable for some components, such as dyes, toxic metals, fertilizers, pesticides etc. Because of its stability and high surface area graphene is a very effective adsorbing agent. Many researchers have found the application of graphene and reduced graphene for the removal of Hg^{2+}, certain antibiotics, Cu^{2+} [21], dyes etc. Other than adsorption, graphene can also be used as membrane filtration. These are also reported to show significant photocatalytic activity against a variety of organic pollutants. Graphene sheets coupled with AgNPs have been reported to show strong antibacterial activity against *S. auereus* [22].

2.4 Dendrimers

Polymeric nanoadsorbents known as dendrimers which are branched structures effectively used for the removal of organic compounds that get adsorbed on the interior hydrophobic body and toxic heavy metals that get adsorbed on the outer branches of the dendrimers. Recently an integrated dendrimer system was found to exhibit significant removal of copper ion from water. Sadeghi-Kiakhani and co-workers [23] fabricated a bio adsorbent chitosan-based dendrimer for the removal of dyes from textile waste. Biggest advantage of using bioadsorbent is its degradability, compatibility and nontoxicity.

2.5 Zeolites

Zeolites are porous membranes in which nanosilver particles can be impregnated, which get exchanged with other cations of water and effectively attack on the germs and retard their growth. In another approach, nanozeolites are also synthesized and used for the purpose of disinfection [24].

For the removal of Arsenic from water, carbon nanotubes and nanometals can be used effectively. Nanometals and zeolites can be directly installed in treatment system in the form of filter bed. On the contrary, CNTs are not cost friendly and require membrane filtration for their installation and to prevent the entry of nanomaterials in the water. But CNTs are very effective against micropollutants having polar organic functional group as CNTs provide intense time and contact surface for the adsorption. As far as the efficiency of the process is considered, polymeric nanoadsorbents are considered as the advanced system for water purification. These remove not only the heavy metals, but also organic pollutants present in water. The only drawback of this system is the requirement of advanced costly technique. All materials discussed here like CNTs, zeolites and nanometals are eco-friendly as obtained from nature itself and nontoxic.

2.6 Nanocomposites

Metal nanoparticles, Nano metal oxides, CNTs, graphene are extensively used for water remediation, but these also possess some drawbacks such as cost, oxidation, product recovery, accumulation, requirement of support etc. In order to fabricate a more usable nanomaterial for water treatment, now-a-days, two types of nanomaterials are combined, and the resultant substance is known as nanocomposites. For example, Carbon Nano tubes and iron nanoparticles are fabricated together to make a composite structure, which has the character for adsorption of toxic ions (which was for CNT) and separable via external magnetic field [25] (which was for Fe nanoparticles). So, the properties of two materials have combined by the synthesis of such type of material.

Uses of all types of nanomaterials discussed are summarized in Table 1

Table 1: Uses of Various Nanomaterials

S. No.	Type of Nanomaterial	Impurities Removed
1.	Metal nanoparticles	Microbial impurities [8], halogen based organic pollutants [10]
2.	Nano Metal oxides	Toxic metals, fertilizers, pesticides, dyes [11], hydrocarbons [16]
3.	Carbon nanotubes	Antibiotics [20], metal ions, dyes, microbes
4.	Graphenes	Dyes, Hg^{2+}, Cu^{2+} ions [21] etc.
5.	Dendrimers	Dyes [22], metal ions etc.
6.	Nanocomposite s	Toxic metal ions [25]

3. LIMITATIONS

Nanomaterials have emerged out as the most advanced, recent and efficient method for water decontamination, but these are also bound with certain limitations like zero valent metal nanoparticles tend to accumulate in water, result in their degradation, oxidation and waste removal after disinfection reactions get over. Some are quite selective against certain pollutants. Besides, metal oxide nanoparticles show activation only in the presence of U. V. radiation; their activity in visible regions is still not reported. Other than this, the preparation and recovery of these nanoparticles are also quite complicated. For their activation purpose, a source of U. V. radiation is also required, which increases the cost of the project. Some nanoparticles tend to show the property of photo-corrosion.

Carbon based nanomaterials like CNTs cost very high, which makes their use limited. Graphene releases toxic substances which are not environmentally friendly. Till date the nanocomposites synthesized are toxic, costly and unstable, so there is a continuous need of fabrication of optimum nanocomposite.

AgNPs are especially used for the removal of E. coli, ZnNPs are used for the removal of OCDD, Nano Fe_2O_3 against dimercaptosuccinic acid, CNTs against Zn (II), Pb (II), Cu (II), Cd (II) and dyes.

4. CONCLUSION AND FUTURE OUTLOOK

In the current scenario, providing decontaminated water to a mass population is a challenging task. Current purification procedures need many modifications. Nanomaterials have come out as the potential factor to serve the need of people to get potable drinking water. Properties like chemical reactivity, high surface area and nano size make them better than the existing process of water remediation. Nanomaterials can be used in the form of particles, sheets, membranes, layers, catalysts, etc. and successfully reported against a variety of water pollutants like organic waste, dyes, inorganic metal cations, compounds, fertilizers, pesticides, pharmaceuticals, industrial wastes and even against microbial impurities of water.

Despite several limitations, nanomaterials are the most widely used agents for water purification. After certain modifications, in their fabrication and usage, these may become the future agent for the same purpose. In order to increase the reactivity of metal nanoparticles, these can be doped with other metals. To make the recovery of nanoparticles easy after disinfection, the nanoparticles can be inserted in membrane like polyvinylidene fluoride [26].

Doping with semiconductors like CdO, CeO_2 [27] has been reported to show enhanced photo-degradation capacity of metal oxide nanoparticles. To make the graphene sheets stable against pressure conditions, their multilayered graphene oxide is synthesized having higher stability. CNTs and graphenes have the capability of removing all kinds of water pollutants even though these are present in very low concentration in water. Incorporation of certain functional groups on carbon nanotubes make them work against a variety of water decontaminants.

Research is still in process to research out nanomaterial which should be environmentally friendly, cost friendly, high stable, non-toxic and effective against organic, inorganic and biotic contaminants, easy to synthesize, use and can be recovered and reused.

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