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Ecofriendly Nanomaterials for Water Remediation: A Review

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ABSTRACT

Water has been the most important amenity of nature that every individual needs for almost each and every aspect of life. To get fresh and hygienic drinking water is the priority and right of each human being. Increasing population, pollution and over exploitation of natural drinking water sources have led to the generation of contamination in water. In order to make the water suitable for drinking purpose, various physical and chemical technologies have been in use, out of these nanotechnology is the most advanced one. But use of synthetic nanomaterials have also caused toxicity and accumulation in environment. This paper mainly focuses on use of eco-friendly nanomaterials for water purification. Nanomaterials extracted from various plant sources and their practical application in disinfection has been described in detail. Besides the use of bio-polymers, cellulose and chitosan based nano materials has also been described. The mechanism of these nanomaterials for the killing of bacteria has also been explained.

Key words : *Ecofriendly nanomaterials, Water, Ecofriendly water treatment*

Introduction

Water is required in every aspect of life, for individual in metabolism, domestic, industrial, agricultural, transportation and geological cycle etc. Due to urbanization and industrialization, human has severely damaged the natural composition of water. Although for the purification of water, many processes have been in practice since ancient times like chlorination, filtration, RO, radiation, ozonolysis etc. Some methods are based on disinfection and some on removal of inorganic and organic impurities of water. In the present time, nanomaterial have come out as the key remedy which can be useful for the removal of all types of impurities in an efficient manner. Nano means the particle with nano size. Such particles have higher surface area so provide more space for reaction as catalyst. The other physical, chemical, electrical properties of nanomaterials are also different than their respective macro particles (Kabir *et al.,* 2018). High reactivity, chemical stability, high surface area, catalytic behaviour, adsorption tendency etc., all these properties enable the nanomaterials to serve as the best agent for water purification.

Nanomaterials for water remediation

Nanotechnology has been proved to be one of the

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most efficient method for water treatment. It is useful not only against the microbial impurities of water but also for the organic and inorganic pollutants. Even for the decontamination of industrial waste water having toxic metals and chemicals, nanomaterials have emerged out as the most suitable method for water disinfection. Owing to nanosize, higher surface area, chemical reactivity, catalytic behaviour and adsorptive behaviour, nanomaterials have been used in various forms like filter membrane, catalysts, tubes, sheets etc. Nanomaterials in the form of zero valent metals, metal oxides, carbon nanotubes, graphenes, dendrimers have found application in the field of water remediation. Ag, Fe, and Zn metal, titanium dioxide, zinc oxide, iron oxide and carbon based nanomaterials in the form of sheets and tubes are much effective. Ag NPs are significantly active against microbial impurities (Danilczuk *et al*., 2006). FeNPs degrade organic pollutants of water via ·OH free radical generation (Wang *et al.,* 2014). Zn NPs are also reported to be effective especially towards halo organic pollutants (Zhao *et al*., 2020).

In the section of nanometal oxides TiO_2, ZnO, Fe_2O_3 and Fe_3O_4 are most commonly studied. In the presence of U. V. radiations, TiO_2 show photocatalytic degradation against microbes, dyes, fertilizers, pesticides, toxic substances etc. Similarly, doped ZnO nanomaterials are also effective against impurities of water. Nano iron oxide materials work as adsorbent for heavy metal ion in water.

Carbon nanotubes have higher surface area which readily absorbs the metal ions and also antimicrobial in nature. Another carbon based nanomaterial which is used as filter or in the form of sheet is graphene. An another form of nanoadsobent is dendrimers which are polymeric materials with branched structure capable of removing organic impurities of water. Now-a-days two types of nanomaterials are combined together to prepare a composite material which contain the properties of both the nanomaterials.

Although the nanomaterials mentioned above are widely used for water technology, but these are associated with several drawbacks like accumulation, degradation, oxidation, selectivity, toxicity etc. So there is a continuous need in the preparation of such eco-friendly nanomaterials, which are non-toxic, stable and cost friendly.

Ecofriendly Nanomaterials

In order to synthesize eco-friendly nanomaterials, green chemistry principles should be applied. Because of the need of reducing toxicity in water, the researchers are much focused on the synthesis of such materials that are not only economical but also eco-friendly in nature. Synthesis of eco-friendly nanomaterials rely mainly on four principles:

- Toxic reagents and solvents should not be used.
- In the adopted synthetic route, there should not be formation of any by-product.
- Shape and size of the particles should be controllable
- And finally the product obtained should be pure.

Chitosan, glycogens and polysaccharides are some bio-molecules which are commonly used as precursors for bio-based nanomaterials. These are also biodegradable in nature and in turn are being prepared from plant extracts and nanocellulose. These are said to be eco-friendly as they do not produce any secondary pollutants.

A researcher named Al-Issai and his coworkers[5]synthesized various nanoparticles of Ag, Cu, ZnO, MgO, SiO_2 and carbon nano tubes and tested their antibacterial activities against various bacterial strains such as *E. coli, Enterobacter, Salmonell and Enterococci*. It was observed that the nanomaterials synthesized from various eco-friendly methods exhibited remarkable activity against infection of water.

Plant based nanomaterials for the preparation of metal and metal oxide nanoparticles

One of the finest methods for the green synthesis of nanoparticles is the use of plant based materials such as plant parts (leaf, root etc.) and the plant products like glucose, sugar, amino acids, extracts from tea, coffee, banana, protein etc. Tea extracts have polyphenols which are chelating and reducing agents, used for the synthesis of nanoparticles. Following are the examples of some plant based materials which have been used for the synthesis of various nanoparticles.

1) Starch: For the synthesis of AgNPs with particle size 25 nm, hydroxypropyl starch is used which in turn is extracted from monosaccharides (glucose and galactose) and disaccharides (maltose and lactose). The nanoparticles thus obtained are significantly active against *E. coli, S. aureus, B. subtilis* and others (El- Rafie *et al*., 2011).

Honey: In an another method, in a controlled environment of pH and temperature, honey is used to synthesize AgNPs (Philip, 2010). At slightly alkaline pH, spherical silver nanoparticles with 4 nm particle size are reported to be synthesized. These nanoparticles exhibit remarkable activity against infection of water.

2) Tea Extract: Polyphenols and epicatechin obtained from tea extract are extensively used for the synthesis of AgNPs. Tea extracts contain caffeine and theophylline work as catalysts for the preparation of nanoparticles. On changing the ratio of water to tea extracts, AgNps ranging from 4 to 100 nm can be prepared.

Vitamin B2: It if found to be the most suitable agent for the synthesis of silver and palladium nanoparticles. Vitamin B-2 has minimum toxicity and also biodegradable in nature. On using water as solvent, rod-like nanoparticles are formed. In the presence of acetic acid, Ag and Pd nanoparticles are formed with the size of 4 to 6 nm in N-methylpyrrolidinone, 5 to 6 nm are synthesized (Nadagouda and Varma, 2006).

3) ***Camellia sinnensis*** **(Green Tea):** For the synthesis of Ag, and AuNPs, green tea extract is used which contains polyphenols. On changing the concentration of metal ion and tea extract, Ag and AuNPs of size 40 nm can be prepared.

Musa paradisiaca **(Banana Peel):** The silver nanoparticles synthesized from banana peel are found to be effective antifungal agents against *Candida albicans* and *Candida lipolytica*and also antibacterial against *E. coli* and *Klebsella* spp. etc. (Deena, *et al.*, 2015).

4) ***Swietenia mahogany:*** Ag, Au, Ag-Au alloy nanoparticles can also be prepared by different polyhydroxylimonoids of dried mahogany leaves.

5) ***Anacardiumoccidentale*** **(Cashew nuts):** In order to synthesize highly crystalline and cubicl structures of gold, silver and Au-Ag alloy nanoparticles, leaf extract of cashew nuts is used as precursor which contains polyols.

6) ***Euphorbia nivulia*** **(Leafy milk hedge):** Silver and Cu NPs of 5-10 nm diameter can be synthesized from the latex obtained from steam of *Euphrbianivulia*. Such NPs are effective against many strains of bacteria (Valodkar *et al.*, 2011)

7) ***Sorghum*** **(Jowar):** Phenolic derivatives obtained from Sorghum are effective reducing and capping agents for the synthesis of Fe and AgNPs at RT.

The summary of various plants or plant products used for the preparation of metal NPs have been depicted in the Table 1.

Microbes for the synthesis of metal NPs

Lactobacillus species and Sachharomycescerevisae: For the preparation of TiO_2 nanoparticles of particle size 8-35 nm, these bacterial species can be used. TiO_2 NPs are found to be highly effective against pathogenic impurities of water (Prasad *et al.*, 2007).

1) ***Trichoderma viride:*** It is a fungal strain commonlyused for the preparation of AgNPs at RT. The metal nanoparticles thus obtained are very active against several gram +ive and –ive bacterial strains.

Fusarium oxysporum: For the synthesis of crystalline SiO_2 NPs of size 2-6 nm, amorphous plant biosilica is treated with rice husk and fungus *Fusarium*

Table 1. Summary of nanomaterials synthesized form various plants or plant products

S. No.	Plant/Plant product	Type of nanomaterial synthesized	Particle size	Used for disinfection of
1.	Starch	AgNPs	25 nm	*E. coli, S. aureus, B. subtilis*
2.	Honey	AgPs	4 nm	Bacterial strains
3.	Tea Extracts	AgNPs	4-100 nm	Bacterial strains
4.	Vitamin B2	Ag and PdNPs	4-6 nm	Bacterial strains
5.	Green tea	Ag and AuNPs	40 nm	Bacterial strains
6.	Banana peel	AgNPs	-	*C. albicans, C. lipolytica, E. coli, Klebsella*
7.	Orange peel	AgNPs	-	*E. coli, S.aureus*
8.	Mahogany leaves	Ag, Au, Ag-Au alloy		
9.	Cashew nut leaf	Ag, Au, Ag-Au alloy		
10.	Euphorbia latex	Ag and Cu NPs	5-10 nm	Gram positive and gram negative bacteria
11.	Sorghum	Fe and AgNPs	10-50 nm	Bacterial strains

oxysporum (Bansal *et al.,* 2006).

2) ***Actinomycetes Thermomonospora Species:*** In an another method, gold nanoparticles can also be synthesized from prokaryotic Thermomonospora species.

Brevibacterium casei: This bacterial species is used for the synthesis of Ag (10-50 nm) and Au (10-50 nm) NPs (Kalishwaralal *et al.,* 2010).

Bio-polymer based nanomaterials

Bio-polymers are biodegradable natural substances with high mechanical strength and can be transformed to water filters, which are effective against bacterial impurities of water (Altintas *et al*., 2015). Due to their larger surface area, their working efficiency is higher than ordinary filters. Among biopolymers, peptides, chitin, cellulose and chitosan derivatives possess remarkable antimicrobial activity. Naturally occurring bio-polymers can be converted to desired nano size, shape and functionality. These disinfectants are not only eco-friendly but also highly reactive, possess high strength and effective against a variety of infectious microbes. As polymeric materials are enriched with functionality of carboxyl, hydroxyl, amino group etc., they cause decontamination of water completely.

Nanocellulose based nanomaterials

Nanocellulose materials are hydrophilic in nature, besides these are renewable and non-reactive in nature. Being cellulose, it is mechanically strong and owing to nano size, its surface area is higher, make it suitable to use as filter membrane for water purification especially against bacteria. Nanocellulose materials can be converted to nanocrystals and nanofibrils by the reaction of catalysis and hydrolysis. Nanocellulose contains both ionic and non-ionic surface groups, which enable them for selective absorption of contaminants. Because of lower surface charge density, cellulose nanocrystals undergo flocculation quite frequently. Despite, the absorption selectivity and Eco friendliness make these membranes a better alternative of conventional membranes.

Chitosan based nanomaterials

Chitosan is prepared from anthropod shells, algae and fungi. It is formed by deacetylation of chitin. It is made up of protein and lipid and proceed to polymerization rapidly. Chemically, its structure shows similarity with cellulose. In water, treatment technology, chitosan works as membrane filter or as surface coating. Other than membrane properties, chitosan is also associated with antibacterial behaviour. It is found to exhibit remarkable antibacterial, antifungal and antiviral properties. Besides, these molecules are not toxic for humans.

The Mechanism of Disinfection

Nanomaterials prepared from natural resources are not only antimicrobial in nature but also their cost of preparation and process of usage are very simple.

Disinfection by plant based nanoparticles

Various nanoparticles like Au, Ag, Pd, Al, Ni have tendency to react selectively with the infected cells like bacterial and viral etc. Due to their larger surface area, their rate of reaction is quite high. These nanoparticles produce reactive oxygen species (ROS) which directly acts on DNA and RNA of infected cells.

AgNPs

Antimicrobial action of AgNPs follow a unique mechanism. AgNPs combine with cell enzymes and prevents replication of DNA, thereby deactivates them. AgNPs enter the cell by rupturing cell membrane and react with protein or glutathione to produce ROS or hydroxyl radical via Fentom mechanism. The ROS attacks on other cell organelles to destroy them like mitochondria, DNA etc., leading to cell death.

ZnO NPs

The action mechanism of ZnO nanoparticles show quite similarity with AgNPs. It also includes release of ROS like peroxide and $HO^{.}$ Radicals which readily damage the infected cells.

TiO_2 NPs

The action of TiO_2 shows photocatalytic degradation of microbes. TiO_2 produces free radical scavengers such as $HO^{.}$ And peroxide which irradiates between the wave length of 300-390 nm (U.V. region). The reaction of TiO_2 depends on several circumstances like concentration of catalyst, microbial nature, radiation energy and pH, O_2 concentration and stability of reactive species etc.

Chitosan Nanoparticles

The mechanism suggested for chitosan against bacterial cell is different from other nanoparticles. Its functioning is related with the electrostatic attraction force between positively charged chitosan and negatively charged cell membrane, causing damage of the membrane and cell organelles get damaged due to action of chitosan. Chitosan works only under acidic media. Several chitosan derivatives containing quaternary ammonium group have been synthesized and reported to be potential antimicrobial agent than the normal compound. Chitosan derivatives form an enclosed layer around microbial cell, result in the breakdown of microbial cell and finally death. Chitosan causes death of cell by inhibiting the enzymatic action of cell via chelate formation with trace metals. But at higher pH, the chitosan action becomes ineffective (Qi *et al.*, 2004).

Conclusion

From the aforesaid observations, it can be concluded that the nanomaterials extracted from natural sources like plant and its parts have been quite effective for not only the disinfection but also for the removal of inorganic pollutants of water. Being eco-friendly, these particles do not cause any toxic effect on environment and on human beings. The biopolymers have also reported to serve the purpose quite effectively. Still, much researches are required to get more form of eco-friendly nanomaterials which are cost friendly, easy to prepare, easy to use, reactive and non-toxic in nature.

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