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RESEARCH ARTICLE

TREATMENT OF CONTAMINATED WATER BY NANOTECHNOLOGY: A REVIEW

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Abstract

In the current scenario, the availability of clean drinking water is decreasing gradually. From a long time, many technologies have been applied for the treatment of contaminated water. The water is contaminated by various sources like industries, human activities, sewage generation and rain. Presently, nanomaterials have good potential for the treatment of drinking water and sewage water. The excellent properties of nanomaterials such as high mechanical properties, more surface area, good chemical reactivity, lower economical value, toxic metal recovery, and pathogen killing. Various types of nanomaterials like carbon nanotubes, metallic nanoparticles, nano-sorbents, bio-active nanomaterial, nano-filtration matrixes, nanoscaled zeolite and nanopolymeric materials are effective and powerful material for the treatment of the contaminated water. In the present review article, we discuss the application of recently advanced nanomaterials for water treatment methods such as adsorption, catalysis, filtration and disinfection. Special attention has been given to three major classes such as organic, inorganic and biological water pollutants. Besides, promises, facts and challenges of these new technologies have been seriously examined. In this review, the most extensively studied nanomaterials, metal oxide nanoparticles, carbon nanotubes (CNTs), and nanocomposites are discussed in brief.

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Introduction:-

Water is an essential component for the living being. Two Hydrogen atom is bound to the one oxygen atom, it creates an asymmetrical molecule with a positive charge on one side and negative charge on the other side as shown in Figure 1. This charge differential is called polarity and dictates how water interacts with other molecules. The polarity of the water molecule plays a key role in the combination of water contaminants.¹⁻⁸ Water has extensive capability to dissolve a variety of compounds due to polar character and it is a designated universal solvent. As per the World Health Organisation's (WHO) report, the requirements of water are a minimum of 7.5 litres per capita per day at normal temperature and general activities. However, in an emergency, a minimum of 15 to 20 litres is required excluded laundry and bathing.

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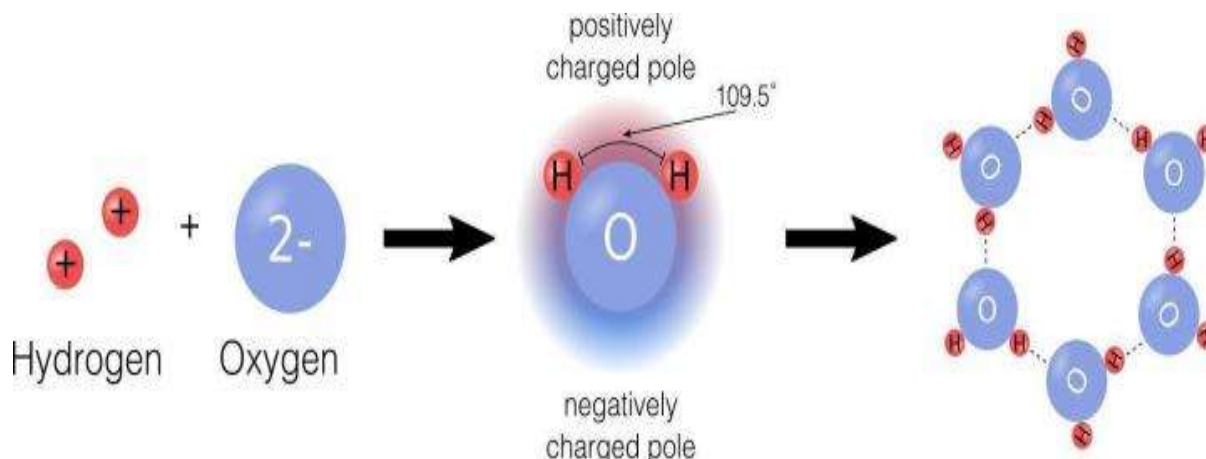


Figure1:- Structure of water molecule.

New scientific concepts and their technologies are replacing traditional water treatment methods. Nanomaterials are very well studied by a great number of investigators for the treatment of contaminated water.⁹⁻¹² Nanomaterials are developed by the engineering and manipulating in natural occurring matters at the nanoscale up to 1–100 nm which generate the novelty in nanomaterials for treatment of water polluted by toxic metals, chemicals, and microbial species. Due to their excellent properties toward reactants, they are more applicable in water purification. The water treatment techniques are revolutionizing by using various types of nanomaterials due to excellent own properties based on particle size.

Several conventional technological developments are used usually for treatment of wastewater while nanotechnology has proved to be one of the advanced tools for wastewater treatment. Developments in nanosized research have change into existing water treatment technology based on an economical level. The excellency of; nanotechnology has floated the good opportunities to fulfil the clean water demands of the new age. It is also suggested that nanoparticle-based techniques can adequately improve the water quality using various nanomaterials.¹³⁻¹⁷ At the nanoscale, materials possess an excellent and significant change in physical, chemical, and biological properties mainly due to their structure, higher surface-area-to-volume ratio offering treatment and remediation, sensing and substrate detection, and pollution control. Nanoparticles can penetrate within the target substrate and thus can treat wastewater which is usually not possible by conventional technologies.

The super high surface area, high reactivity, and catalytic properties of nanomaterials are expected to greatly enhance the kinetics and efficiency of various chemical and physicochemical processes used in water and wastewater treatment, and therefore reduce system size as well as chemical and energy consumption. These unique features have the potential to enable the paradigm shift towards distributed wastewater treatment and water supply, a much-needed change in large metropolitan areas facing challenges of rapid population growth and ageing infrastructure. On the other hand, like any new family of materials, the potential impact of nanomaterials on human health and the environment is unclear.

Table 1:- Some limitations for conventional water treatment processes.

S. No	Methods	Some limitations
1.	Distillation	Most of the heavy contaminants like metals and other compounds not removed and high energy required
2.	Chemical	The huge amount of chemical required and create secondary sludge disposal environmental issue.
3.	Coagulation and flocculation	Complex and not efficient to remove contaminants due to pH problem
4.	Microbial	A very slow process, more time required and generate micronutrients which are not removed easily.
4.	Ultraviolet	More expensive and not efficient in killing the microorganism
5.	Reverse Osmosis	Requires high energy, not capable to remove chemicals organic volatile compounds, chlorine and chloramine.

6.	Nanofiltration	Requires high energy and pre-treated water-limited salts and univalent ions removed, Fouling affect membrane filtration capacity.
7.	Ultrafiltration	Does not remove dissolved inorganics requires particulate plugging and difficult to clean.
8.	Microfiltration	Nitrate, fluoride, metals, volatile organic matters, colours not removed. Require regular cleaning. Less sensitive to microbes
9.	Carbon filter	Does not removed nitrate, fluoride, metals, sodium. Requires regularly changing of filter units.

Mostly water pollutants are compounds of organic, inorganic and microbial species. Among metals, some carcinogenic such as arsenic, chromium, cadmium, lead, cobalt, nickel, mercury etc. which are directly influence leaving being and environment. Anions like Nitrates, chlorides, sulfates, phosphates, fluorides, oxalates, selenides, and chromates show hazardous effects at various concentrations. Water is also polluted by organic pollutants, like pesticides, fertilizers, hydrocarbons, detergents, phenols, plasticizers, biphenyls, oils, and greases.¹⁸⁻²²

The most important technologies are applying for water treatment such as crystallization, coagulation, filtration, micro/ ultra-filtration gravity separation, ion exchange, sedimentation, flotation, flocculation, oxidation, precipitation, solvent extraction, evaporation, distillation, reverse osmosis, electro-dialysis, electrolysis, adsorption, setting-out, centrifugal and membrane separation, fluidization, neutralization, and electrochemical process.

Some important limitations for conventional water treatment processes for the removal of pollutants from water are summarised in Table 1. Literature survey indicates that any single technique is not capable to recover the pollutants from water.^{23,24}

Treatment of wastewater by nanotechnology:

Nanomaterials play an important role in the water treatment process because chemical, physical and microbial properties are changed and create novelty in performance.²⁵⁻²⁸ The advantage of some nanomaterial-based techniques for the treatment of wastewater are summarised in Table 2 and briefly discussed below.

Table 2:- Application of nanomaterials for wastewater treatment.

S. No	Nanomaterials	Advantages	Limitations
1.	Nanoadsorbents	More surface area, good adsorption capacity, chemical pollutants and bacteria removed	More costly
2.	Nanometals and oxides	Very high surface area, less abrasive, magnetic	Less reusability
3.	Membrane and their process	Excellent reliable, frequently used in wastewater treatment processes	More energy require
4.	Photocatalysis	High stability, low cost, Activity performed in UV-visible range	Very selective response
5.	Disinfection and microbial growth control	Act very strong antimicrobial activity, less toxic to human health, ease application	Residue disposal problem

Nanadsorption process:

Adsorption is a surface phenomenon. Adsorption is depending upon nature of adsorbate and adsorbent and also influenced by physical forces and chemical bonds between them. Due to excellent properties of nanoadsorbents such as nanosize, catalytic properties, good reactivity, more surface area, huge active sites, good catalytic power, they are easily interacting with cations and anions of pollutants and removed from water bodies. Recently, carbon, metal and other material based nanoadsorbents frequently applied water treatment.²⁹⁻³² Nanomaterials have excellent absorption capacity, interaction power, and reaction capabilities, and they are mixed with aqueous suspended contaminants which eventually can also quantum size effects reflect.³³⁻³⁷

Carbon nanotube used as nanoadsorbents:

Carbon nanomaterials are fascination materials because they have a unique structure and specific electron characteristics which plays a major role in the adsorption process. Due to more pollutants adsorption power, fast kinetics, more surface area and excellent selectivity, they are utilised in many fields including wastewater treatment.

Carbon nanotubes are graphene sheets rolled up in cylinders with the diameter as small as 1nm.³⁸ The structure of carbon nanotubes is cylindrical (Figure 2). Carbon nanotubes (CNTs) are generally two types as single-walled and multi-walled nanotubes contain activated carbon as substituents. The surface areas and active sites of carbon nanotubes which are chemically modified for achieving high adsorption goal. Ultimately, the hydrophobic surface of carbon nanotubes reduces the active surface area which accelerates the adsorption of organic pollutants. A large number of pores and active sites in the bundle of carbon nanotubes play a major role in the adsorption process.

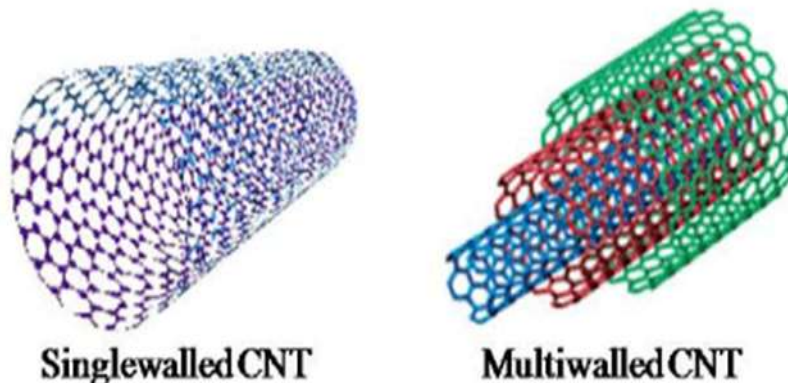


Figure 2:- Structure of single-walled carbon nanotube and multi-walled carbon nanotube.

According to well documented scientific studies, CNTs have excellent properties and are attracted research interest in the adsorption process. Due to larger surface area and good pores density, CNTs possess super adsorption capabilities and excellent adsorption efficiencies for pollutants, like dichlorobenzene, ethylbenzene, Zn^{2+} , Pb^{2+} , Cu^{2+} , and Cd^{2+} , and many dyes.^{39,43}

Hydrogen peroxide, $KMnO_4$ and nitric acid are used for the recovery of Cadmium ion from water by the oxidized surface of carbon nanotubes. This CNTs have good adsorption property for metals because oxidized surfaces have functional groups, like carboxylic acid, hydroxyl, carbonyls. They have the excellent adsorbing capacity with metal. Many investigators have been reported that ions of Cu, Pb, Zn are also removed with the help of the same process. Regeneration of CNTs are achieved by change pH in acidic condition.⁴⁴⁻⁴⁸

Metal-based nanoadsorbents:

Iron oxide, titanium oxide, zinc oxide are metal-based nanoadsorbents. They are frequently used for the removal of toxic metals from water bodies. The nanosize based metal oxides are cheaper, easy applicable and highly reactive. The oxygen atom of metal oxide is easily attached with water contaminants and automatically formed complex with nanoadsorbents. Magnetic nanoadsorbents like maghemite ($\gamma-Fe_2O_3$), hematite ($\alpha-Fe_2O_3$), and spinel ferrites ($M^{2+}Fe_2O_4$, where $M^{2+} = Fe^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Mg^{2+}$) are excellent adsorbing metals for the recovery from polluted water.⁴⁹⁻⁵¹ Many investigators reported that the adsorption capacity of nanoadsorbents are directly based on particle size because surface area increases when particle size decreases.⁵²⁻⁵⁴ The capacity of CNTs to adsorb toxic metals is also reported by several investigators.⁵⁵⁻⁵⁷ Toxic metals are easily removed from polluted water by magnetic nanoadsorbents and they are separated with help of applied external magnetic field.

Polymer-based nanoadsorbents:

Due to good thermal stability, unreactive in acid or basic medium and excellent adsorbing capacity, polymeric nanoadsorbents are used by many researchers for removal of toxic metals from wastewater.⁵⁰⁻⁶² The polymeric matrix of nanoadsorbents was prepared by the modification of Fe_2O_4 magnetic nanoparticles with the help of 3-aminopropyltriethoxysilane and copolymers of acrylic acid and crotonic acid. This modified polymeric nanoadsorbents matrix are capable of removed toxic metal ions like Cd^{++} , Cu^{++} , Pb^{++} and Zn^{++} from polluted water.

Membrane:

The porosity of membrane plays a key role in the filtration of microorganism and materials which are influenced by pressure-driven force or electrical method. The automation process of membrane technology depends on pore density and molecule size for wastewater treatment. Due to the requirement of high energy consumption for creating pressure-driven force and adhering of contaminants on membrane develops complexity and reduces the

membrane life.^{63,64} The quality of membrane technology is modified by the addition of nanomaterials into the membrane which improves thermal stability, permeability, selectivity, fouling resistivity, and chemical and thermal stability. Electrospun nanofibers have a good surface area, excellent porosity which forms complex nanofiber matrixes.⁶⁵⁻⁶⁷ They are easily fabricated for different uses. Preparation properties and uses of nanofibers have been well documented in the literature. An electrospun nanomembrane is capable to remove the bacteria and viruses from the aqueous environment due to appropriate pore size which is also calibrated as per the requirement of purposes. Nanocomposite membranes are also fabricated by a combination of mixed matrices surface and functionalised membrane. In another process, the thin-film membrane of nanocomposite is prepared by incorporation of nanoparticles such as nanozeolites, nano-silver CNTs and nano-titanium oxide within a thin layer of polymers to improve the quality of membrane.⁶⁸⁻⁷⁰

Nanoparticle-based Photocatalysis:

Titanium oxide and zinc oxide nanoparticles play an important role in photocatalytic degradation of water pollutants. The electrochemical photolysis of water on TiO₂ semiconductor electrode has been reported in literature.⁷¹⁻⁷³ Recently, photocatalytic degradation technology has been successfully used for the degradation of pollutants in wastewater. At the presence of light and catalyst, chemical pollutants can be gradually oxidized into low molecular weight intermediate products and ultimately converted into CO₂, H₂O, and anions such as NO₃⁻, PO₄³⁻, and Cl⁻. The photocatalytic characteristics of titanium oxide nanoparticles are efficient to kill algae, fungi, Gram-negative, Gram-positive bacteria, protozoa and viruses. In a recent study, the CZTS/ZFO p-n heterostructured nano-photocatalyst exhibited remarkably stable and easy separated performances, suggesting a promising application for the photo-oxidative degradation of organic contaminants.⁷⁴

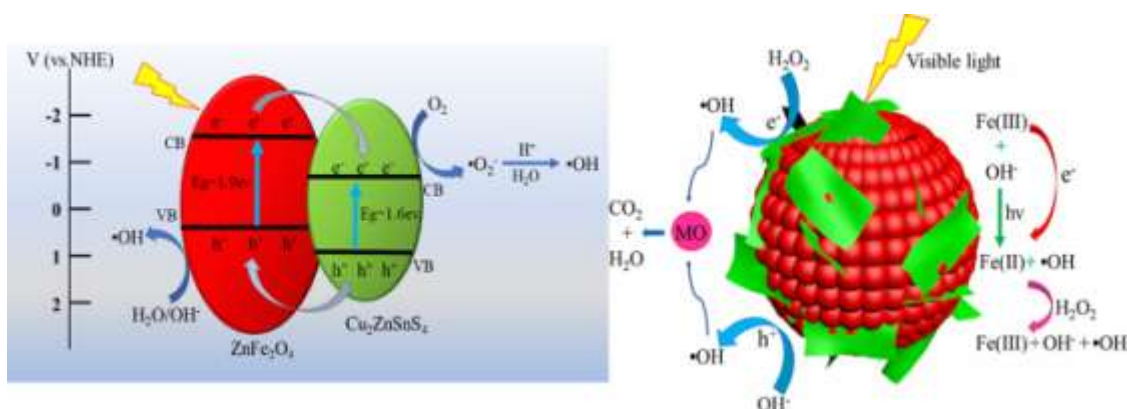


Figure 3:- Graphical representation of heterostructured nanophotocatalyst.

Inhibition of microbial growth and Nanomaterials:

Inhibition of microorganism is a big challenge from a long period to the scientists working on the aqueous environment. Traditionally, several chemicals such as potassium permanganate, chlorine, chloramines, ozone etc. have been used as a disinfectant for killing the pathogen in water and wastewater. Presently, many materials like nanoparticles of AgO, ZnO, TiO₂ fullerenes and CNTs act as some good antimicrobial agents. The antimicrobial mechanism of TiO₂ is well established by many researchers which are based on reactive oxygen species present in titanium oxide because it is capable to disrupt the cell wall of microorganism.⁷⁵⁻⁷⁷ In the same fashion, Ag nanoparticles, ZnO nanoparticles and CNTs have been used for the killing of microorganisms. The detailed work on TiO₂ nanocomposites based polymeric membranes has been reported.^{78,79}

Silver nanoparticles are prepared from its salts such as Ag(NO₃)₂ and AgCl₂, and their antimicrobial effects have been well documented by many investigators.⁸⁰⁻⁸⁴ The antimicrobial property is directly related to the nanoparticle size⁸⁵, when particles sizes are small nearly 8 nm, they were more effective in comparison to large particle sizes (11–23nm).⁸⁶

Regeneration of nanoparticles:

After wastewater or water treatment, regeneration of nanoparticles is a very tough and essential process. the pH of the medium plays an important role in the regeneration of nanoparticles. Magnetic separation is another good process to the magnetic nanoparticle separation from the bulk solution. Regeneration of nanoparticles and its reuses

are more economical for treatment of water.⁸⁷⁻⁸⁹ Presently, fast, sensitive and selective nanoparticle-based technology is in great demand for the treatment of wastewater. Environmentalists suggest that reuse of nanoparticles is highly recommended after they've been recovered from the pollutants of the wastewater. The fundamental concept of nanotechnology is the fast recovery of treated water and minimizing hazardous by-products.

Conclusions:-

Present age requires advance and excellent technologies for the treatment of polluted water which is also capable of killing microorganisms. Nanoparticle-based techniques have created a new horizon in the field of water/wastewater treatment. Due to unique characteristics of nanoparticles even when they are used in trace amount, they are capable of removing toxic metal ions, chemical pollutants and also killing of bacteria, fungi and viruses. As per the discussion mentioned in this communication, nanoparticle-based technologies promise to achieve the goal. Moreover, the nanotechnologies used in the treatment of wastewater were discussed in brief. Considering the fast development process and application, nanomaterials look extremely promising for wastewater treatment

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