

A review on nanomaterial applications in wastewater treatment and toxicity to human beings

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Abstract:

Background: Deficiency of water and contamination are most significant issues for many of countries in the world. Different kinds of nanomaterials are utilized on larger scales in water and waste water treatments.

Materials and Methods: We review applications of four kinds of nanomaterials e.g. nano-filtration membranes, nano-adsorption materials, nano-reducing materials and nano-photocatalytic materials are largely used in water treatments and pollution control. We discuss their general properties and significant applications in waste water treatments.

Results: The use of these nanotechnologies is increasing and anticipated to result in raised human exposure to nanomaterials. The impact of nanomaterials in the human environment is zone of rising scientific interest. More research is required on nanomaterial characterization, human exposure to nanomaterials and mechanisms of different health related problems related to nanotoxicity.

Conclusion: Techniques that are standardised and validated are essential for risk assessment of nanomaterials. The advantages of nanomaterials discovered at present in human environment are numerous, however their general toxic effects on human beings are limited.

Key Word: Wastewater; Nanomaterials; Treatments; Nanotechnology; Toxicity.

Date of Submission: 07-10-2022

Date of Acceptance: 19-10-2022

I. Introduction

Water is a legendary substance whose material presence is optional contrasted with the representative incentive as it is indicated in our thoughts as the sign of life. Sustainable supplies of fresh water are integral to the world's health, environment and financial system. Because water is a primary regular asset, a basic human need, and a significant public resource, its use requires appropriate arrangements, advancements, and executives. Wastewater is constantly growing, and without the proper analysis and management procedures, the available freshwater resources are becoming contaminated¹. Fresh drinking water is one of the essential human requirement. After such a large amount of progression in science and innovation, the misfortune is 78 crores of individuals around the globe don't have approach to clean and fresh water even today. Likewise, around 0.25 crores of the individuals around the earth don't have satisfactory approach to hygiene because of barriers in fresh water supply².

Quick improvement of economy, substantial utilization of toxic chemical substances and defects of water executive arrangements brought about a progression of water issues including water lack and contamination³. Nanotechnology, offers the capability of durable explanations to expand effectiveness and decrease prices, through the modification of developed materials that empower more significant water quality and reuse. The distinctive properties of nanomaterials and their exposure with ongoing water processing technologies present incredible options to alter water treatment⁴. Over the most recent twenty years, nanotechnology has risen essentially with its applications in practically all parts of science and innovation. In reality, different nanomaterials have been arranged and utilized for the removal of water contaminants⁵. Nanoparticles are assumed to occupy an important part in water treatments⁶. As yet, numerous relative surveys on nanomaterials in water analysis and treatment have been described. Although, a comprehensive view on nanomaterials toxicity is still lacking. The environmental hazards and harmfulness of a material are basic issues in materials choice and plan for water treatments. There is no doubt that nanotechnology is better than other strategy utilized in water treatment yet today the information about the environmental hazard, transportation and toxicity of nanomaterials is still in outset⁷.

Nano-filtration membranes, nano-adsorption materials, nano-reducing materials, and nano-photocatalytic materials are the four categories of nanomaterials we will discuss in this article for the treatment

of water and wastewater. Also mentioned is the toxicity of nanomaterials to the environment and to humans. Due to the possible introduction of a wide range of nanomaterials into the human environment, interest in their potential toxicological effects is growing⁸.

II. Nano-filtration Membranes

Application of nano-filtration membranes is currently advancing very quickly across all industries. This membrane was previously utilized in filtration operation in the finish of 1980s⁹. The nano-filtration membrane is a type of semi permeable membrane that allows some low molar mass solutes, dissolvable particles, and low ion pervasion. Surface water, waste water, and ground water might all be studied and treated using nano-filtration membranes. Water conditioning is the most often used application for nano-filtration membranes¹⁰. According to current research, nanofiltration has also been used to remove arsenic and other growing contaminants including hormones, medicines, and personal care products in addition to the reasons for removing turbidity, hardness, fluorides, sterilization effects, and pesticides^{11,12,13}. However, current studies on the use of nano-filtration membranes to remove active medicinal components from drinking water and surface water are often insufficient¹⁴. There were further numerous applications on domestic division, for example treatment of municipal wastewater¹⁵, vehicle wash wastewater¹⁶, Leachate¹⁷, and eatery sewage. On industrial scale, a few applications of nano-filtration membranes process are to isolate colors in textile industry¹⁸, metal recuperation, olive factory polluted water treatment¹⁹. Nano-filtration membranes are represented in (Table no 1).

Table no 1: Representative nanofiltration (NF) membranes for water treatment

Polymeric membranes	Mixed Matrix Membranes (MMMs)	Ceramic Membranes
Cellulose based membranes	Polymeric membranes with metal oxide fillers	Metal oxide membranes
Thin-film composite membranes	Polymeric membranes with carbon-based fillers	Carbon based membranes

III. Nano-adsorption materials

Carbon based nano-adsorbents

Due to their microscopic size, carbon-based nanomaterials in pure form often cannot be used effectively for water treatment, making their recovery from water treatment systems is challenging. As a result, researchers have been searching for methods to combine these nanomaterials with membranes, add them to polymeric beads, or modify them with magnetic metal oxides to facilitate their removal from water²⁰.

For the removal of heavy metals including Cd²⁺, Pb²⁺, Zn²⁺, and Ni²⁺, carbon nanotubes, including single- and multi-walled carbon nanotubes, are suitable adsorption materials. Carbon nanotubes are also used for the removal of organics from water^{21,22}. Su and Lu reported that the normal weight reduction of the carbon nanotubes (2.65%) was less than that of granular activated carbon (6.40%) and that the adsorption limit of carbon nanotubes on naturally diffused organic materials (11.61 mgg-1) was higher than that of granular activated carbon (3.55 mgg-1)²³. Due to the natural compound-carbon nanotube interlinkage as well as hydrophobic influence, hydrogen bonding, p-p interactions, and electrostatic relation, carbon nanotubes strongly adsorb low molecular mass polar natural compounds in an aqueous environment^{24,25}. The cost-benefit ratio of carbon nanotubes is significantly influenced by recovery. According to Lu et al. (2006), 0.1 mol. L-1 nitric acid solutions can be used to recover single-walled carbon nanotubes and multi-walled carbon nanotubes with adsorbed Zn²⁺, and the adsorption property was still preserved after ten iterations of reconstruction and reuse. It suggested that by lowering the pH of the mixture, carbon nanotubes may be recovered²⁶.

Metal based nano-adsorbents

Inorganic nanomaterials with a metal or metal oxide basis are used frequently to remove heavy metal particles and colours. Metal oxides are acknowledged as sorbents to remove heavy metals and dyes because of their minimal ecological impact, low solubility, and lack of connection to the creation of secondary pollutants²⁷. The three most well-known kinds of iron oxide nanoparticles used in water and wastewater treatment are nFe₃O₄, n-Fe₂O₃, and n-Fe₂O₃. Iron oxide nanomaterials could adsorb different categories of heavy metals (e.g., Cu²⁺, Pb²⁺ and Zn²⁺)²⁸, natural toxins (e.g., 1-naphthylamine, red dye, polycyclic aromatic hydrocarbons)²⁹ and radionuclides²⁵. Although, the use of iron oxide nanomaterials for adsorption of heavy metals is quiet at laboratory scale³⁰. Other than iron oxide nanoparticle, compelling adsorbents for the removal of heavy metals, metallic pollutants, and radionuclides included nZnO, nTiO₂, and nAl₂O₃³¹. Like carbon nanotubes, metal oxide nanoadsorbents could likewise be recovered by changing mixture pH value³² and afterward the adsorption limit remained moderately stable³³. However, inverse outcomes were also described. As⁵⁺ adsorption on akagane'ite-type nanocrystals can be reversed, however the adsorption limit would fall by around 25–30% after each round of recovery and reuse, according to Deliyanni et al³⁴.

IV. Nano-reducing materials

As a category of reasonable reductant for pollutants reduction in water, nanoscale zero-valent metals have engaged a lot of consideration since 1980s. The standard redox potential of iron metal is -0.44V ($E^0 = -0.44\text{V}$). Iron is therefore a reasonable reductant when used for reaction with oxidized contaminants in water. Currently, the treatment of water and wastewater contaminated with chlorinated organic contaminants³⁵, heavy metals like chromium³⁶, copper³⁷, cadmium³⁶, zinc³⁷, silver³⁷; colors³⁸; and phenol³⁹ has been successfully applied using nanoscale zero-valent iron (nZVI).

The removal efficiency of eight metal particles, including Cd^{2+} , Ni^{2+} , Zn^{2+} , Cr^{6+} , Cu^{2+} , Pb^{2+} , and Ag^+ , from nanoscale zero-valent iron (nZVI) was characterized by Li and Zhang as being 36.5, 71.0, 92.5, 97.5, 99.7, and 99.8%. The chemistry of the contaminants varies greatly. There are many practical methods for contaminant reduction, including sorption, (co)precipitation, surface-mediated chemical reduction, and complexation³⁷. Different alterations are utilized with the objective of more successful conveyance of reactive nanoparticles to the purification sector^{40,41}. Alterations of nanoscale zero-valent iron (nZVI) expanded strength, reactivity, versatility, and diminished aggregation of nZVI. Although, changes of nanoscale zero-valent iron (nZVI) may cause the formation of materials that are not only utilized in contaminants removal more adequately, yet in addition multiply in living beings, drift over broad areas, sedimentation on bottoms of water supplies, or become transporters of different contaminants⁴². Various researches show that nZVI has significant capability to become an effective, flexible and experimental approach for water treatment on huge scale. Nanoscale zero-valent iron (nZVI) has strong reducing ability, relatively low cost, outstanding adsorption properties, good mobility and high reaction activity (Figure no 1).



Figure no 1: Characteristics of nanoscale zero-valent iron nZVI.

V. Nano-photocatalytic materials

Currently, nanomaterials used in photocatalysis most frequently include nTiO_2 , nWO_3 , nZnO , nAl_2O_3 , and nBiVO_4 . Due to its high sensitivity, heat resistance, and abundance as an unprocessed material, nTiO_2 is the most often used nanomaterial in waste water treatment⁴³. nTiO_2 is considered as a really effective and clean photocatalyst because it does not get utilized during consumed in the reaction⁴⁴ or reflection⁴⁵. Wang et al. described that nTiO_2 indicated its ability to eliminate water contaminants under bright (UV) radiation. Additionally, they performed treatments of desulphurization wastewater in the presence of nTiO_2 photocatalytic effect that can eliminate the contaminants over seventy five percent⁴⁶. Cho et al. (2010) utilized nTiO_2 in the treatment of contaminated groundwater. This contaminated water was polluted by the addition of toluene, benzene, ethyl benzene, and total petroleum hydrocarbons⁴⁷. Although, nTiO_2 has several defects that include low absorb capability of visible light and low reuse rate. To defeat previously mentioned defects, a few methodologies have been described to alter nTiO_2 , which include doping, coupling and dye sensitization⁴³.

VI. Human exposure to nanomaterials

A significant route for human interaction with nanoparticles is by ingestion. Human exposure to nanomaterials can occur either directly through food consumption or indirectly through the dissolution of

nanoparticles from food packaging materials⁴⁸. When these nanoparticles enter into the body they might be transferred from one part of the body to another part by blood dissemination. It is feasible that their circulation in the body might be a concern of their size and surface qualities, for example, lipophilicity, polarity, hydrophilicity and catalytic activity^{49,50}. The nanoparticles are assumed to reveal improved chemical and biological activity in human body, when the nanoparticle size reduces and surface area per unit mass grows up^{51,52}. As a result, it is reflected that lighter nanoparticles may be more poisonous than larger ones. The light weight nanoparticles are transported on faster rate by human cells than larger particles. Another important path of human exposure to airborne nanomaterials is inhalation process⁵³. One of the significant way of human exposure to nanomaterials is skin absorption⁵⁴.

VII. Challenges and assessment of nanomaterials toxicity

Nanomaterials are increasingly present in both the environment around people and in consumer goods. It is assumed that human exposure to nanoparticles will continue to rise. In comparison to their bigger size counterparts, nanomaterials are thought to have a wide range of biological functions. These particles might be metabolized or changed in living organisms. The significant properties of these particles are dependent on their size, shape and creation. The metabolized nanoparticles might have different impact on biological system as compared to original material. The inadequate understanding of interrelation between nanomaterials and biological systems needs well classification and integration.

The utilization of nanomaterial and its exposure passage is associated with its potential toxicity. The exposure pathway extremely depends on particle behavior⁵⁵, while risk assessment is dependent on perfect toxicity evaluation⁵⁶. It is reflected by our literature search that currently assessable knowledge on general risk assessment of nanomaterials is not enough⁵⁵. Moreover, there are no globally acquired standard strategies for toxicity assessment or for chemical classification of nanomaterials. There is limited information available on exposure of human to nanomaterials. A lot of attention is required and more information is essential on nanoparticle characterization, exposure pathway, metabolism and action procedure preliminary to systemized quantitative risk assessment protocols will become accessible. Present hazard assessment of nanomaterials will keep on depending for the upcoming intensely on extrapolation of rodent dose-response study⁵⁷.

Nanomaterial toxicity largely depends on its intrinsic physicochemical properties for example area, design, surface properties and chemical structure. Generally, the nanoparticles which are extremely small moves quickly and taken up by body cells faster than larger particles. Nanomaterials of a same size and shape might show non identical toxicological profiles. Nanomaterials that are similar in size and form can aggregate into different sizes and shapes that can affect how hazardous and active they are biologically. Apart from information and data space distinguished above, following are uncertainty concerning aspects of toxicity assessment:

- a) Characterization of the particles that may support toxicity
- b) Transport of nanomaterials through environment and its environmental significance
- c) Direct and indirect pathways of human exposure to nanomaterials
- d) Cytotoxicity, hepatotoxicity and immunotoxicity of nanomaterials
- e) Different mechanisms nanotoxicity and related diseases

VIII. Discussions

Generally, different physical and chemical techniques are utilized for water and waste water treatments. Water and wastewater treatment using nanotechnology promises to not only overcome substantial challenges faced by current treatment technologies but also to assign new treatment proficiencies that could allow financial use of unreliable water sources to increase water supply. We have described some advantageous applications of four kinds of nanomaterials in this paper. Currently, four different types of nanomaterials including nano-filtration membranes, nano-adsorption materials, nano-reducing materials and nano-photocatalytic materials are largely utilized in the water and waste water treatments.

Nano-filtration membranes could be extensively used in the production of drinkable water, the removal of harmful metals, and the elimination of pesticide residue from contaminated water. Carbon nanotubes including with iron oxides nanomaterials and nTiO₂ have demonstrated high adsorption limits. Additionally, hazardous metals and organic pollutants could be eliminated by reduction or oxidation using nanoscale zero-valent iron (nZVI). As an outstanding photocatalyst, nTiO₂ gives amazing performance in the wastewater treatment, particularly paper factory wastewater and dye wastewater. Nanomaterials have obtained broad consideration in water contamination remediation and examining process. However, few issues are still required to be studied and resolved, including cost-efficacy, technical barriers and hazard assessment of nanomaterials. Some of the possible health related risks of nanomaterials are given in the (Table no 2).

Table no 2: Potential hazards of nanomaterials

Nanomaterials	Potential Hazards
Carbon Nanomaterials, Silica nanoparticle	Pulmonary inflammation, fibrotic scarring, Lung granuloma ^{58,59,60}
Carbon, silver and gold nanomaterials	Dispersing into different organs together with central nervous system ^{61,62,63}
Quantum dots, carbon and TiO ₂ nanoparticles	Skin penetration ^{64,65}
MnO ₂ , TiO ₂ , and carbon nanoparticles	May enter brain through olfactory epithelium which contains olfactory sensory neurons ^{61,62}
TiO ₂ , Al ₂ O ₃ , carbon black, Co, and Ni nanoparticles	May be more poisonous than micron sized particles ^{66,67}

The environmental hazard and possible risks of a material are basic issues in materials determination and plan for water treatment. A few examination groups have discovered harmful impacts of nanomaterials, the reasons for the toxicity are generally unknown. Huge gaps are still present in the information about the interaction of nanoparticles in the human environment. To fully understand the possibility for human exposure to the nanoscale materials of currently available products and future items, additional tests are anticipated to evaluate the constancy of these matrices in a variety of test settings. Significantly, scientific strategies are required that license constant, in situ checking to advance manufacturing procedures, that reduce waste and vitality costs. The availability of common analytical methods that address these problems is essential to advancing our understanding of the mechanisms governing the formation and reactivity of nanoparticles.

IX. Conclusion

The utilization of nanomaterials in water quality administration has gained wide consideration because of their significant properties for example reactant, magnetic, electrical, mechanical, optical and photonic properties. Water lack and contamination are significant difficulties for many countries of the world. Four types of nanomaterials are largely utilized in the water and wastewater treatments with a lot of applications in this field. Water conditioning and the eradication of various impurities from water are the most widespread uses of nano-filtration membrane. Nano-adsorption materials are used in the removal of heavy metals and dyes from water. Nano-reducing materials are used for treatment of water contaminated with chlorinated organic contaminants. Nano-photocatalytic materials have large number of applications in the chemical industry wastewater treatment and contaminated groundwater treatments.

Nanomaterials have acquired much importance in the waste water treatment and analysis. Future predictions predict an increase in human exposure to nanomaterials. To evaluate the safety of nanomaterials, better equipment are necessary. There is little current study on the effects of human exposure to nanoparticles. The potential risks of nanomaterials to humans and the environment must be discussed in the future before they are produced in large quantities. More research is needed on nanomaterial characterization, human exposure to nanomaterials and mechanisms of diseases related to nanotoxicity. Expected toxicity of nanomaterials is additional challenge for their broad application. The test methods need to be accepted. Recognizing the positive and negative controls for nanotoxicity is still necessary. There is a deficiency of standardized and validated techniques which are necessary for risk assessment of nanomaterials. Therefore, any specific administrative testing requirements for nanomaterials are now premature in the absence of standardized approved methodologies. Nanomaterials have recently been discovered to have numerous benefits for the environment and water treatment, but they also have few negative side effects on human health.

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Junaid Abid, et. al. "A review on nanomaterial applications in wastewater treatment and toxicity to human beings." *IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)*, 16(10), (2022): pp 48-54.