NANOTECHNOLOGY IN WATER PURIFICATION AND TREATMENT: CURRENT OUTLOOK AND FUTURE PERSPECTIVES

Abstract

Meeting the world's water needs will be extremely difficult due to the rapidly growing population, varying environmental conditions and climate change. It is projected that by 2050, there will be 6.4 billion people on Earth, necessitating an increase in water availability and production to meet human needs. Because of the worldwide industrial revolution, a variety of harmful pollutants are finding their way into water bodies. A multitude of industries, including textile, leather, electronics, metal polishing, etc., regularly discharge large amounts of heavy metals into the environment.

Nano-based materials have a very high area/size ratio, which makes them useful for improving the properties of existing materials. The novel treatment techniques employ nanoparticles to eliminate dissolved gases, heavy metals, and organic pollutants in addition to a variety of ailments. With the development of cutting-edge next-generation technologies, this technology offers new possibilities to make water treatments reach new heights. The paper describes the emergence of state-of-the-art next-generation technologies and explores its opportunities for water treatment methods.

Keywords: Nanomaterials, Water treatment, Technology, Membrane, Biodegradation

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I. INTRODUCTION

The rapid climate change and exponentially increasing population pose serious challenges to fulfilling global water needs. The population all over the world is rapidly rising and will touch 6.4 billion by 2050. This requires growth for water production and availability by then to meet human requirements. Agricultural requirements for freshwater account for 70 % of available water usage[1]. Every year around 65 billion freshwater is consumed to achieve human needs. As per the demands, there lies an immediate need to develop novel techniques for wastewater treatment and water production. Industrialization in all the developed and developing countries is discharging several pollutants like heavy metals, microplastics, pathogens, dyes, organic and inorganic compounds into freshwater bodies [2]. The stringent norms for water discharge to control emerging contaminants enable us to look into new ways for wastewater treatment. The development of nanomaterials for water treatment may help to resolve the global challenges of marine pollution [3].

Various hazardous materials are entering into water bodies due to the global industrial revolution. Several industries including textile, leather, electronics, metal finishing, etc. are discharging large quantities of heavy metals on a continuous basis. The removal of heavy metals is essential as they can enter into the bodies of land and marine animals accumulate and lead to death [4]. Some metals like copper and zinc are necessary for the human body but can be dangerous if present in excess amounts. They also disturb the ecosystem and natural cycle of the environment. These toxic metals need to be removed from environment to prevent its harmful impacts on humans and nature. Recently, various techniques are evolving for removal of toxic metals. These include electrochemical treatment, ion exchange, chemical precipitation, coagulation, adsorption, membrane filtration, and reverse osmosis etc [13]. Among the mentioned processes adsorption is the most common method because of its economic value and due to its low cost and simple operation and accessibility/regeneration of different adsorbents. Despite all the benefits it is difficult to operate on a commercial scale.

To overcome the limitations of conventional techniques nanotechnology presents one of the innovative areasto reduce water pollution and its reclamation. Besides, existing technologies give higher efficiencies and lower inputs. Various nanomaterials like nano-membranes, nano-metals, and nano-adsorbents are available along with nano-catalysts. This technique provides economic and sustainable use of the resources to overcome the limitations posed by existing treatment technologies [14]. The nano-materials have sizes between 1-100 nm with diverse size-based characteristics due to their higher surface area. They offer features like more reactivity, strong sorption, rapid dissolution, quantum effect, super-magnetism, and par magnetism, etc. the developed nano-sized materials can be used as membranes, catalysts, coatings, reagents, coatings, and adsorbents. For the nano-based substances, the area/size ratio is very high, due to which they can be employed to improve the existing properties of the materials [15]. The advanced treatment systems employ nanomaterials to remove heavy metals, organic contaminants, and dissolved gases, along with different pathogens. This technique presents new ways to make water treatments pave new heights with the development of advanced next-generation systems.

In this chapter, the properties of nanomaterials for water treatment and production are discussed (Figure 1). The advantages and impacts of using these materials in this field are reported. Nanomaterial classification and its various uses are well discussed. The removal strategies of heavy metals and future directions for sustainable environment are also discussed in this chapter (Figure 2).

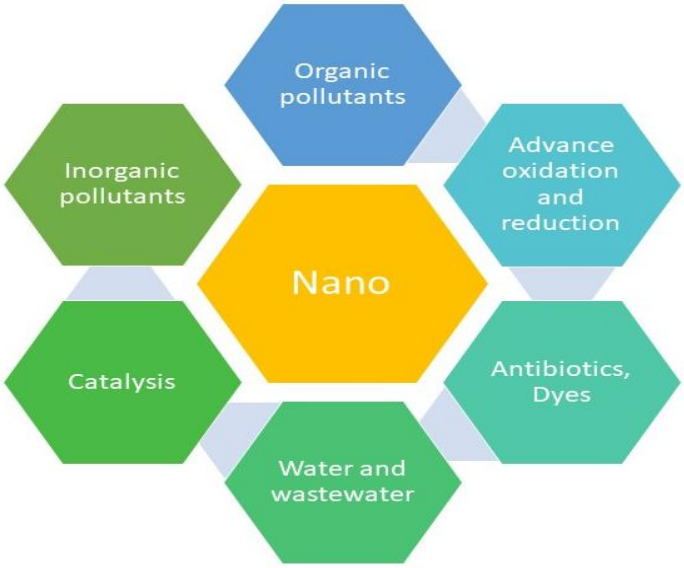

Figure 1: Broad Application of Nanoparticles

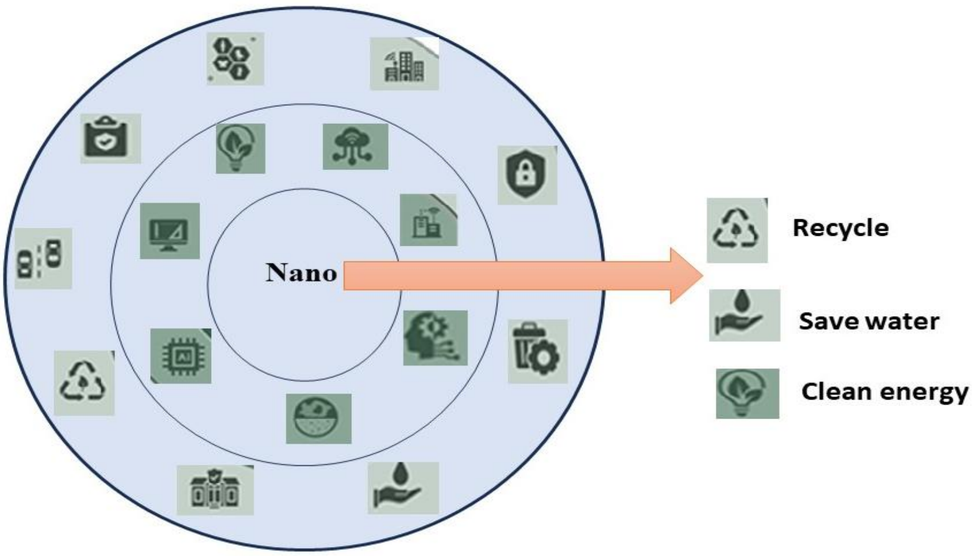

Figure 2: Nano for Sustainale Goal and Sustaible Environment

II. DIFFERENT TYPES OF NANOMATERIALS

1. **Nanometals and Metal Oxides:** The metal in their oxides form are a promising alternative to traditional coagulants like activated carbon for heavy elements removal from wastewater. The size is small which reduces the diffusion distance and makes them compressible without reducing the surface area. Usually, nano-metals and nano-metal oxides are transformed into pellets which are porous in nature for their applications on industrial scale. Some of the commonly used metal oxides include FexOy, Al_2O_3, TiO_2,

MgO, MnO_2, CeO_2 etc. They have higher levels of reactivity due to the quantization effect and unsaturated metal surface that provides higher active sites for metal binding.

2. **Nanozerovalent Iron:** Nano-iron with zero valency is one of the most promising materials for adsorption. It has higher reduction potential, good mobility with excellent reactivity and adsorption performance. It can be synthesized by chemical and physical processes like lithography, grinding, and abrasion. Chemical reactions such as combination of liquid metal-hydrogen, gas phase thermal decomposition, and reduction of gas-metal can all be used to create it. Due to its ease of usage, it is most frequently synthesized through chemical reduction,and the product obtained has a uniform structure and strong reactivity.

3. **Iron Oxides:** The nano-sized iron oxides includegoethite (α-FeOOH), Haematite (α-Fe_2O_3), maghemite (ϒ-Fe_2O_3), and magnetite (Fe_3O_4). Nano iron oxide like goethite can be used for heavy metals like arsenate, cadmium, cobalt, mercury, chromium, lead, tin, and zinc removal from wastewater [24]. Some researchers studied the performance of goethite for arsenate removal and observed that it is getting adsorbed on iron oxide surface through binuclear complex formation. Also, some researchers employed goethite for As(V) removal with good adsorption performance at neutral pH. It was found that the surface hydroxyl groups are responsible for arsenate removal at acidic pH while at neutral pH electrostatic attraction plays a key role for metal ion removal [25]. The goethite presents good arsenic adsorption capacity which can be improved by adding biodegradable polymeric functional groups.

   - **Magnetite (Fe_3O_4):** This iron-based nanoparticle has higher adsorption characteristics for metal removal of Hg(II), Cu(II), Cr(VI), As(V), Ni(II), Sb(V), and V(V). Due to its more magnetic property, it can removed from dilute solutions by application of outside magnetic potential. They can be synthesized by hydrothermal or solvothermal methods. Apart from easy synthesis and separation, they have the capability to agglomerate in aqueous systems that reduce their specific surface area and adsorption capacity. Also, they are not stable under acidic conditions so chemical modifications are needed to use them in strong acidic environments. Functional groups like amines, and silanes, can be added to its surface to improve its adsorption capacity under extremely acidic conditions. By adding polymer groups to Fe_3O_4 they can remove Cr (VII) ions by electrostatic interactions.

   - **Aluminium Oxide (Al_2O_3):** Al_2O_3 can effectively remove heavy metals like Zn(II), Ni(II), Cr(VI), Cd(II), and Pb(II). Nano-alumina can be used in even harsh chemical environments as it has excellent chemical resistance and regeneration capability [22]. Smaller-sized alumina particles have higher adsorption capacities for Cr (VI). It can also be reduced to Cr (II) and Cr(III), by binding with active sites on the alumina surface. The adsorption capacity of nano-sized alumina is not altered by the presence of other foreign species in water. However, for groundwater the potential to adsorb is significantly decreased because of the presence of other contaminants. They have regeneration capacities of around 91 % when treated with sodium hydroxide [23].

- **Silica (SiO_2):** Silica is available in different pore sizes and has a unique shape, higher surface area, and dimensioned pore size. It has number of hydroxyl groups on its external that can be functionalized with silane modifiers to improve its adsorption capacity. It has excellent acid and alkali resistance and many nitrogen-containing functional groups can be added like polyaniline and polypyrrole [16]. Different organic and inorganic functional groups can be conjugated with hydroxyl groups of silica through vander waals forces, hydrogen bonding, and reversible covalent bondings. Also, various coordinating structures can be formed with by combination of heavy metals ions and hydroxyl groups [17]. Metals like Pb(II), Cd(II), As(III), Fe(II), and Mn(II) are separated from water suitable for human intake by these silica nanoparticles.

- **Titanium Dioxide (TiO_2):** Titanium dioxide being photocatalytic in nature has greater advantages for wastewater remediation. It has low cost and higher chemical stability. Similarly, it has more lifetime compared to other nanomaterials [18]. It can be successfully employed as a disinfectant by activating it under UV rays. Titanium-basednanowires were successfully employed to remove heavy metals like Pb^{2+}, Cu^{2+}, Fe^{3+}, Cd^{2+} and Zn^{2+} from contaminated water with an adsorption efficiency of 97 %. Therefore it can be successfully employed in water filters as a promising alternative for water purification [19]. Apart from this, they have excellent electrical and optical properties and can be employed in coatings, anticorrosive, solar cells etc.

4. **Metal-Organic Frameworks (MOFs):** These are nano-porous organic-inorganic materials with topological structures in 1D, 2D and 3D. The unique structure is formed by connecting metal clusters with organic ligands. MOFs present one of the leading and promising classes of nanomaterials at present. They have superior applications in gas sensing, liquid separations, gas storage, drug delivery, catalysis, along wastewater treatment [26]. They have unique features of high crystallinity, large porosity and specific surface area which is very high compared to other porous materials. The structure of MOFs is highly flexible and it can be adjusted due to bridging ligands and coordination bonds. Their structures can be reversed or deformed due to the existence of several sigma-bonds. Compared to traditional porous materials like molecular sieves, MOFs are highly flexible. This feature imparts peculiar physiochemical properties with great adsorption/desorption characteristics [27]. The unique feature of reversibility, makes them change their structure through functionalized chemical modification.

   ZIFs are a class of MOFs that have emerged as excellent adsorbent materials within the past three decades. They have three-dimensional lattices with metal ions and organic linkers that contain tetrahedral Zn^{II} atoms that are connected by imidazole ligands. There are numerous zeolite-like shapes can be formed by combining different ligands and metals.

   ZIFs offer higher stabilities owing to its chemical, hydrothermal and thermal properties. Their 3D framework offers accessibility and diffusion of contaminants through the structure. They have the great advantage of modifying their pore size and shape by changing the linkers and metal ions connectivity. To combat the limitations of inorganic membranes they are the building blocks for membrane preparation with high efficiency for water treatment applications [28]. They are used as fillers in mixed matrix membranes due to their integrated organic-inorganic properties. The interaction of organic ligands with polymers increases the affinity between the polymer matrix and ZIFs. The pore of the ZIFs is flexible in nature and they can easily trap the target molecules resulting in more separation efficiency. The polymer characteristics can be upgraded by changing the polymer chain packaging and enhancing the free volume by these fillers.

5. **Nanoadsorbents:** Various metal oxides can be used as low-cost adsorbents for heavy metal removals along radionuclides. Some of the nanoadsorbent includes carbon-nanotubes-based nanoadsorbent, metal oxide nano adsorbent, polymer nanoadsorbent, and zeolites. The oxygen metal present in metal oxides like titanium dioxide, iron oxide and alumina is responsible for metal sorption [11]. The nano-sized adsorbents allow fast adsorption of metal ions along with diffusion inside particle through its microporous boundaries. It allows rapid kinetics due to more available specific surface area, more number of adsorption sites and shorter diffusion rates. Various heavy metals like arsenic, lead, mercury, copper, cadmium, chromium, and nickel can be used using titanium dioxide nanoparticles [12]. They also have the unique feature of switching to higher valency, lower valency and zero valency. Hexavalent chromium ions can also be removed by some iron-based nanoparticles along with arsenic and lead at acidic pH from water pH. Some nanorods-based magnetic adsorbents can also be used for heavy metal removal as they have good adsorption capacities. Mercury can be removed by super-magnetic nanoparticles with faster and more selective adsorption. Iron-based materials like nano-haematite can remove lead, zinc and cadmium from water. These nanoadsorbents offerthe advantages of higher adsorption capacities along with limitations of higher toxicity, production cost, bulk volume production handling etc.

6. **Carbon Nanotubes (CNT) Nano Adsorbent:** These are the carbon allotropes with cylindrical nano-pores. They are present either as uni-walled or multi-walled nanotubes. They have the unique feature of higher active adsorption sites with adjustable surface chemistry and antimicrobial properties. They can be effectively used to adsorb the contaminants along with their detection in various water streams [20]. The electrostatic attraction or chemical bonding is responsible for their adsorption. To overcome the disadvantages of ozonation and chlorination without any byproducts this process can be used. The regeneration of CNTs is simple by changing of various parameters like Ph shift, temperature, and pressure etc. They can be simply regenerated through appropriate adjustments of operating conditions, like pH shift. Recently, CNTs were transformed into sponges with a dash of boron that can be used effectively for oil-water separation. If it is scaled up it can be used to separate oil from oil spills. They can be transformed into oxidized CNTs, molecule-modified CNTs, metal-oxide-modified CNTs, and polymer-modified CNTs [21]. Due to their higher production costs, they are still in the phase of production for their application of municipal and wastewater treatment from industries. But some effluent like pharma needs smaller quantities of CNTs to separate antibiotics and pharmaceuticals from wastewater.

7. **Polymeric Nano Adsorbent:** Dendrimers are a class of polymeric adsorbents that are used for heavy metal removal. The dendrimers have unique internal and external structures. They have internal shells that can adsorb organic compounds due to their hydrophobic walls and the external bifurcations can adsorb heavy metals. Metals like

copper can be removed by using these adsorbents in an ultrafiltration system. The adsorbent can be regenerated easily by a small pH change. Textile water dyes can also be removed by these adsorbents based onchitosan-dendrimer nanostructure. They have the advantages of nontoxicity, biodegradability and biocompatibility.

III. WATER TREATMENT BY NANOMATERIALS

Major challenges in water treatment and reclamation includethe removal of micro-pollutants, organic dyes, heavy metal uptake, brackish water etc. New water treatment membrane includes MOF-based membranes. They provide various interaction paths along with strong mechanical and chemical strength. They can be synthesized by continuous growth of MOF layers on a polymer substrate [4]. They have excellent controllable porosity, that imparts good permeability and makes them potential candidates for practical water treatment applications. For large-scale, industrial applications the nanoparticle can be formulated into a packed bed to reduce the pressure drop and equipment size or it can be immobilized on an inert carrier. Some researchers have used lithium-ion imprinted adsorbents as short beds to remove lithium from wastewater. They recovered lithium with 98 % purity by using different series-parallel combinations [5]. This technology does not rely on larger infrastructure for wastewater treatment. They have low economic utilization of available water resources and great advantage of increasing water supply.

Membrane separation technology can be employed for water treatment with nanoparticle addition. It represents a greener technology due to its operational simplicity, low area requirements, environmental protection, energy conservation, and higher separation efficiency [6]. The nanoparticles can be embedded into membranes to improve their rejection efficiencies. Some expensive materials like gold, silver, palladium, and ruthenium can be immobilized on the membrane surface and applied for heavy metal removal with greater efficiency. Several nanoparticles like silica, zirconia can be embedded into membrane structures to improve their properties [7]. The membrane feature like mechanical strength and permeability can be greatly improved by addition of nanofillers. The inorganic oxides also enhance the tensile strength of the membranes. Some researchers employed zeolite nanoparticles in polysulfone polymer and removed nickel, and lead ions from water solutions [8].

IV. CASE STUDY

In a recent study at CSIR-IICT, the nanoparticles of zinc and copper were synthesized using either co-precipitation, precipitation, or calcination methods. The antimicrobial activity of the material was tested for *E-coli*, *Staphylococcus aureus*, *Klebsiella planticola* and *Micrococcus luteus*. The antimicrobial activity of the synthesized was compared with streptomycin as a control. It was observed that the incorporation of metal oxide reduced the activity in the case with a 12-14mm zone of inhibition *E.coli* (Fig. 3). The pristine CuO nanoparticles have shown antibacterial activity and were incorporated into the matrix. The synthesized membranes are tested for the water flux in the test system.

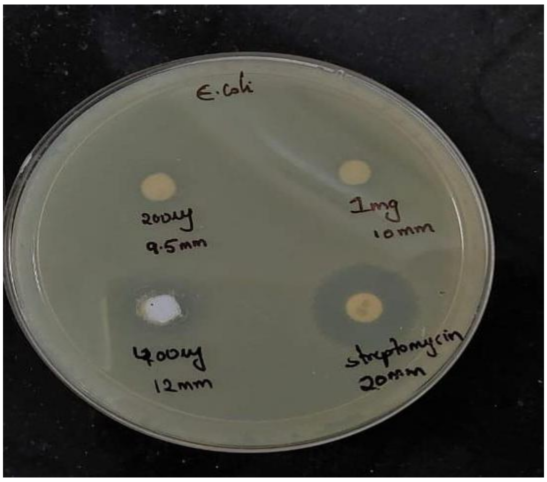

Figure 3: Antimicrobial activity showing for *E-coli*

Membrane techniques like ultrafiltration, nanofiltration can be employed for wastewater remediation with photocatalytic membranes. Materials like titanium dioxide and zinc oxide can be used for such operations. The organic pollutants can be reduced along with heavy metal removal [9]. The nanoparticles have strong oxidative free radicals that can destroy pollutants present in wastewater. The poor reusability of adsorbents can be overcome by membranes thatuse nanoparticles in immobilized form [10]. The removal of heavy metals from water is a one-step process using membranes without any use of harsh chemicals. The combination of polmer+nanomaterial provides higher adsorption sites along with greater water permeability. Photocatalytic materials like graphitic carbon nitride, graphene quantum dots and titanium dioxide can be used in membranesfor simultaneous photocatalysis and membrane filtration.

V. FUTURE SCOPE AND LIMITATIONS

The nanomaterials are of great value in water treatment applications. Apart from several advantages, there are some limitations to using the materials which include the aggregation of material in the membrane, susceptibility to pathogens and bacteria for real-time applications, immature production methods, uncertain life cycle etc. also, the synthesis of MOFs with controllable shape/size is relatively complex that requires many efforts to develop for industrial applications. Nanotechnology can be very useful for developing countries, which are more prone to water quality degradation regularly. It represents one of the innovative areas to develop and maintain water quality standards. Nanotechnology-based water monitoring, treatment and recycling can be opted for in the near future. However, the loading of nanoparticles onto polymeric membranes has some drawbacks of aggregation and poor dispersion. The search continues for production of low cost membranes, more selectivity and rejection along with an increase in number of usage cycles. The incorporation of nanoparticles into membranes is tried in various ways by researchers to provide different features of nanomaterials to membranes. Porous nanomaterials like MOFs can be employed to overcome the problems of pressured drop and leakage along with regeneration.

Nanotechnology can be combined easily with conventional technologies and it holds a huge potential to be developed as a water treatment tool in the near future. It needs still more work done for the complete removal of heavy metal ions from wastewater. Many studies can be done on the development of these nanomaterials for target pollutants. To employ these materials commercially in water treatment it needs lower cost and more reusability. The nanomaterial-based membrane possesses good potential to be used on a commercial scale. Besides, several issues on the uses and toxicity of nanomaterials on the environment and human beings have also started. Subsequently, the stability, antifouling, dispersibility and compatibility of the nanomaterials can be widely studied. Further research can be focused on the use of these materials for large-scale commercial applications. With these limitations, new research should be focused on the use of nanomaterials along with their reuse and biodegradation capability.

VI. ACKNOWLEDGMENT

The author would like to acknowledge the CSIR for the financial support under FBR. The manuscript has the publication no. **IICT/Pubs./2023/349**.

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