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NANOMATERIALS IN WASTEWATER TREATMENT: ADVANCEMENTS AND APPLICATIONS

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ABSTRACT

Nanotechnology has received a lot of attention as a new method of removing dyes, heavy metals and other pollutants from water and wastewater. Numerous studies on the synthesis, manufacturing, and improvement of nanoparticles have shown that they are effective adsorbents for removing a variety of dyes, heavy metals and other pollutants from wastewater. This review aims to educate researchers on effective nanoadsorbents, their mechanism of adsorption towards particular dyes, heavy metals, and the basic building blocks of nanoadsorbent materials synthesis. The development of nanocomposites and additional focus on nanoadsorbent modification are also highlighted in this research as value-added products to boost heavy metal removal and increase adsorption capacity. Regarding their ability to remove dyes, metals and cost-effectiveness, possible obstacles and directions for using nanocomposites for heavy metal, dyes and other pollutants removal in actual wastewater effluent are reviewed. Future studies should focus on finding an affordable method of producing nanocomposite materials and assessing the toxicity of nanoparticles in wastewater applications. To verify the viability of the nanoadsorbents for the removal of specific dyes, heavy metals from actual wastewater, more research on the efficacy of the nanoadsorbents at the pilot or industrial scale is urgently required.

Keyword **:** Wastewater; Contaminants; Nanotechnology; Nanoadsorbents; Treatment

Introduction

Water is a common natural resource that is essential for the survival of every human being and the advancement of human civilization. Water demand is rising swiftly along with urbanisation and industrialization, making it crucial for developing economies to find a solution to the issue of water scarcity. Numerous industries, including those producing batteries, mining, poisons, and electroplating discharge a significant amount of polluted effluent. Wastewater toxins have a variety of negative effects on the living organisms and the ecosystem (Ashraf *et al.*, 2019; Reddy *et al.*, 2012). It ultimately proved to find a more effective and reasonably priced tool for treating industrial wastewater. The types of pollutants present in the industrial wastewater depend on the manufacturing process (Lakkaboyana *et al.*, 2021). Industrial wastewater typically contains high levels of toxic organic compound, a higher pH, hazardous heavy metal, greater salinity, and enhanced turbidity from the presence of inorganic component contaminants. The treatment of industrial wastewater includes adsorption, flotation, chemical precipitation, membrane filtration, flocculation, and coagulation (Banch *et al.*, 2019; Lakkaboyana *et al.*, 2019). Sometimes, these wastewater treatments fall short in their ability to get rid of specific contaminants, like hazardous heavy metals, oil, and bacteria.

Residential, commercial, industrial, and agricultural settings are just a few of the places that produce waste water. The composition of wastewater varies greatly and is mostly based on the source from which it is produced. Excreta, natural organic matter, plant matter, protein, food, heavy metals, metal ions, gases, and other contaminants found in surface water, ground water, and industrial water are examples of complex organic compounds that are frequently found in wastewater. Typically, hazardous and nonhazardous waste can be separated into two groups. Nonhazardous industrial wastes are made from iron, glass, organic waste, cardboard, plastic, stone and do not pose risks to the environment or human health. Contrarily, hazardous wastes are industrial wastes such flammable, biodegradable, and hazardous compounds that may be damaging to human health or the environment (Hanafiah *et al.*, 2018a). Air leaks, solid trash, and wastewater are the three categories for industrial waste. Due to the possibility of both suspended solids and liquids in wastewater as well as the possibility of liquids, gases, and some liquids in the precipitation of solid waste, there is a few overlap between the physical properties of the substances present in these three groups. A material known as particle emission as well as a fluid that emits air may make up particle and air exposures (Carboni *et al.*, 2016). Industrial waste, which is waste that is dumped into the ground and contains a higher percentage of non-recyclable or recyclable metals, is typically an excellent choice for landfill.

Typical wastewater sources and types

- **Domestic and municipal wastewater:** Wastewater that has been discharged from homes, institutions (including hospitals, schools, and clinics), and commercial buildings (like malls, eateries, and so on).
- **Industrial wastewater:** Wastewater is removed during industrial processes, such as those in the pharmaceutical, textile, and poultry sectors.
- **Inflow/Infiltration:** Water from establishment channels, leaking pipes, flooded manholes, groundwater invasion, etc. that eventually enters the sewage system.
- **Storm water:** Discharge from precipitation and snowmelt (Hanafiah *et al*., 2018b; Palani *et al*., 2021a)

Environmental and health impact of wastewater

It degrades water quality and causes water pollution when released into natural water bodies. Wastewater contains organic material, nutrients, and pollutants that can deplete the oxygen in water bodies, killing aquatic life and creating "dead zones." The natural equilibrium being upset can have a domino effect on aquatic flora and animals, affecting biodiversity and the general health of the ecosystem. The higher quantity of nutrients in wastewater, such as nitrogen and phosphorus, can cause eutrophication of water bodies, which promotes excessive algal growth and further deteriorates water quality. Industrial effluent can produce contaminants and heavy metals that can build up in the environment, eventually infiltrate the food chain, and pose dangers to both animals and human consumers. Wastewater must be treated before disposal since, if not, its contents could threaten both the environment and living beings. Numerous health issues were raised as wastewater was used to irrigate crops and due to percolation of wastewater groundwater also contaminated. According to Chen *et al.* (2013), there was a higher danger when residential water was mixed with industrial effluent prior to irrigation. The heavy metals are non-biodegradable in nature and having a longer biological half-life, risk factors are increased as a result of pathogen and heavy metal pollution (Chaoua *et al*., 2019; WHO, 2006). Zn, Mn, Cr, Cu, Fe, Pb, and Ni are among the hazardous elements that it contains (Mahfooz *et al*., 2020). These heavy metals build up in the topsoil (at a depth of 20 cm) and enter the body of humans and other animals by ingestion of leafy vegetables and inhalation of polluted soils (Mahmood *et al*., 2014). Using wastewater for irrigation lowers crop quality and raises health concerns. Children who consume too much copper develop anaemia, renal and liver damage, headache, nausea, and vomiting (Madsen *et al*., 1990; Bent & Bohm, 1995; Salem *et al*., 2000). A higher concentration of arsenic causes osteopenia or osteoporosis (Puzas *et al*., 2004) and may cause bone and kidney cancer (Jarup, 2003). According to Fukushima *et al.* (1970), cadmium causes musculoskeletal disorders, but mercury directly harms the nervous system (Azevedo *et al*., 2014; Keshari *et al*., 2021). For this Wastewater treatment is required before releasing into natural bodies. The wastewater treatment is done using a number of chemical, physical, and biological treatment procedures.

Methods for wastewater treatment

Membrane treatment, ultrafiltration, coagulation, precipitation, solvent extraction and reverse osmosis are costly and ineffective in treating such effluents when heavy metals, dyes and other pollutants are present in high concentrations. Other methods, such as chemical coagulation, electro-coagulation, and solvent extraction, are also not effective in the complete removal of metals, dyes and other pollutants from wastewater (Qiu *et al.,* 2020). They require huge amounts of reagents for the process, and disposal of toxic sludge also leads to problem of solid waste disposal. Upon considering all the above methods, adsorption seems to be a potential and promising technology for the treatment of dyes, heavy metals and other contaminants with high efficiency (Kour *et al*., 2021). It is a mass conversion method where the waste is transferred on active sites present on the adsorbent by physical or chemical bonding (Ojedokun *et al.,* 2021). The adsorption technique is used to treat both high and low-concentration effluents having dyes and metals (Burakov *et al.,* 2018). Nowadays, for the removal of heavy metals, dyes, pesticides and other pollutants the adsorption process is upgraded using nanotechnology by using nanoadsorbent to enhance its adsorption capacity.

Nanotechnology and Nanoadsorbents

With applications in many industries, including environmental remediation, nanotechnology has emerged as a promising topic. Nanoadsorbents are crucial in this context. Nanoadsorbents are nanomaterials with special properties at the nanoscale that are intended to efficiently adsorb or remove contaminants from water, air, or other fluids.

The field of industrial and municipal wastewater treatment has seen extensive use of nanotechnology (NT) and, in particular nanoparticles, (NPs). Industry sectors that frequently produce industrial wastewater include those in the textile, leather, chemical, pharmaceutical, and medical sectors. Advanced NT applications in municipal wastewater treatment are currently being established by adsorption processes mostly.

Nanoadsorbents are used in water treatment to absorb a variety of impurities, such as heavy metals, organic pollutants, and colours. For instance, due to their high affinity for metal ions, nanoparticles like graphene oxide, carbon nanotubes, and other metal oxides have showed outstanding adsorption capabilities for heavy metals. These nanomaterials can be functionalized to increase their affinity for certain contaminants and selectivity when binding to them.

Adsorption is a straightforward physico-chemical technique used for removal of hazardous heavy metals and/or organic pollutants from wastewater. In this particular instance, electrostatic forces drive surface adsorption onto solid sorbents. These can result in a positively or negatively charged sorbent surface, and can be brought on by, for instance, hydroxyl groups and/or other functional groups. Adsorbents with opposite charges are used, depending on the charge of the pollutants to be removed. Chemical interactions on the surface of the sorbents define the efficacy of the adsorption. The primary factors affecting adsorption are pH, temperature, the amount of stirring, contact time, the initial concentration of the chemical to be adsorbed, and the amount of adsorbent used. Major benefits include a wide spectrum of target pollutants, high operational flexibility, and a straightforward process design (i.e., equipment and setup), particularly when activated carbon (AC) is utilized as an adsorbent. The cost-effectiveness of the heavy metal adsorption method can be increased by producing absorbents like AC or biomaterials many times (Chai *et al.*, 2021). Unfortunately, regeneration is not always able to accomplish their preferred removal efficiency.

Conventional adsorption uses AC because of its versatility and wide variety of applications as well as because surface doping makes chemical modification simple and increases the selectivity of particular target contaminations. However, it is still pricey because it is made from natural materials like coconut shells and coal. Common costs, for instance, can range between USD 0.30 kg and USD 1.37 kg for the removal of chromium utilising commercial AC absorbance, with adsorption capacities of 2.18 kg and 15.47 kg, respectively. If larger chromium adsorption capabilities up to 50 g /kg are required, the cost can easily rise to USD 20 and even more (Babel and Kurniawan, 2004). Adsorbents at such high prices are by no means practicable and are a barrier to wider commercial use, which is not limited to wastewater treatment.

Scientists were therefore driven to investigate and create different adsorbent materials, notably with regard to the removal of heavy metals, as a result of low adsorption capabilities in comparison to relatively expensive adsorbent costs (Chai *et al.*, 2021). In addition to future advancements using AC with various surface modifications, innovative nano-absorbents have been gaining interest for a few years already. Nano-adsorbents have more accessible adsorption sites, better reactivity, and a larger affinity for heavy metals because of their increased surface-area-to-volume ratio (Kuhn *et al.*, 2022).

Applications of Nanoadsorbents for Wastewater Treatment

One of the numerous effective removal methods is the electrostatic interaction between heavy metal ions and carbon nanotubes (CNTs) (Rajendran *et al.*, 2022). Puri *et al.* (2021) claim that the usage of both Single wired nanotubes and multi-wired nanotubes (SWNTs and MWNTs) for eliminating hazardous ions of Cr(VI) is effective and has demonstrated good adsorption efficiency. Though SO_4^{2-} ions may cause the competitive inhibition of active sites, the introduction of carbon nanotubes has provided a more dependable alternative. It is preferable to employ nanotubes since it only required a few minutes for adsorption to occur on the surface and ion diffusion into the pores of CNT. In order to decontaminate the water, Mura *et al.* (2018) reported using a mixture of graphene oxide (GO)/FeO-Fe(VI). It covers the elimination of an organic synthetic rhodamine B dye, an organic non-ionic insecticide called diethyl 4-nitrobenzyl phosphonate (DNBP), as well as the medication diclofenac (DCF) from water samples. The removal of the aforementioned chemicals from water was accomplished with about 99% efficiency using graphene oxide nanomaterial (Asghar and Mushtaq, 2023).

Nanomaterials of metal complexes, such as titanium dioxide nanoparticles in arsenic adsorption and nanosized magnetite, demonstrated being preferable for the removal of heavy metals over activated carbon. The use of photocatalysts, such as nanoparticles of titanium dioxide, has been thoroughly studied to reduce the hazardous metal ions in water. According to a study, titanium dioxide nanocrystalline has shown to be more effective as photocatalysts than commercially available nanoparticles of titanium dioxide, removing arsenic with almost extreme efficiency at a pH value of about neutral. Chromium (VI) was converted to chromium (III) in daylight using a titanium dioxide nanocomposite, which consisted of titanium dioxide nanoparticles added to a graphene sheet. Palladium nanoparticles were used to treat chromium comparably. Most analysts assess the ability of arsenic (a heavy metal) to be removed by using Fe_2O_3 and Fe_3O_4 as simple adsorbents. Utilizing iron oxide nanocrystals with a high specific surface area allowed for the exploration of As removal (Palani *et al.*, 2021b).

Due to its distinct qualities and features, nano-clay has gained increased interest in recent years. Clay and other naturally occurring clay minerals are essential for maintaining the ecology. Clay is mostly made up of unprocessed minerals and exhibits a variety of geometry and morphology. These clay minerals have been utilized to clean contaminated water, store hazardous materials, and dispose of them. Clay minerals have been used as raw materials in a number of industries for hundreds of industrial applications due to their wide availability and inexpensive cost. Clay is used as a nano-adsorbent in a variety of adsorption procedures because of its distinctive features and high removal effectiveness. It has been demonstrated that nano-clays are a highly effective and efficient property enhancer for water purification. Numerous researchers have thoroughly investigated the use of clay minerals as adsorbents for the adsorption of several harmful substances, including heavy metals, dyes, antibiotics, biocide compounds, and other organic molecules (Awasthi *et al.*, 2019).

For the adsorption of COD, BOD, Fe(III), Cr(VI), and chloride from tannery effluent, kaolin and kaolin/ZnO nanocomposites were studied (Mustapha *et al.*, 2020). Kaolin/ZnO nanocomposites and ZnO nanoparticle were created using the sol-gel and wet-impregnation techniques, respectively. The clay structural network was successfully immobilized on the zincite hexagonal lattice layers of ZnO nanoparticles, according to the HRSEM/EDS/XPS study. When compared to pure kaolin (17 m2/g), kaolin/ZnO nanocomposites had a larger surface area (31.8 m^2/g), according to BET measurements. The kaolin/ZnO composites removed the most BOD (94%), COD (95%), Fe(III) (98%), Cr(VI) (100%), and chloride (78%). While kaolin was able to remove 89% BOD, 91% COD, 91% Fe(III), 78% Cr(VI), and 73% chloride under the same circumstances. Due to the greater surface area of the kaolin/ZnO nanocomposites than kaolin, they performed better in terms of adsorption.

Patio Ruiz *et al.* (2020) synthesized composites from chitosan beads that were altered with iron oxide (FeO) and titanium dioxide (TiO_2) nanoparticles via ionic cross-linking (Ch-FeO/TiO_2) in order to eliminate PAHs. By removing naphthalene from water and seawater samples, the improved adsorption mechanism of Ch-FeO/TiO_2 was discovered. Ch-FeO/ TiO_2 showed a greater adsorption capacity of 33.1 mg/g in comparison to unaltered chitosan beads (un-Ch) 29.8 mg/g. This adsorbent can be an excellent alternative for restoration of water sources contaminated with complicated substances because it is affordable and environmentally friendly.

According to Xin *et al*. 2021; Keykhaee *et al*. 2020; Icten and Ozer 2021 with the impressive micro-pollutant sequestration capacities and rapid adsorption kinetics at the laboratory scale, magnetic nanoadsorbents are becoming more and more useful functional materials. For instance, magnetic coal-based activated carbon has a specific surface area of 1188 m^2g^{-1} (Liu *et al*., 2021). High pore volumes (Li *et al*., 2020; Azam *et al*., 2020; Pan *et al*., 2021), sturdy architectures (Lingamdinne *et al*. 2019), and deeply interconnected porous networks (Tan *et al*., 2020) are further properties of magnetic nanoadsorbents. For the purpose of removing Ca^{2+} and Cu^{2+} metal ions from oilfield wastewater, He *et al*. (2021) developed Fe_3O_4/GO-COOH nanoadsorbents by magnetising and carboxylating graphene oxide (GO). The Fe_3O_4/GO-COOH adsorption capacities for Ca^{2+} and Cu^{2+} were 69.3% and 49.3%, respectively, after 30 minutes, and 78.4% and 51%, respectively, after 60 minutes. Additionally, the nanoadosorbent maintained a high recovery rate and clearance percentage after five adsorption/desorption cycles.

To synthesize different nanocomposites, a new method of nanoadsorbent modification that combines nanoparticles with metal, polymer, and carbon-based materials has been used. Many different kinds of nanocomposites, such as organic-polymer, inorganic-polymer, and also magnetic nanocomposites that benefit from various nanomaterials, have recently been synthesized (Yang *et al*., 2019). To achieve higher adsorption capacity and higher removal efficiency for heavy metals from wastewater, these nanocomposites would enhance adsorption performance and offer more precise interaction with the targeted pollutants (Yang *et al*., 2019). Nanocomposites, according to Barak *et al*. (2018), have a number of benefits, including as stability, low cost, improved mechanical capabilities, reduced energy consumption, and susceptibility to high temperature and harsh chemical conditions. In addition, the creation of hybrid nanocomposite adsorbents has amazing advantages for wastewater treatment applications in terms of magnetic characteristics and physiochemical stabilities (Nizamuddin *et al*., 2019). The longevity and reusability of nanocomposite adsorbents have also been reported by numerous studies, indicating that these adsorbents have excellent regeneration capabilities as a key component of a cost-effective strategy for removing heavy metals from wastewater (Nasir *et al*., 2019).

Potential advancements and future directions

1. Integration with Hybrid Systems: By integrating nanoadsorption with other treatment techniques like membrane filtration, biological processes, or enhanced oxidation; hybrid systems can be created that make the most of each method's advantages while also improving pollutant removal in general.
2. Real-time Monitoring: By incorporating nanosensors into nanoadsorbents, it may be possible to track the concentrations of contaminants in real-time, enabling flexible treatment plans and minimizing over treatment.
3. International cooperation could speed up the advancement and application of nanoadsorption technology on a global scale by facilitating the exchange of knowledge and best practices between researchers, businesses, and governments.
4. Public Awareness and Acceptance: Addressing concerns and ensuring responsible deployment of nanoadsorption technology can be accomplished through interacting with the public and stakeholders to highlight the advantages, safety, and potential of this technology.
5. Regulatory Framework: Establishing clear regulatory guidelines for the production, use, and disposal of nanoadsorbents will ensure their safe and ethical application in wastewater treatment.

Conclusion

In order to solve water scarcity and satisfy public demand for drinking water, the worldwide water situation must be improved. This requires novel water purification technologies. These challenges are brought on by population expansion, climate change, fast urbanization, and industry. Recent advances in engineering have made it clear that nanotechnology can be used to protect and sustain the environment.

This study has so far provided a succinct overview of a variety of nanoadsorbents that have been used to successfully remove heavy metals from wastewater with perfection. However, the data on the use of nanoadsorbents on actual wastewater are insufficient and urgently require additional research on pilot and large-scale studies. To increase the effectiveness and viability of the nanoadsorbents in actual wastewater treatment, it is therefore necessary to optimise them while taking into account their synthesis, cost, removal capability, and reusability. However, much more research is needed to support this claim.

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