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# Advancement of Nanoadsorbents in remediation of heavy metals from polluted water

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Abstract— The processing of nano-adsorbents and their feasibility for wastewater detoxification in the process of heavy metal extractions are quantitatively described in this review. The effects of certain key characteristics, including surface area, segregation, and adsorption capacity, on the functions of nano-adsorbents were thoroughly assessed. A thorough examination of the properties of nanomaterials, including their restricted ability has been made available to adsorb specific heavy metal ions.. The effects of temperature, electrostatic force, adsorbent dosage, pH, substrate concentration, reaction time, and response duration on the uptake of metal ions have all been investigated as experimental factors. Therefore, this review article's goal is to offer fresh information on the study and the improvement in this specific field, and to provide a version of the uses, benefits and restrictions of nanosorbents for the cleanup of wastewater .

*Keywords*— Nanoadsorbents, wastewater, composites, surfactants, adsorption

# I. INTRODUCTION

Water is one of the most prevalent components that make up life on Earth. It is essential to the global economy, since agriculture uses around 70% of freshwater resources. Water contamination is a worldwide problem that can have an impact on the health of people, plants, trees, and animals. Furthermore, a major environmental issue that the globe is currently dealing with is a lack of water[2]. Owing to advances in science that both benefit and introduce harmful contamination into the environment. This pollution is caused by mining activities, surface runoff from farms,untreated garbage dumping by municipalities, and inadequate release of industrial effluents into the soil and water bodies. These actions degrade our environment's fundamental qualities and endanger human health and life. There will undoubtedly be more demand placed on water supplies as the world's population grows. Toxin-containing unprocessed household and industrial waste is separated, Degradation of surface and ground water quality poses a serious risk and adversely affects the current fauna and flora[1]. Over the past few decades, heavy metal contamination has grown in severity as an environmental issue, leading to a multitude of illnesses and ailments[31]. The refractory consequences cause heavy metals—natural constituents of the earth's crust and economically significant minerals—cause heavy metal pollution, which lowers water quality and has an impact on the food chain[1].

Increasing demand of pure water with low concentration of heavy metals makes it obligatory to effectively eliminate poisonous heavy metals from industrial runoffs prior to their release into the ecosystem[3].

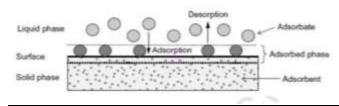
Consequently there will be a growing need for more affordable and efficient water treatment solutions on a global scale. There are several methods for extracting dissolved heavy metals from aqueous solutions, such as adsorption, electro dialysis, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and ion-exchange[31]. Even though the strategies listed above are effective and achieve the discharge standards, however, most of them generate secondary waste. Adsorption's high efficiency and ease of use have drawn a lot of attention from the scientific community and industry, especially when employing inexpensive adsorbents[31]. Adsorption, therefore, is believed to be a promising choice for the exclusion. Recently, numerous studies reported that the nanosorbent materials have a great and quite promising effect on water and wastewater treatment such as carbon tube, polymeric zeolites, metal and metal oxides nanosorbents[32].

In addition to addressing the present shortcomings of conventional approaches, nanotechnology and nanoparticles (NPs) based waste water treatment systems

Correspondence: Kriti Shrivastva, Centre for Renewable Energy and Storage, Suresh Gyan Vihar University, Jaipur Corresponding author. E-mail addresses: kriti.shrivastva@mygyanvihar.com 42 | P a g e provide the opportunity to optimally utilise previously untapped unconventional water sources[4].

Nanostructures, with their small size, huge surface area, and simplicity of functionalization, present unique prospects to create more efficient catalysts and redox active media for wastewater purification. It has been demonstrated that nanoparticles may successfully remove a wide range of contaminants from wastewater, including biological toxins, colour, heavy metals, organic and inorganic solvents, and microorganisms that cause diseases like cholera and typhoid[12].

The adsorbate builds up on the surface of the adsorbent during the adsorption process, which is a surface phenomena. When a solution containing absorbable solute comes into contact with a solid that has a highly porous surface structure, some of the solute molecules from the solution concentrate or deposit on the solid surface because of liquid–solid intermolecular forces of attraction. When it comes to bulk materials, other atoms inside the material satisfy all of the bonding requirements (ionic, covalent, or metallic) of the substance's constituent atoms. Adsorbates can be drawn to the atoms on the adsorbent's surface because they are not completely encircled by other adsorbent atoms. The specifics of the species involved determine the particular form of the bonding, but the adsorption[2].



# II. NANOADSORBENTS USED IN THE WASTEWATER REMEDIATION PROCESS

The affinity between the adsorbent and the adsorbate is the primary interaction force governing adsorption. As the surface area of the adsorbent rises, so does the adsorption process. Despite its great success in eliminating heavy metal ions and other kinds of pollutants, commercial activated carbons, zeolites, commercial activated alumina, silica gels, ion-exchange resins, and other adsorbents do have certain drawbacks[12].

Some of them are very costly, some need to be pretreated, and their removal and regeneration provide further issues. Since they have surmounted these restrictions, adsorbents such magnetic adsorbents, Saudi natural clay, and nanoadsorbents have been employed to remove pollutants in recent years[12].

Nanomaterials are materials with nanoscale dimensions (ranging from 1-100 nm) exhibit the potential to be used in removing a variety of toxic metals, especially heavy metals[14]. Nanoparticles are preferred over other adsorbents due to their multiple sorption sites, high specific surface area, low-temperature modification, porosity, surface capabilities[15]. The characteristics and effectiveness of nanosorbent materials are also influenced by additional physicochemical variables, including size, shape, chemical composition, crystal structure, physicochemical stability, surface energy, surface area, and surface roughness. It was discovered that by decreasing in size, nanomaterials might be made more reactive, increasing their surface area in relation to their volume[16].

#### A. Types of Nano-Adsorbents

Waste water treatment employs a wide range of nanoadsorbents. They have proven to be quite successful at removing contaminants from water. However, as it depends on a number of factors, such as the NPs' size and shape, the operating parameters (pH, temperature, reaction duration), the experimental design (batch vs column runs), and other factors, a direct capacity comparison is not possible [4]. The following major categories apply to the nano-adsorbents:

#### 1. Carbon-based nanoparticles:

The two most crucial and distinctive qualities of any nano-adsorbent would be its porosity and vast surface area. Published research indicates that there are numerous varieties of in the market, including polymers, metalorganic frameworks, zeolites,[31] activated carbon, and pillared clays [18]

The top four hazardous heavy metals are chromium (Cr), lead (Pb), mercury (Hg), and cadmium (Cd). These metals are non-biodegradable, bioaccumulative, and extremely harmful. The health of humans, animals, and plants is seriously endangered by these heavy metals even at trace concentrations. Adsorption of aqueous heavy metals has been accomplished by the use of functionalized carbon nanotubes[28] and graphene nanostructures.[38]

The most well-known group of all, though, may be carbon-based adsorbents, such as, activated carbon, porous carbon, graphene, [33] and fullerenes [37], all of which have excellent adsorption capacity and good thermal stability [21,22]. Typical carbonaceous materials, carbon layered silicate nanocomposites have recently attracted a lot of study interest because of their superior qualities over their counterparts. These days, water supplies contain a variety of hazardous substances such as lead, arsenic, mercury, zinc, nickel, chromium, and zinc [31].

Graphene oxide (GO) has a strong hydrophilic character because of the existence of oxygen-containing functional groups on its surface, which causes a fine dispersion in water. Given its unique functional groups and large surface area, graphene oxide (GO) is a viable option for decontaminating waste water. The process of removing heavy metal ions involves complexing metal ions with graphene's oxide binding site by adsorption[1][38].

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Adsorption of heavy <u>metal ions</u> by various kinds of <u>nanoparticles</u>.



To remove heavy metal ions, functionalized calcium silicate nanofibers were made from oyster shells; for Cu(II) and Cr (VI) cations, the removal capacities were 203 and 256 mg g-1. Many studies have been conducted on cement-based materials for the stabilization or solidification of heavy metals [34]

2. Metal based Nano Particles

Metallic nanoparticles NPs have become a promising material for heavy metal ion removal in recent years. Au-NPs, or gold nanoparticles, are utilised in cosmetics and other goods for human health. The anti-cancerous and distinctive visual features of Au-NPs have significant medical significance. The production technique of Au-NPs intended for pancreatic cancer therapy provided a comprehensive explanation of how Au-NPs work against Escherichia coli.[25]

Ag-NPs the most commonly utilised Metal NPs. Silver has been utilised from ancient times to cure ulcers, reduce body infections, and function as an antibacterial agent on minor wounds. Food rotting can also be avoided with the use of silver [23]. Ag-NPs/Graphene Oxide composites are used to measure the amounts of quercetin and morin in a variety of fruits and vegetables [24]. Because of their instability, bare metallic nanoparticles (NPs) are less frequently used as adsorbents because they tend to agglomerate. Furthermore, the procedure of separating bare nanoparticles from wastewater is difficult. Thus, in order to improve their stability and facilitate the separation process, these nanostructured adsorbers must be functionalized or capped.

## 3. Nanoscale Zerovalent Iron

In order to eliminate harmful heavy metal ions found in groundwater and waste water, nanoscale zerovalent iron or NZVI, has been employed. Strong reactivity, many reactive surface sites, and controlled particle size make it an ideal choice for nanoscale zerovalent iron (NZVI). According to earlier reports, NZVI demonstrated encouraging potential to eliminate HMs due to their unique structure. NZVI is a good option for the decontami-nation of As, Cu, and a number of other hazardous metals. In the same way,100% conversion of Cr(VI) to Cr(III) was seen within the aqueous medium in order to eliminate Cr(VI)[34].

4. Metal Oxide based Nanomaterials

There are some nanosized metal oxides, such as TiO2, Fe3O4, MnO2, MgO, CdO, ZnO, CuO, Al2O3, CeO2, ZrO2 and so on, which serve as a common adsorbent.

Many metal oxide-based nanomaterials, such as Fe3O4, TiO2, and ZnO, as well as their composites, have been employed. Nano-metal oxides have gained popularity in the past several years. A group of metal oxide compounds that have diameters between one and one hundred nanometers is known as nano-metal oxides. Their nanoscale size, which provides them a relatively high surface area, active surface, and diffusion activation energy, offers them a potent quantum effect. Generally speaking, nano-metal oxides have improved redox and adsorption capacities, are reasonably priced, and have no adverse effects on the environment [27]. For the purpose of adsorptive removal of arsenic, chromium, lead, cadmium, and mercury-based ions from contaminated water, the current study critically evaluates recent advances in surface chemistry and structural engineering of changeable metal oxides and their composites[36]. Metal oxides functionalized with surfactants exhibit improved adsorption efficiency. Because the majority of metal oxide nanoparticles have a propensity to aggregate, their surface area decreases. As a result, adding surfactant to the s Alumina (Al2O3), another essential metal oxide, is found in natural soils and has multiple structural phases ( $\alpha$ ,  $\beta$ ,  $\nu$ ,  $\Theta$ , and  $\chi$ ).  $\alpha$ -Al2O3 is used in conventional procedures as a naturally occurring adsorbent with higher stability. Strong interatomic bonding makes alumina an attractive sorbent due to its interesting features, which include good electrical insulation, wear and corrosion resistance, compressive strength, and thermal conductivity[1].In an investigation titanium dioxide examined the adsorption capability of Al2O3, or sodium dodecyl sulphate (SDS) modified alumina, towards NH4 (I) ions. The authors noted that the application of SDS to alumina's surface results in a notable boost in removal efficiency because the coating of an anionic surfactant alters the surface charge [42].

Another class of metal oxide nanoadsorbents, silicabased nanomaterials, have a lot of potential for metal ion adsorption because of their special qualities, which include a large surface area, controlled surface properties, and welldefined pore size. Furthermore, nano silica offers a safe and environmentally beneficial adsorbent[43]. Nitrilotriacetic acid (NTA) modified silica gel is an effective way to remove Cu (II), Cd (II), and Pb (II) from waste water. The produced substance demonstrated rapid metal ion removal in a matter of 2 to 20 minutes, exhibiting adsorption capacities of 63.5, 53.14, and 76.22 mg g -1 for Cu (II), Cd (II), and Pb (II), in that order. Another study looked into the improved removal of Cu (II) ions using amino-functionalized (3-aminopropyl and phenyl groups) silica nanospheres [43],[44].

Fe3O4 magnetic nano adsorbent has been synthesized without and with additional materials using a combination

Correspondence: Kriti Shrivastva, Centre for Renewable Energy and Storage,, Suresh Gyan Vihar University, Jaipur Corresponding author. E-mail addresses: kriti.shrivastva@mygyanvihar.com 44 | P a g e method of coprecipitation and milling, namely Fe3O4 Magnetic (FM), Fe3O4 Magnetic/Activated Carbon (FMAC), Fe3O4 Magnetic/Chitosan (FMCH), and Fe3O4 Magnetic/Glutaraldehyde (FMG)(46). A combination of coprecipitation and milling techniques are utilized to create Fe3O4 magnetic nanoadsorbent, which is created by concentrations of FAS (ammonium iron sulfate) III and FAS (ammonium iron sulfate) II compounds. In order to recover water contaminated by different heavy metals including Mn, Fe, Pb, and Zn, it needs to produce appropriate surface modifications and heterogeneous particle sizes[46].

## 5. Polymer based nanoparticles

Some polymer based nanoparticles are porous resins, polyaniline, polyacrylamides, cellulose acetate, cellulose or carboxymethyl cellulose, chitosan, alginate, and so forth[8]. Polymer-based nanofibrous membranes have also been employed to increase their adsorption efficiency. This is because of their large specific surface area, minute interfacial pore size, higher gas permeability, and welldefined porous nature. Their ideal adsorbent features are their easily degradable properties, strong skeletal strength, and changeable surface functional moieties. Metal ions are adsorbed on functional groups of integrated sorbent in the nanomembrane, allowing waste water to pass through the membrane during the membrane adsorption process on the surface of polymeric nanofibers. Unique functional groups such as -NH 2, -COOH, -SO 3 H, and so on improve the polymer-based nanomembrane's capacity to adsorb substances and its selectivity.

## 6. Chitosan nanopolymer

A hydrophilic, non-toxic, environmentally benign, and biocompatible polymer, chitosan can combine with different metal ions to form complexes. The selectivity and sorption capacity of chitosan are further enhanced by chemical modifications, and the presence of amino groups promotes the interaction with metal ions through chelation[45] Chitosan-alginate nanoparticles (CANPs) were created in order to adsorb mercury (II) ions from water[44]. The positive and negative ions of alginate and chitosan, respectively, cause them to interact electrostatically with calcium and tripolyphosphate ions. In this investigation, the highest possible adsorption level of CANPs for Hg (II) ions was shown to be a very high value of 217.39 mg/g at 30 °C[44].

## B. Synthesis of Nanosorbent Materials

Nanosorbent materials are typically synthesised using either the top-down or bottom-up technique. Depending on which approach is more advantageous than the other, it is used; in the top-down approach, bulk material is reduced to nanoscale through particle size erosion by mechanical alloying, micromechanical, electrochemical [39], sonochemical exfoliation, acidic dilution (oxidation), highenergy ball milling, and reactive milling; in the bottom-up approach, nonabsorbent materials are synthesised by atomic layer deposition, where atoms are deposited on atoms, molecules on molecules through arch discharge method, unzipping of carbon nanotubes, reduction of graphene oxide, sol-gel method, and chemical and physical vapour deposition [17].

## **III. CONCLUSION AND FUTURE PROSPECTIVE**

There are numerous wastewater remediation techniques; however, adsorption has emerged as the most potent and widely used technique. The adsorption technique can efficiently reduce numerous classes of pollutants (both inorganic and organic) with limited or no formation of poisonous by-products(s) or intermediates. Therefore, these materials are applicable in removing pollutants from the water source gaining wider recognition in water remediation, having unique potential in the adsorption process. In comparison to traditional adsorbents, nanoadsorbent's properties increase their application and have become more bneficial in numerous fields than traditional adsorbents. Hence, nanoadsorbent materials can be considered next-generation adsorbents useful in environmental purification and pollutant control in wastewater. This review study discusses all the assets about treating waste water using nanoparticles Nevertheless, a lot of issues and advancements must be resolved before these nanomaterials can be used in the future. One of the main problem is the post-management of the utilized nanomaterials, since there is limited literature accessible and many of them do not focus on this topic. Since recovered pollutants have the potential to pollute the environment again, it is important to dispose of exhausted nano adsorbents safely. Further studies are needed to be done with these nanoadsorbent materials, including surface adaptations and chemical stabilization for improving their application in wastewater.

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