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Adsorptive Remediation of Wastewater Pollutants using Different Nanomaterials

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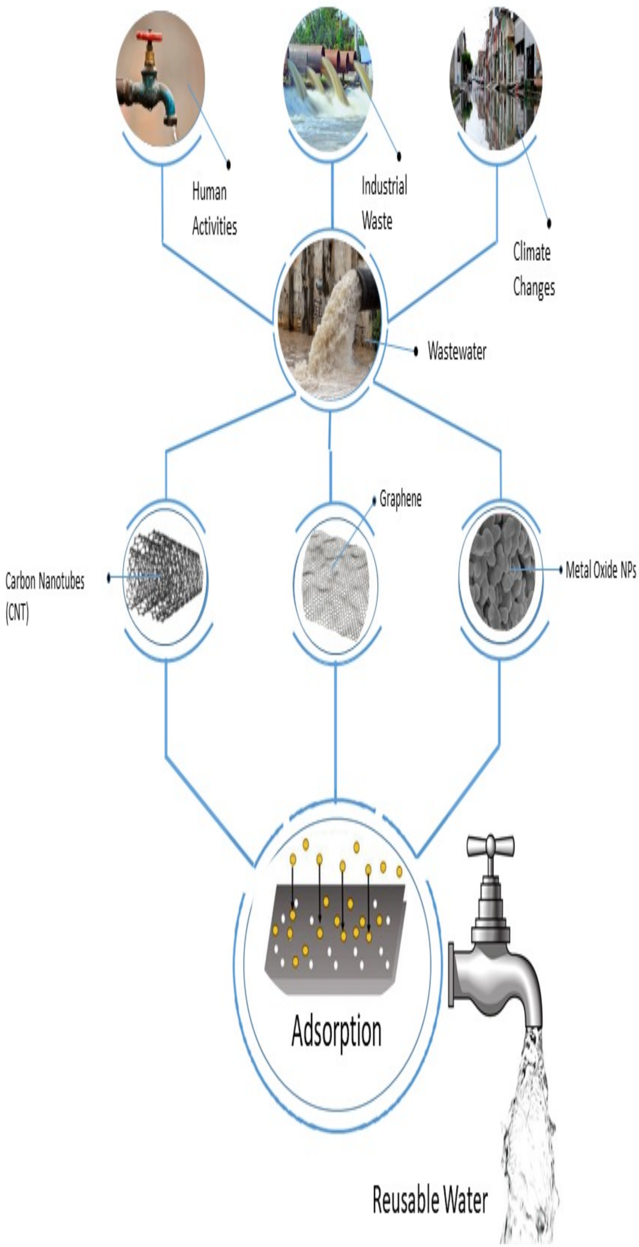
ABSTRACT

Keeping in view the scarcity of water resources, effective use of water is an essential element for humans. The contamination of water with toxic pollutants is the biggest challenge globally. Therefore, it is crucial to develop and implement water treatment approaches which limit water wastage. Water is contaminated with various toxic, inorganic (heavy metals) and organic (dyes) pollutants. Primarily, water pollution is created by man-made activities, including household chores, agricultural consumption, and industrial waste. On the contrary, nanotechnology promisingly ensures safe and healthy drinking water. The current review article provides a brief overview of recent developments in nanomaterials, biosorption capacities (presented in tabular form for comparison), and future perspectives of nano-based sorbents. Moreover, nanomaterials for adsorptive remediation of pollutants (heavy metals and dyes) are categorized as organic (carbon and graphene-based) and inorganic (metals and metals oxides-based). To increase their adsorption capacity, they can be modified with various functional groups. The adsorption capacity of nanomaterials to adsorb the pollutants depends on pH, adsorbent dosage, pollutants concentration, and contact time. These nanomaterials are a powerful alternative to conventional treatment approaches due to their improved adsorption capacity. However, nanotechnology requires to overcome the environmental concerns and cost-effectiveness of nanomaterials. The regeneration and reuse of nanomaterials can enable it.

Keywords: adsorption, carbon nanotubes, graphene oxide, nanomaterials, treatment, wastewater

GRAPHICAL ABSTRACT



INTRODUCTION

Due to industrialization, environmental contamination has become a serious problem affecting developing and established countries. Fundamentally, no specie can live on this earth without water because water, soil and air are essential human resources. Environmental remediation, water, soil and air pollution production are primary concerns worldwide, especially in developing regions. However, the environmental remediation is still a major challenge, particularly when four common points, cost, recycle-ability, eco-friendliness, and efficiency are taken into consideration. The primary pollutants in water (like tape, surface, and groundwater) are mostly composed of inorganic contaminants for instance heavy metals, organic contaminants (like pesticides, pharmaceuticals, detergents, and biomaterials) and arsenic ions [1].

Since the urbanization and industrial revolution, a number of metal ions has been released into the water by different human activities, like chemical manufacturing, mining, electroplating, and applications of fertilizer and pesticides. Due to this technological advancement, heavy metal pollutants in water and soil become a big challenge globally, due to their toxic nature, persistent and non-biodegradable, like Cr(VI), Cu(II), Hg(II), Cd(II), Pb(II), the human health, and ecological environment which seriously threatened the human existence, while affecting the various utilization materials of humankind. Besides, the heavy metals even at the low concentration present in water may cause health and environmental problems [2].

Organic pollutants in water may also cause serious health and environmental issues. Several harmful organic dyes are released into the water by various industries such as cotton, leather, paper, wool, and silk. These organic dyes are water soluble, and their continuous release in water even at low concentrations is very toxic and hazardous to humans. For example, methylene blue is a common water-soluble dye, the contamination of water with methylene blue can cause cyanosis, shock, heart attack, irritation to the skin, vomiting, quadriplegia, and jaundice in humans. On the other hand, malachite green (cationic dye) is also soluble in water, and it may cause mutagenesis, carcinogenesis, and teratogenicity [3]. According to one projection from the World Health Organization (WHO), more than half of the total population would live in water-stressed areas by 2025 [4].

Out of total earth, surface 70.8% is embodied by water. Just about 2.7% is clean water and out of 0.4% can be directly utilized. This tiny fraction of fresh water supports approximately 100,000 species out of nearly 1.8 million, which is about 6% of all identified species. The consumption of water is essential from both, qualitative and quantitative point of view. Consequently, a very important world crisis is water pollution [5].

Water treatment typically consists of several treatment barriers that vary in terms of supply requirements and water security in general [6]. Different methods for wastewater treatment havebeen established in recent decades. These include micro and ultrafiltration, solvent extraction, gravity separation and sedimentation, coagulation, precipitation, flotation, oxidation, distillation, evaporation, adsorption, reverse osmosis, electrolysis, and ion exchange. Adsorption is one of the primary wastewater treatment techniques mentioned above, owing to its low cost, easy to operate, and provision of a large scale of adsorbents [7]. So many treatment processes have been set up to extract contaminants from wastewater. Still, it is not possible to expect a 100% reduction of incoming waste load [8].

Nanotechnology-enabled, highly reliable, flexible, and multifunctional processes, which are intended to supply high-performance, wastewater treatment solutions and safe water that not only solve major issues facing current water treatment systems but also provide new treatment technologies, which allow additional water supplies to be used effectively to expand existing water treatment technologies. Recent developments in nanoscale science and engineering have brought tremendous improvement in wastewater treatment systems. Nanomaterials have a particle size less than bulk-sized materials. Most of these nanomaterials were investigated and identified as products for water and water treatment applications in the fields of adsorption, microbial control monitoring and detection, photo-catalysis and membrane filtration, and disinfection [9].

The use of nanoparticles as adsorbents to treat water has been important in the recent years. As the safest approach for chronic and emerging contaminants, nanotechnology has demonstrated considerable potential [10]. Due to their higher appearance and reactivity, nanomaterial-based adsorbents provide attractive alternatives for conventional adsorbents, resulting in higher adsorption capacity [11]. Furthermore, the small size of the particles also allows the construction of modular treatment systems. Recent research has also shown that nanoparticles can be engineered to attack several pollutants, simultaneously [12]. One main concern of the current research is to summarize the useful results which can be used to remove aquatic contaminants of various forms of nanomaterials in wastewater treatment, such as adsorbents.

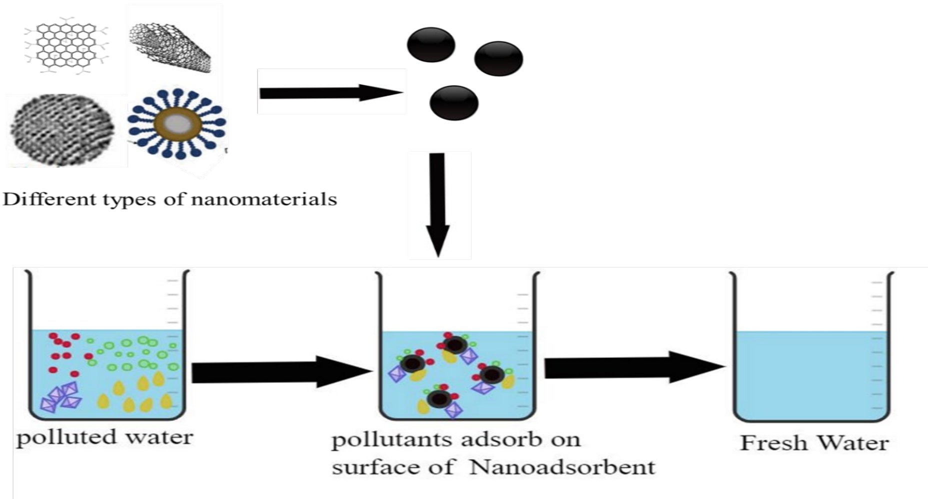


Figure 1. The adsorption mechanism of nanomaterials to adsorb the water pollutants

2. ADSORPTIVE APPLICATIONS OF NANOMATERIALS

In recent times, nanomaterials have procured great attention in removing pollutants from wastewater. The nanoscale characteristics like adsorption, reactivity, high surface area and catalysis make the nanomaterials more effective for wastewater treatment. Different types of nanomaterials are used to remove pollutants from wastewater [13] which include carbon-based, zero-valent, and nanocomposites. There are various methods to synthesize the nanomaterial like sol–gel, co-precipitation, chemical vapour deposition, sputtering spinning and pyrolysis. Removal mechanisms include adsorption, chemical precipitation, coagulation ion exchange, and membrane filtration [14].

2.1.Carbon Based Nanoadsorbents

2.1.1. Carbon Nanotubes (CNTs)

CNTs are the allotropic form of carbon. CNTs have 1nm diameter with a few centimeters in length [15]. Usually, CNTs have a cylindrical structure wrapped up in a tube-like frame. There are two types of CNTs, single-walled carbon nanotubes and multi-walled carbon nanotubes. SWCNTs are generated by the roll-up of the signal graphene sheet, and the roll-up of several graphene sheets forms the MWCNTs. Fig.2 reveals the structure of SWCNTs and MWCNTs. CNTs have good sorption capacity and high performance relative to traditional powder and granular activated carbon [7].

Experimental results have shown that both nature of sorbate and the substrate functional groups are dependent on the adsorption potential of CNT [16].The functionalization surface of CNTs can be modified with N, O, and P containing group, which ensures the efficiency in the precise surface area [17]. For the surface grafting of CNTs with a strong adsorption of heavy metals from liquids, numerous organic polymers have been introduced [18].

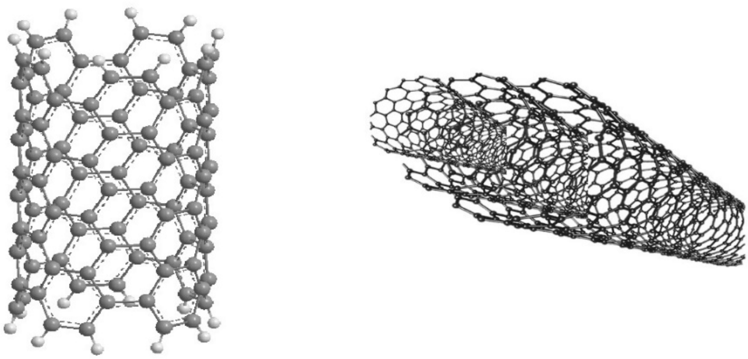


Figure 2. Structure of SWCNTs and MWCTNs

2.1.1.1.Removal of organic pollutants

In the adsorption of several organic chemicals, CNTs have demonstrated higher efficiency than activated charcoal [19]. The broad surface area and the multiple interactions between pollutants and CNT are mostly due to the high adsorption capacity. The field on which individual CNTs can be adsorbed is centered on the external surfaces [20]. CNT aggregates contain pore space and loops that are strong adsorption active sites for organic compounds [21].

The main downside of activated carbon is its poor adsorption ability for polar organic compounds that have lower-molecular weight, due to various interactions between pollutants and CNT. It strongly adsorb all of these polar organic materials. The carbon nanotubes (CNTs) surface rich in π electrons makes $(\pi - \pi)$-interactions with organic molecules [22, 23]. The graphite CNT surface forms hydrogen bonds with organic compounds that have functional groups of -OH, $-NH_2$, and -COOH, which donate electrons [24]. Electrostatic attraction promotes the absorption at an acceptable pH of positively charged chemical compounds like some antibiotics [25]

The overall, mechanism involved in adsorption of organic pollutants onto the CNTs, include $(\pi - \pi)$-interactions, Lewis's acid–base interactions, hydrogen bonding, hydrophobic interactions, and electrostatic interactions. However, there have been no specific procedures for addressing the specific contribution of such mechanisms for a specific adsorption, which suggest that this field requires more investigation [26].

Table 1: The Adsorption of Organic Pollutants onto Different Types of Carbon Nanotubes CNTs

Sr. No.	Carbon nanotubes CNTs types	Organic pollutants	Adsorption capacity (mg/g)	References
1	Oxidized SWCNTs	Basic red 46 (BR 46)	49.45	[27]
2	Untreated MWCNTs	Tetracycline (TC)	269.54	[28]
3	SWCNTs	4-Chloro-2-nitrophenol	1.44	[29]
4	Untreated SWCNTs	Dissolved organic matter (DOM)	26.1–20.8	[30]
5	Alkali-activated MWCNTs	Methylene blue	399	[31]
6	Untreated SWCNTs	Reactive red 120 (RR -120)	426.49	[32]
7	Untreated MWCNTs	Methylene blue	59.7	[33]
8	Carboxylated MWCNTs	Norfloxacin	90.3	[34]
9	KOH activated MWCNTs	Toluene, ethylbenzene, m-xylene	87.12, 322.05, 247.83	[35]
10	Pristine and hydroxylated MWCNTs	Sulfamethazine	24.78, 13.31	[36]
11	MWCNTs	Methyl orange	52.86	[37]
12	MWCNTs/CoFe2O4	Sulfamethoxazole	6.98	[38]

Sr. No.	Carbon nanotubes CNTs types	Organic pollutants	Adsorption capacity (mg/g)	References
13	Chitosan/Fe2O3/MWCNTs	Methyl orange	66.90	[39]
14	Single, double and multi-walledd carbon nanotubes	Ciprofloxacin	933.8, 901.2, 651.4	[40]
15	Calcium alginate/MWCNTs	Methyl orange	12.5	[39]
16	Single, double and multi-walledd CNTs	Oxytetracycline	554, 507, 391	[40]
17	MWCNTs	Tetracycline	192.7	[41]
18	CNTs-c@Fe-chitosan	composite Tetracycline	104	[42]
19	multiwalled carbon nano-tubes (MWCNTs)	4-Chloro-2-nitrophenol	4.42	[29]

2.1.1.2. Removal of heavy metals

Oxidized carbon nanotubes (CNTs) have strong adsorption potential for metals with fast kinetics. The functionalization can modify the carbon nanotubes' surface with hydroxyl, phenol, and carboxyl-containing group primarily, through chemical bonding and electrostatic attraction [43]. Consequently, the adsorption potential of CNTs can be greatly increased by surface oxidation. Various experiments showed that carbon nanotubes CNTs are adsorbents for metal ions and then activated carbon(for instance, Zn^{2+}, Cu^{2+}, Cd^{2+},and Pb^{2+}) [44, 45].

Carbon nanotubes (CNTs) based nanomaterials can be used to track and remove metal ions electro-chemically [46]. For example, the order of affinity of the metal ions towards carbon nanotubes at pH = 9 is $Cu^{2+} > Pb^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$ [47].

Multiwall carbon nanotubes (MWCNTs) can be utilized to remove rare earth metals like strontium Sr (II) and Europium Eu (III) from an aqueous medium [48, 49]. Multiwall CNTs, coupled with chitosan, effectively adsorb heavy metals like Cu^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+} [50]. Multiwall carbon nanotubes (MWCNTs) can be modified using ethylene diamine to remove Cd^{+} ions from an aqueous medium [51]. The polydopamine-functionalized carbon nanotubes CNTs were prepared by different methods and introduced to extract Cu^{2+} ions. [52]. The nanocomposites of graphene oxide and biochar-based CNTs displayed enhanced specific surface area and expanded sorption potential for ions Cd^{2+} and Pb^{2+} ions [53]. Carbon nanotubes CNTs have strong absorption capacity when functionalized with polyethyleneimine and utilized to extract Cu^{2+} metal ions [54].

Modified MWCNTs have two main kinds of mechanisms between adsorbate and adsorbent: physical and chemical adsorption. The possible mechanism of metals ions on modified MWCNTs are demonstrated, such as complex formation, chemical interaction, electrostatic attraction and physical adsorption between surface functional group of modified MWCNTs, and metals ions. The formation of complexes and electrostatic attraction between the surface functional groups and metals ions of modified MWCNTs is the most important adsorption mechanism [55].

Table 2: The Adsorption of Different Heavy Metal ions onto Various Types of Carbon Nanotubes CNTs

Sr. No.	Adsorbents	Metal ions	Adsorption capacity mg/g	References
1	CNT dendrimer	Pb (II)	4870	[56]
2	CNTs (HNO_3)	Pb (II)	49.95 at pH=7.0	[17]
3	MWCNTs	Ni (II)	7.53 at pH=7.0	[57]
4	CNTs	Pb (II)	17.44 at pH=7.0	[58]
5	SWCNTs	Ni (II)	9.22 at pH=7.0	[57]
6	MWCNTs (HNO_3)	Pb (II)	97.08 at pH=5.0	[44]
			Adsorption capacity mmol/g	
7	CNTs	Hg (II)	1.068	
8	$CNT\text{-}COO^-$	Hg (II)	3.300	
9	CNT-OH	Hg (II)	1.284	
10	$CNT\text{-}CONH_2$	Hg (II)	1.658	
11	CNTs	Cd (II)	1.291	
12	CNT-COO-	Cd (II)	3.325	[59]
13	CNT-OH	Cd (II)	1.513	
14	$CNT\text{-}CONH_2$	Cd (II)	1.563	
15	CNTs	Cu (II)	1.219	
16	CNT-COO-	Cu (II)	3.565	
17	CNT-OH	Cu (II)	1.342	

Sr. No.	Adsorbents	Metal ions	Adsorption capacity mmol/g	References
18	CNT-$CONH_2$	Cu (II)	1.755	
19	CNTs	Pb (II)	1.406	
20	CNT-COO^-	Pb (II)	4.672	
21	CNT-OH	Pb (II)	2.07	
22	CNT-$CONH_2$	Pb (II)	1.907	

2.1.2. Graphene-Based Nanomaterials

Graphene triggered dramatic advancements in the built environment due to its unique form and outstanding physicochemical properties [60]. The graphene-based materials have drawn enormous global attention [61]. GO is a modified graphene with several oxygen groups like carbonyl, epoxy, hydroxyl, and carboxyl groups [62].

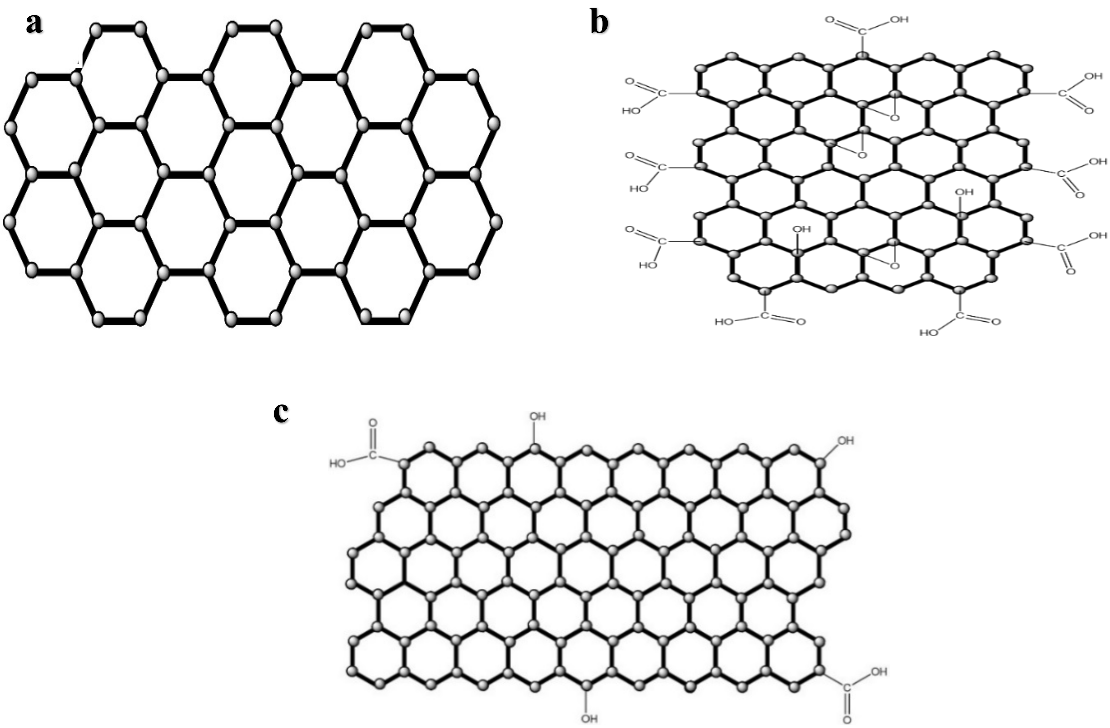


Figure 3. Structure of (a) graphene, (b) graphene oxide (GO) and (c) reduce graphene oxide (rGO)

2.1.2.1. Removal of dyes

Dyes are abundant water contaminants, which are released from many factories, such as textiles, printing, dyeing, tannery and painting, paper, and pulp. Some dyes are more durable and harder to biodegrade because they have a complex molecular structure. The existence of dyes in water creates problems for aquatic organisms and certain dyes are harmful for human health [63]. Recent research primarily, concentrates on the chemical improvements in graphene and its ability to adsorb dyes [64].

Graphene Oxide (GO) can absorb the methylene blue (MB) dye to a large degree with very high absorption potential (714 mg/g) [65].The nanocomposite of the tannic acid-graphene adsorbent can utilized to extract blue rhodamine [66].

Adsorption capacity of acid orange on GO has been studied by [67]. GO has a high adsorption potential (2158 mg/g), it sufficient for treatment process. The adsorption potential reduced to 976 mg g^{-1} when the GO concentration was doubled, but the removal efficacy increased to 95%. [68]. Graphene-SO_3H/Fe_3O_4 was observed which removed almost 93% of cationic dye in 10 minutes.

The nanocomposite of magnetite reduced graphene oxide, which can be utilized for the adsorption of dyes. The material revealed considerable malachite dye removal (94%) in two hours at optimal condition [69]. Acid Blue 92 can be removed by surface-modified graphene oxide nanosheet [70].

Graphene based nanomaterials have several mechanisms involved in adsorption of different types of dyes at molecular level, based on adsorbate-adsorbent, adsorbate solvent which mainly depend on physical and chemical interaction. The primary mechanism of interaction can also be induced by the π-π interactions since all carbon atom of GO has an π-electron which is perpendicular to the surface of GO [71].

Table 3: The Adsorption of Dyes onto Different Types of Graphene

Sr. No	Adsorbents	Dye	Adsorption capacity mg/g	References
1	rGO/ hydrogel	MB	7.85	[72]
2	GO/Fe_3O_4	MB	167.2	[73]

Sr. No	Adsorbents	Dye	Adsorption capacity mg/g	References
3	PES/GO	MB	62.50	[74]
4	Fe_3O_4-GO	MB	167.2	[73]
5	TiO_2-GNs	MB	83.3	[75]
6	GO	AO	1428	[76]
7	GNs Sodium	AO	3333	[76]
8	Fe_3O_4-GO	NR	171.3	[73]
9	Fe_3O_4-GNs	CR	33.7	[77]
10	$CoFe_2O_4$-GNs	MO	71.5	[78]

2.1.2.2. Removal of heavy metals

GO is a functionalized graphene with oxygen that contains groups that can adsorb the heavy metal complexes through both coordinate and electrostatic approaches. [79] prepared graphene oxide nanosheets are checked for the extraction of metal ions like Cd^{2+}, Co^{2+}, Pb^{2+} [80], and U(VI) [81] aqueous media. [82] synthesized a functionalized graphene oxide (GO) with thiol groups(R-S-H). The adsorption capacity increased by this surface-modified graphene oxide (GO-SH).

A flower-like composite of GO-TiO_2 was synthesized, which is used to separate the metal ions from water such as Cd^{2+}, Pb^{2+}, and Zn^{2+}. The composite of graphene oxide with titanium oxide (GO-TiO_2) has high adsorption capacity like 65.6,72.8 and 88.9 mg/g for Pb^{2+}, $Cd^{2+}$and Zn^{2+} respectively, at pH of 5.6 [83]. [84] synthesized a magnetite (Fe_3O_4/GO) composite to separate Co^{2+} ions from solution and studied adsorption kinetics, thermodynamics, and equilibrium.

The adsorption mechanism depends on the surface and electrostatic interaction between surface functional groups and metals ions. The adsorption mechanism of graphene-based nanomaterials also depends on the additional properties and characteristics of functionalization [85].

Table 4: The Adsorption Capacity of Graphene Base Nanomaterials to remove Different Heavy Metals

Sr. No	Adsorbents	Heavy metals	Adsorption capacity mg/g	References
1	GO	Cd (II)	14.9	[83]
2	TiO_2/GO	Cd (II)	72.8	[83]

Sr. No	Adsorbents	Heavy metals	Adsorption capacity mg/g	References
3	GO/ Fe_3O_4/sulfanilic acid	Cd (II)	55.4	[86]
4	GO	Cu (II)	46.6	[87]
5	GO/ Fe_3O_4	Cu (II)	18.3	[88]
6	GO-gelatin/Chitosan	Cu (II)	120	[89]
7	GO	Pb (II)	35.6	[83]
8	GNs	Pb (II)	22.4	[90]
9	GO-EDTA	Pb (II)	479	[91]
10	GO	Hg (II)	35	[82]
11	GO-SH	Hg (II)	190	[82]
12	GNs-polypyrrole	Hg (II)	980	[92]

2.1.2.3. Removal of pharmaceutical waste

Pharmaceutical traces have been identified as an emerging contaminant owing to their presence in the water body. Pharmaceutical waste is produced during agricultural processes, antibiotics that have been only partially used have expired, and a significant amount of bacterially resistant antibiotic waste has been released into the environment. In addition, the sewage system could excrete drugs not fully metabolized inside the body. Adsorption is an effective approach to remove micro pollutants due to its low-cost, simple design, and high efficiency [93].

Dorzolamide (Dorzo), a pharmaceutical component common in biomedical effluents, is removed using the composite graphite oxide (acrylic acid) grafted chitosan (GO/CSA). The GO/CSA composite has a very high adsorption capacity (334 mg/g) at room temperature [94]. Graphene nanoplatelets have great adsorption potential, and it is utilized to remove aspirin, caffeine, and acetaminophen [95]. The synthesis of reduced graphene oxide/magnetite (RGO–M) is used in norfloxacin (NOR) and ciprofloxacin adsorption (CIP) [96]. [97] performed a laboratory adsorption analysis using GO as an adsorbent to extract sulfamethoxazole and diclofenac solution.

[98] synthesized reduced porous graphene oxide nano sheets loaded on ribbon-shaped boron nitride (BN) foam were used to remove the

gemfibrozil (GEM). Its distinctively fast adsorption kinetics towards GEM, with 90% removal potential in less than 5 min in terms of reliability

Table 5: The Adsorption of Pharmaceutical Waste onto Different types of Graphene

Sr. No	Adsorbents	Pharmaceutical waste	Adsorption capacity mg/g	References
1	GO	Tetracycline	313	[97]
2	Graphene nanoplatelets	Aspirin,	13.02	[95]
3	GO	Tetracycline	323	[99]

2.2. Metal Oxide-based Nanomaterials

Metal oxides are inorganic nanomaterials, commonly utilized to remove organic pollutants and heavy metal ions from the aquatic environment. Metal oxide nanomaterials, such as Fe_3O_4, ZnO, TiO_2, MgO, MnO_2, and CdO, offer specific affinity and high specific surface area.

2.2.1. Iron Oxides (Fe_3O_4) Nanomaterials

2.2.1.1. Removal of heavy metals

Iron oxide nanomaterials have attained substantial attention owing to their simplicity and availability. Various types of iron oxide nanomaterials are utilized as nano adsorbents to adsorb the heavy metals ions from wastewater [100, 101].

The surface modification of iron oxide nanomaterials can increase the adsorption capacity [102]. The surface-modified Fe_3O_4 nanoparticles have a high potential for rapid adsorption of heavy metals like As^{3+}, Cr^{3+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, and Pb^{2+} from wastewater [103]. [104] used carbon-encapsulated magnetic nanoparticles for adsorption of Cd^{2+} and Cu^{2+} ions. They found that the ion adsorption attain 95% of copper and cadmium.

The adsorption mechanism of metal ions from wastewater by functionalized iron oxide nanomaterials include magnetic selective adsorption, surface site binding, modified ligands combination, and electrostatic interaction [105].

2.2.1.2. Removal of organic pollutants

Fe NPs are widely being investigated for the adsorption of organic dyes, especially for the successful treatment of large quantities of water and rapid extraction by utilizing a powerful external magnetic field [106].

Organic contaminants are usually adsorbed via surface-exchange reactions till all the active sites on the surface are occupied [107]. Based on this process, nanomaterials development for the extraction of dye pollutants needs the addition of surface functionalization [108].

2.2.2. Zinc Oxides (ZnO) Nanoparticles

Zinc oxide (ZnO) nanoparticles are found as effective candidate for the treatment of wastewater due to their specific characteristics. Kataria et al. experimented with removing the Victoria Blue (VB) B dye using zinc oxide (ZnO) nanoparticles [109]. The maximum adsorption of dye was attained at pH 6. VB B dye's highest adsorption capacity on nano adsorbate was 163.93 mg/g, which was measured using the Langmuir model.

Zinc oxide (ZnO) nanomaterials can remove toxic heavy metals Pb (II) from wastewater. Pb (II) 's highest adsorption capacity on nano adsorbates was observed to be 19.65 mg/g in an aqueous solution at70 ºC temperature under pH 5 [110].

Zinc oxide (ZnO) nanomaterials were synthesized and utilized to remove alizarin red S colour. The maximum adsorption efficiency was attained when pH was 4, for 35 min, adsorbent dose was 0.4 g/L, and dye concentration was10 mg/L [111].

[112] synthesized the zinc oxide (ZnO) nanomaterials through biological process was investigated through its adsorption potential to remove the Ismate violet 2R. The 99% removal efficiency was attained when pH was 6, for 120 min, adsorbent dose was 0.08 g/L, and temperature was at 55 °C.

2.2.3. Titanium Dioxide (TiO_2) Nanoparticles

In the past few years, titanium dioxide (TiO_2) nanoparticles can also be utilized as sorbents for removing and separating metal ions, like Cu^{2+}, Pb^{2+}, Hg^{2+}, and Ag^{+}. TiO_2 nanoparticles displayed strong adsorption efficiency.

Titanium dioxide (TiO_2) nanoparticles entrapped poly (vinylidenefluoride) (PVDF) hybrid membranes are utilized to remove heavy metal like Cu. The adsorption rate of poly (vinylidenefluoride) PVDF(CTAB)/TiO_2 at pH of 7 was 68.80% [113].

Titanium dioxide (TiO_2) nanoparticles containing polyacrylamide-grafted gum ghatti (PAAm-g-Gg) of hydrogel nanocomposite (HNC) was applied for the removal of toxic cationic dyes like MB from water. The adsorption potential of the hydrogel nanocomposite was relatively higher than that of the neat gum ghatti Gg or Gg-cl-PA Am hydrogel. The hydrogel nanocomposite removed 98% of the MB dye from the aqueous media [114].

2.3. Metal-based Nanomaterials

2.3.1. Silver (Ag) Nanoparticles

Ag NPs are widely utilized as adsorbents owing to their non-toxicity, large surface-to-volume ratio, and cost-effectiveness. Ag NPs are applied to organic pollutants like methylene blue. The highest adsorption capacity of MB dye at pH 7 is 147 mg/g [115].

Ag NPs combine with yttrium oxide (Ag-Y_2O_3) form a nanocomposite, which has a larger surface area (18.05 m^2g^{-1}) and adsorption potential for metals such as Cr (VI) and Cu (II) [116].

2.3.2. Iron (Fe) Nanoparticles

Zerovalent iron nanoparticles are a suitable adsorbent to absorb heavy metals like arsenic (As). Zerovalent iron nanoparticles showed high efficiency at pH >5 for the removal of arsenite than arsenate. The adsorption potential of arsenate and arsenite is 12.0 mg/g and 18.2 mg/g, respectively, at pH 6.5, which was much better than other commonly usable adsorbents of arsenic. In the presence of silicate or phosphatic, arsenic's adsorption efficiency decreased, significantly [117].

2.3.3. Iron/Zinc (Fe/Zn) Bimetallic Nanoparticle

A novel (Fe/Zn) bimetallic nanoparticle was used as an adsorbent to remove the organic pollutants like CR and MG from water. The adsorption capacity of CR and MG dyes was impaired by pH, contact duration, and adsorbent dose at the start. It was the maximum for MG and CR at pH 9 and 4, respectively [118].

In the field of adsorptive remediation of wastewater by metal-based nanomaterials, it is extremely important to understand the adsorption mechanism. Majority of studies have clarified the process based on adsorption patterns, which was observed at different pH ranges. A few researches, have focused on the characterization of metal-loaded adsorbents and attempted to provide a support for the possible mechanistic route [119].

2.3.4. Nickel/Zinc (Ni/Zn) Nanocomposite

Punia et al (2022) [120] synthesized the Ca doped Ni/Zn nano-ferrites for the removal of metal ions (Cd and Cr). Various batch experiment and adsorption results revealed that maximum uptake by chromium and cadmium was 51.00% and 98.25%, respectively.

The Ni/Zn based nanohybrid was used to remove the organic dye (Azorubine dye). The maximum adsorption efficiency was attained when pH was 5, time was 60 min, adsorbent dose was 0.68 g/L and dye concentration was 10 mg/L [121].

Table 6: Adsorption Capacity of Metal and Metal Oxides Nanomaterials to remove Heavy Metals and Organic dyes

Sr. No	Adsorbents	Pollutants	Adsorption capacity mg/g	References
1	Goethite (α-FeOOH)	Cu (II)	149.25	[122]
2	γ-Fe_2O_3	Cu (II)	26.8	[123]
3	Amino-modified Fe_3O_4	Cu (II)	12.43	[124]
4	Fe_3O_4 magnetic nanoparticles	Cu (II)	61.07	[125]
5	δ-MnO_2	Ni (II)	30.63	[126]
6	Modifying Fe_3O_4 microspheres	Hg (II)	37.4	[127]
7	TiO_2	Pb (II)	401.14	[128]
8	δ-FeOOH-coated γ-Fe_2O_3 MNPs	Cr (VI)	25.8	[129]
9	Modified Al_2O_3	Pb (II)	100	[130]
10	TiO_2	Cd (II)	16.69	[131]
11	Flower-shaped ZnO	Victoria Blue B	163.93	
12	ZnO	acid fuchsin AF	3307	[132]

Sr. No	Adsorbents	Pollutants	Adsorption capacity mg/g	References
13	Co_3O_4/SiO_2 nanocomposite	MB	53.87	[133]
14	ZnO	CR	1554	[132]
15	TiO_2	MO	85.39	[131]
16	Zn-Fe_2O_4 hollow fibers	Acid fuchsin AF	150.37	[134]
17	ZnO	Malachite green MG	2963	[132]

3. CONCLUSION

Water is one of the most abundant natural resources on earth. However, only 1% of that natural resource is available in pure form for human consumption. A sustainable approach to affordable and clean water is perceived as one of the biggest global challenges. Nanotechnology has the potential to overcome this challenge efficiently and inexpensively as it is an advance wastewater treatment approach. A wide variety of nanomaterials has been reported to remove inorganic (heavy metals) and organic (dyes) contaminants. Nanomaterials for remediation of contaminants (heavy metals, dyes) are categorized as organic (carbon-based and graphene-based) and inorganic (metals and metals oxides-based) nanomaterials. These nanomaterials have specific physiochemical properties. For instance, carbon and graphene-based nanomaterials have a high surface area and can be modified with different functional groups to increase their adsorption efficiency. The metal oxides-based nanomaterials have a minimum environmental impact and low solubility with numerous active seats and a specific affinity. The nanomaterials provide a powerful alternative to conventional treatment approaches due to improved adsorption capacity. However, due to environmental concerns, technical difficulties, and cost-effectiveness, most implementations are not still ready for the market and thus, only a few nano-sized products are commercially available.

3.1. Recommendations

The following aspects should be taken into consideration for prospective work to enhance the adsorption applications of nanomaterials:

- Efficiency of nanotechnologies experiments should be performed to introduce more practical conditions for the optimization of process parameters. Synthesized materials could be more effective in pollution sensing technologies.
- Long-term performance –future experimentation should concentrate on the recycling ability of sorbents. The more they would be recyclable, the more they would be cost friendly.
- Environmentally friendly–for the nanomaterials to be efficiently applied, the overall process should be secure and environmentally friendly.
- Waste management – more studies are required to resolve the management of recovered contaminants and depleted nanoparticles. Recently, potential disposal strategies for the contaminant of saturated nanoparticles involved stabilization and solidification of waste in the form of bricks and cement.

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