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REVIEW

The role of nanomaterials as effective adsorbents and their applications in wastewater treatment

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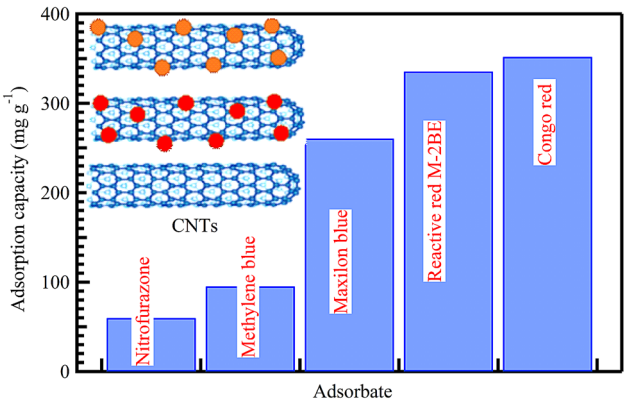
Abstract Nanomaterials have been extensively studied for heavy metal ions and dye removals from wastewater. This article reviews the role of nanomaterials as effective adsorbents for wastewater purification. In recent years, numerous novel nanomaterial adsorbents have been developed for enhancing the efficiency and adsorption capacities of removing contaminants from wastewater. The innovation, forthcoming development, and challenges of cost-effective and environmentally acceptable nanomaterials for water purification are discussed and reviewed in this article. This review concludes that nanomaterials have many unique morphological and structural properties that qualify them to be used as effective adsorbents to solve several environmental problems.

Graphical Abstract



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Introduction

Treatment processes for wastewater as well as drinking water are one of the major prerequisites for developing, growing the economy as well as health maintaining. Therefore, it is crucial to develop and implement innovative technologies for treating water at high efficiencies and low energy consumption. On a global scale, waterborne diseases are still a major cause of death in developing countries where access to safe drinking water is often limited. With the introduction of disinfection processes (mainly using chlorine), waterborne infectious diseases have been significantly reduced. However, it is known that the application of disinfection agents such as chlorine, chlorine dioxide or ozone is associated with the formation of disinfection by-products (e.g., trihalomethanes, halophenols, ketones, aldehydes) with a high mutagenic and/or carcinogenic potential [1–4]. Chlorination also affects the taste and odor of drinking water. Therefore, the reduction/elimination of toxic by-products formation resulting from disinfection processes is necessary. Further, many toxic materials such as heavy metal ions and azo dyes in wastewaters cannot be completely removed during wastewater treatment processes that are commonly used on a large scale [5–10]. Thus, these toxic materials are permanently introduced into rivers and streams by wastewater discharges, while diffuse sources such as runoff from agricultural fields are possible, but frequently contribute to a much smaller extent to the overall pollution [7, 11, 12].

The most common toxic materials in wastewaters responsible for particular problems are heavy metal ions and azo dyes [13–18]. Despite the fact that the human body needs low doses of metal ions such as for example Zn(II) ions, their excess may cause eminent health problems such as depression, lethargy, neurological signs and increased thirst. In addition, exposure to metal ions, often toxic, can cause health problems such as liver or kidney damage, Wilson disease, insomnia, cancer, diarrhea, nausea, vomiting, dermatitis, chronic asthma, coughing and headaches [19–21].

Removal of toxic materials from wastewater is necessary for health and environmental protection. For this purpose, conventional methods such as reduction, precipitation, adsorption, oxidation and ion exchange are commonly used. However, among them the adsorption process is the most suitable method because of its high efficiency and economic consideration [22–26]. Such adsorbents such as activated carbon (AC), zeolites, biomaterials, polymers, have been used extensively for wastewater treatment [22–31]. However, the adsorption efficiency of these materials is relatively low [26]. Therefore, it has become essential to find more efficient adsorbents.

Recently, there has been a remarkable potential for the remediation of environmental problems as a result of nanoscience and nanotechnology developments [32, 33]. In comparison to conventional materials, the nanostructured adsorbents, mainly due to the exceptionally high surface area, show much higher efficiencies and faster adsorption rates in water treatment [34–36]. A variety of efficient, low-cost and eco-friendly nanomaterials with unique functionalities have been proposed for potential applications in detoxification of industrial effluents, groundwater, surface water and drinking water [34, 37]. An ideal adsorbent for wastewater treatment purposes should satisfy the following criteria [26]: (1) should be environmentally benign; (2) should demonstrate a high sorption capacity and high selectivity especially to the pollutants occurring in water at low concentration; (3) the adsorbed pollutants can be easily removed from its surface, and (4) should be recyclable. In recent years, many studies have proved that the nanomaterials can satisfy most of these requirements [38–40].

It was demonstrated that the nanomaterials such as carbon nanotubes (CNTs), graphene, ferric oxide (Fe_3O_4), manganese oxide (MnO_2), titanium oxide (TiO_2), magnesium oxide (MgO) and zinc oxide (ZnO) may play an important role in the waste water treatment processes [41–49]. The nanomaterials may be successfully used as efficient, cost-effective and environmentally friendly adsorbents for the removal of various toxic substrates from wastewater such as heavy metals, azo dyes, etc. [2, 5–9, 34, 37–46, 49–51].

Adsorption phenomenon

The adsorption process is a surface phenomenon in which the adsorbate is accumulated on the adsorbent surface. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited on the solid surface [46–48]. In case of bulk materials, all the bonding requirements (ionic, covalent, or metallic) of the material constituent atoms are filled by other atoms in the material. However, the atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms, therefore they can attract adsorbates [48–52]. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (an adsorbate bound to the surface by weak van der Waals forces), chemisorption (an adsorbate tethered through covalent bonding [53] or due to electrostatic attraction [26]).

The equilibrium stage of adsorption between the solution and adsorbent is attained (where the adsorption of solute from the bulk onto the adsorbent is minimum) and the adsorption amount (q_e, mmol g^{-1}) of the molecules at the equilibrium could be calculated according to the following equation [48, 53]:

$$q_e = \frac{V(C_0 - C_e)}{m}, \quad (1)$$

where V is the solution volume (L); m is the mass of adsorbents (g); and C_0 and C_e are the initial and equilibrium adsorbate concentrations, respectively. In addition, adsorption maybe defined as the mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions [54]. It is worth pointing out that the large surface area of adsorbent allows achieving a high adsorption capacity and surface reactivity [54].

Adsorption isotherm models

The adsorption isotherm models present of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature [52, 54–56]. There are many isotherm models such as: Langmuir and Freundlich, Temkin, Harkin–Jura and Dubinin–Radushkevich. Among of them, Langmuir and Freundlich models are commonly used for the description of adsorption data [48, 55–57].

The Langmuir equation is expressed as [48, 56]:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}K_l} + \left(\frac{1}{Q_{max}}\right)C_e, \quad (2)$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}), and Q_{max} and K_l are Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent toward adsorbate, respectively.

On the other hand, Freundlich isotherm describes heterogeneous surface adsorption. The energy distribution for adsorptive sites (in Freundlich isotherm) follows an exponential type function which is close to the real situation. The rate of adsorption/desorption varies with the strength of the energy at the adsorptive sites. The Freundlich equation is expressed as [48]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e, \quad (3)$$

where k (mg g^{-1}) and $1/n$ are the constant characteristics of the system [56, 58]. An example of the linear relation of Freundlich and Langmuir isotherms is displayed in Fig. 1 for MB adsorption on Co_3O_4/SiO_2 nanocomposites [57].

Kinetic models

An applicable kinetic model is necessary to analyze the rate and the mechanism of adsorption processes (e.g., mass transfer and chemical reaction). Several kinetic models such as simple-first-order, pseudo-first-order, pseudo-second-order and intra-particle diffusion models [48, 53, 57, 59, 60] have been applied to disclose the adsorbate-adsorption phenomenon.

The simple-first-order and pseudo-first-order rate equations are given by Eqs. (4) and (5), respectively [48, 56, 57]:

$$\log q_t = \frac{k_s}{2.303}t + \log q_e \quad (4)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t, \quad (5)$$

where q_e and q_t are the amounts of adsorbate (mg g^{-1}) at equilibrium and at time t, respectively. k_s and k_1 are the rate constants (h^{-1}).

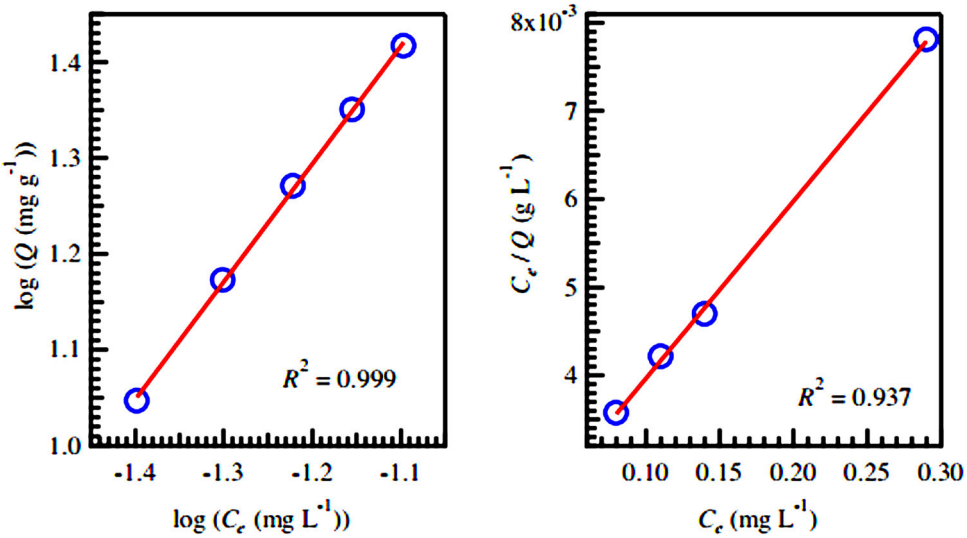

Fig. 1 Freundlich (*left*) and Langmuir (*right*) isotherms for MB adsorption on Co_3O_4/SiO_2 nanocomposite, The *solid lines* are the linear fits (copied form Ref. [57])

On the other hand, the pseudo-second-order rate formula is as following [48, 56, 57, 60]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (6)$$

where k_2 is the equilibrium rate constant (g mg^{-1} h^{-1}). The slopes and intercepts t/q versus t plot are used to calculate k_2.

In addition, intraparticle diffusion model which can be described as follows [56, 57]:

$$q_t = k_p t^{1/2} + C, \quad (7)$$

where C is the intercept and k_p is the intra-particle-diffusion rate constant (mg g^{-1} $h^{1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$.

Development of nanomaterials as adsorbent for wastewater treatment

The most widely studied nanomaterials for wastewater treatment are AC, CNTs, graphene, Fe_3O_4, MnO_2, Co_3O_4, TiO_2, MgO and ZnO, etc. [22, 43, 46, 52, 57, 61–68]. They may be prepared in different morphological forms such as particles, tubes and sheets [26].

Hereby we review recent advances in heavy metals and dye removal from wastewater using nanomaterials as effective adsorbents and perspectives in this area of research.

Carbon-based nanomaterials

Different types of carbon-based nanomaterials have been used widely for heavy metals and dye removal in recent decades due to their nontoxicity, abundance, ease of preparation, high surface area and porosity, stable structure and high sorption capacities [38, 41, 52, 69–71].

Activated carbon (AC)

AC was used initially as sorbents; however, due to the difficulties associated with heavy metals and dye removal at ppb levels, CNTs, fullerenes, and graphene were used as nanosorbents to overcome this difficulty. AC typically has high porosity, high surface area, and can be prepared from readily available carbonaceous precursors such as coal, wood, coconut shells and agricultural wastes [72–75]. AC is extensively used for the removal of inorganic and organic pollutants from effluent streams and in water treatment [22]. In addition, it possesses a significantly weak acidic ion exchange character, enabling it to remove metal contaminants and to adsorb pollutants from wastewater [22]. The sorption of pentavalent arsenic on granular activated carbon (GAC) was experimentally studied [75]. AC prepared from coconut tree sawdust was used as an adsorbent for the removal of Cr(VI) from aqueous solution [76]. Sorption and stability of mercury on AC for emission control were also reported [72]. Powdered activated carbon (PAC) prepared from *Eucalyptus camaldulensis* Dehn bark was studied and showed a sorption capacities (q_m) at 60 °C, of 0.85 and 0.89 mmol g^{-1} for Cu(II) and Pb(II), respectively [73]. A novel sodium polyacrylate grafted AC was produced using gamma radiation to increase the number of functional groups on the surface which increased the efficiency of metal ions sorption by AC [74]. Their high sorption ability and low price make AC promising materials for heavy metals and dye removal.

Carbon nanotubes (CNTs)

CNTs (Fig. 2), which were first developed by Iijima [77], have a unique structural, electronic, optoelectronic, and semiconductor, as well as mechanical, chemical and physical properties [22, 23]. CNTs have been applied widely to remove heavy metals and dyes in wastewater treatment [6, 7, 9, 11–16, 41, 71, 78–82].

CNTs are considered to be one of the most promising adsorbents for wastewater treatment because of their large adsorption capacity for synthetic dyes [15]. Multi-walled carbon nanotubes (MWCNTs) have been shown to surpass cadmium hydroxide nanowire-loaded AC ($Cd(OH)_2$–NW–AC) with respect to their efficient removal of safranin O (SO) from wastewater [83]. However, only few studies were reported on the application of CNTs for dye removal from aqueous solution [41, 69, 76, 84–86]. Moreover, CNTs were typically used directly without further treatment [41, 69, 85]. Therefore, CNT functionalization has been initiated to introduce various functional groups that provide new adsorption sites [15]. Among such modifications, oxidation is an easy method for introducing hydroxyl and carbonyl groups to the sidewalls of CNTs. Oxidized MWCNTs were found to be effective in the removal of methylene red (MR) and methylene blue (MB) from aqueous solutions [87, 88]. Yao et al. [89] reported an adsorption capacity of 41.63 mg g^{-1} at 333 K for the removal of MB onto CNTs. Shahryari et al. [90] performed the same batch of experiments on MWCNTs having a higher surface area of 280 m^2 g^{-1} as compared to that of CNTs (160 m^2 g^{-1}) used by Yao et al. and reported a higher MB adsorption of 132.6 mg g^{-1} at 310 K. In addition, cellulose grafted with soy protein isolate/hydroxyapatite rod-like nanocrystals showed a high MB adsorption capacity of 454 mg g^{-1} [91].

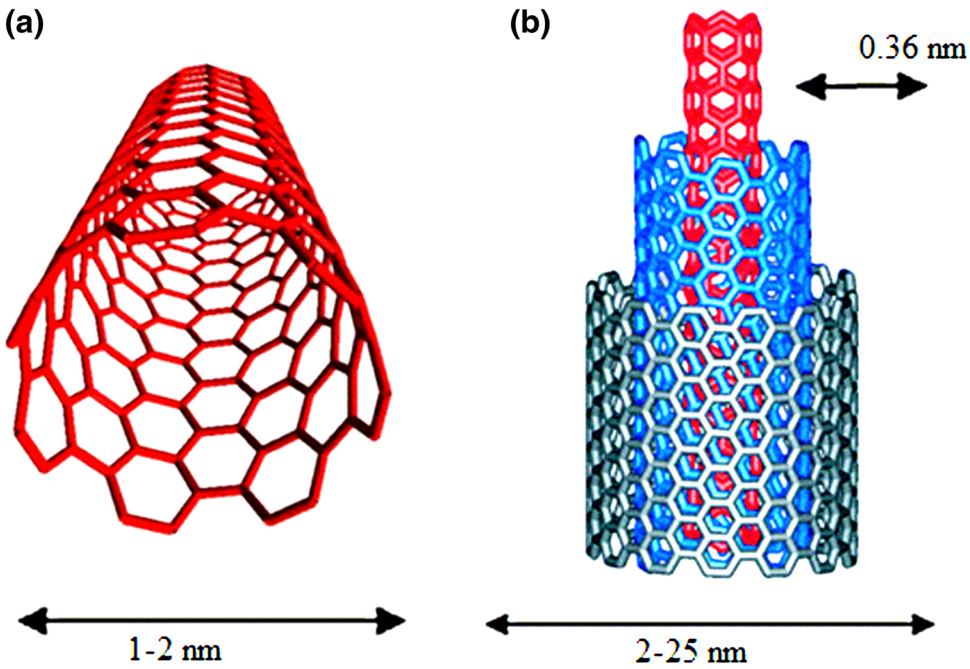

Fig. 2 Schematics of SWCNTs (**a**) and MWCNTs (**b**) (copied form Ref. [22])

The adsorption capacity also depends on the experimental conditions, nature and type of adsorbent. The comparative adsorption of anionic orange II (OII) from aqueous solution using MWNTs and carbon nanofibers (CNF) as adsorbents was studied in batch experiments by Rodríguez et al. [75]. They found that the adsorption of II (OII) onto MWCNTs was slightly higher than CNF (the adsorption capacity in case of MWCNTs was 77.83 mg g^{-1}, while it was 66.12 mg g^{-1} in case of CNF [75]). In addition, MWCNTs showed higher adsorption than PAC for removal of reactive red M-2BE (RRM). The maximum amounts of RRM uptake were 335.7 and 260.7 mg g^{-1} for MWCNTs and PAC, respectively [76]. The higher adsorption capacity can be explained on the basis of higher average pore diameter of MWCNTs, which was 7.62 nm as compared to 3.52 nm of PAC. It seems that dye molecules can easily be diffused from the surface to pores of MWCNTs due to larger pore size.

CNT-impregnated chitosan hydrogel beads (CSBs) have been developed for the removal of congo red (CR). CSBs demonstrated a higher maximum adsorption capacity (450.4 mg g^{-1}) than chitosan without impregnation (200 mg g^{-1}) based on Langmuir adsorption modeling [72]. A new generation of CSBs has been prepared by sodium dodecyl sulfate and MWCNTs to improve the mechanical properties [73]. The new CSBs have demonstrated a high maximum adsorption capacity for CR of 375.94 mg g^{-1} [73]. Compared to MWCNTs and hybrid CNTs (HCNTs), single wall carbon nanotubes (SWCNTs) can demonstrate better adsorption properties for organic contaminants because of their higher specific surface area. SWCNTs are more efficient for removing benzene and toluene and have shown maximum adsorption capacities of 9.98 and 9.96 mg g^{-1}, respectively [74]. A maximum adsorption capacity of 496 mg g^{-1} was achieved when a reactive blue 29 (RB29) has been removed from aqueous solution by using SWCNTs [92].

On the other hand, CNTs showed high sorption efficiency of divalent metal ions. The advantages and drawbacks of Co(II) and Cu(II) removal using AC, CNTs, and carbon-encapsulated magnetic nanoparticles were reported by Pyrzyńska and Bystrzejewski [80]. The results showed that the carbon nanomaterials have significantly higher sorption efficiency compared to commercial AC. Meanwhile, Stafiej and Pyrzynska [79] found out that the solution conditions such as pH and metal ion concentrations could affect the adsorption characteristics of CNTs. Oxidized CNTs have also shown exceptionally high sorption capacity and efficiency for Pb(II), Cd(II) and Cr(VI) from water [78, 93, 94]. CNTs were also reported as good adsorbents for multi-component sorption of metal ions [71]. The sorption mechanisms were reported to be governed by the surface features, ion exchange process and electrochemical potential [95]. The latter plays a significant role in multi-component sorption where redox reactions, not only on the adsorbent surface but also among the different adsorbates, are likely to occur. MWCNTs were found to adsorb ^{243}Am with extraordinarily high efficiency by forming very stable complexes [96]. The sorption characteristic of Pb(II) from aqueous solution was studied using oxidized MWCNTs [81]. The reported results showed a slope of V/m and intercept of C_o V/m for the same initial concentration of Pb(II) and the same content of oxidized MWCNTs for each experimental data [81].

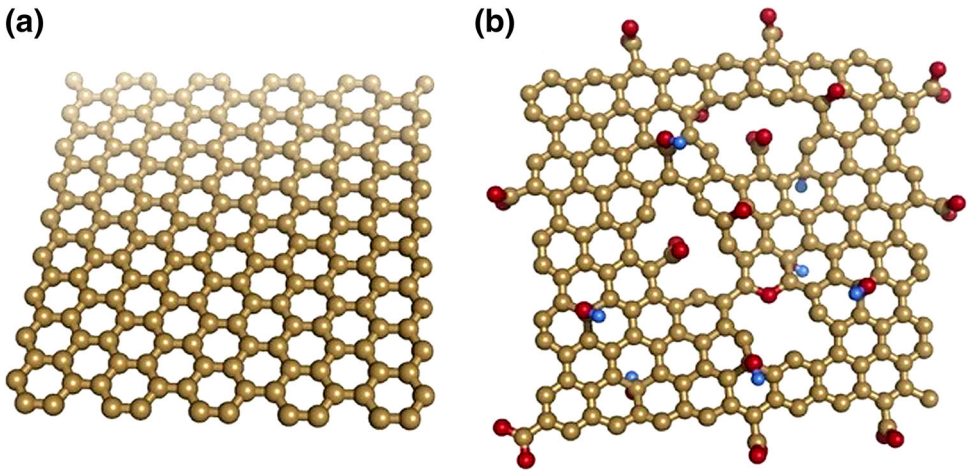

Fig. 3 Schematics structure of graphene (**a**) and graphene oxide (**b**) (copied form Ref. [57])

Oxidized MWCNTs were also applied to adsorb Ni(II) from aqueous solution [41]. The predominant mechanism of Ni(II) sorption onto MWCNTs was reported to be ion exchanged at low pH values and by strong surface complexation at high pH values [41]. It was also reported that oxidized MWCNTs can be potentially promising materials for the pre-concentration and solidification of heavy metal ions [70].

The sorption and kinetic desorption of $^{152+154}$Eu(III) on MWCNTs have also been studied [97]. It was found that MWCNTs were a suitable material for pre-concentration of lanthanides from large volumes of aqueous solutions in radioactive nuclear waste management with the strong surface complexation and/or chemisorption mechanism [97]. With the aid of FITEQL 3.2, Chen et al. [82] characterized the surface properties of MWCNTs at different ionic strengths and pH values, and modeled Sr(II) and Eu(III) sorption onto oxidized MWCNTs by applying surface complexation model, and found that the diffuse layer model (DLM) fit the experimental data very well. The removal of divalent metal ions [Cd(II), Cu(II), Ni(II), Pb(II), Zn(II)] from aqueous solution using various kinds of CNTs have been studied [98]. It has been proved that the CNTs are very promising adsorbents for environmental protection applications because of their superior sorption capacity and in the same time ability to effective desorption of divalent metal ions [98].

It is worth noting that the CNTs can be potentially produced on a large scale using different methods such as chemical vapor deposition to reduce the cost of production and increase their future use in environmental protection applications.

Graphene

Graphene (Fig. 3), which can be used as nanosorbents, typically consists of one or more atomic-layered carbon

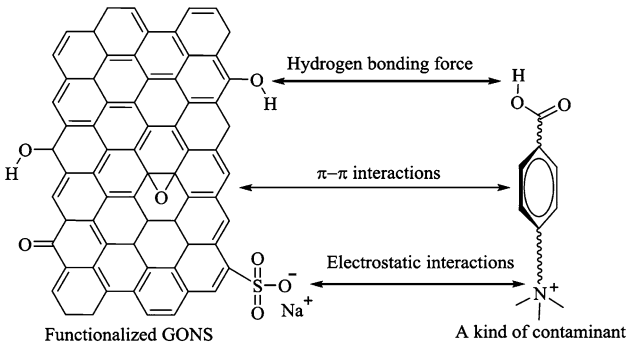

Fig. 4 Schematic representation of possible interactions between GONSs and pollutants (copied form Ref. [110])

atoms, and possesses a unique two-dimensional structure and excellent mechanical, thermal and electrical properties [99, 100]. Using Van der Waals' forces and π–π stacking interactions, the adsorption of dyes on few-layered graphene nanosheets can be realized (see Fig. 4). For modify the chemical and physical properties and improve the manufacturing of reduced graphene oxide (rGONSs) graphene oxide nanosheets (GONSs), it can be first incorporated into composite materials. Both rGONSs layers and single GONSs layers have high aspect ratios and large π-electronic surfaces that provide strong intermolecular forces among adsorbates [101]. Due to the opened-up layer structure, rGONSs exhibit markedly faster adsorption kinetics than CNTs [63, 102]. Among different carbon-based materials (coal base AC (HD4000), SWCNTs and MWCNTs), rGONSs exhibited better adsorption capacities for two synthetic organic compounds (SOCs; phenanthrene and biphenyl) in aqueous solutions [52]. More importantly, rGONSs are much cheaper than SWCNTs [103]. rGONSs have already been used as adsorbents for the removal of cationic red X-GRL [104], MB [66, 105], methyl orange (MO) [106], CR [107] and other organic materials from aqueous solutions. The maximum adsorption capacities of

p-toluenesulfonic acid (*p*-TA), 1-naphthalenesulfonic acid (1-NA) and MB on GNS reach up to 1430, 1460 and 1520 mg g^{-1} at 303 K, respectively, which are the highest among all nanomaterials studied in this field to date [108]. The observed adsorption capacities for the adsorption of three types of pesticides [chlorpyrifos (CP), endosulfan (ES), and malathion (ML)] onto GONSs and rGONSs from water are as high as 1200, 1100 and 800 mg g^{-1}, respectively, and GONSs and rGONSs were unprecedented substrates for these adsorption technologies [109].

The few-layered GONSs through the modified Hummers' method have been synthesized [111]. These rGONSs can be used as sorbents for the removal of Cd(II) and Co(II) ions from aqueous solution [111]. It was reported that heavy metal ions sorption on nanosheets is dependent on pH and ionic strength [111]. The abundant oxygen-containing functional groups on the surfaces of graphene oxide nanosheets were reported to play an important role on sorption [111].

Magnetite–graphene composite adsorbent with a particle size of $\sim$10 nm was reported to give a high binding capacity for As(III) and As(V) [112]. The high binding capacity was due to the increased adsorption sites in the graphene composite [112]. The strong functional groups on the graphene oxide (GO) surface make it a potential adsorbent for metal ion complexation through both electrostatic and coordinate approaches. Generally, GO showed high adsorption capacity for cationic metals. rGONSs can be used for adsorption of both cationic and anionic metals. After modification of GO with organics or metal oxides, its composites can also be used for anionic metal removal due to functionalization. Cu(II)–GO interaction in aqueous solution showed that Cu(II) causes GO sheets to be folded and form large aggregates [113]. The coordination between Cu(II) and oxygen atoms on GO was the primary driving force. GO has a Cu(II) adsorption capacity of 46.6 mg g^{-1}, which is higher than that of CNTs (28.5 mg g^{-1}) and AC (4–5 mg g^{-1}) [113].

The removal of Cd(II) [71, 111], Co(II) [111], Pb(II) [71, 114], and U(VI) [115] ions from aqueous solutions have been studied using few-layered GONSs. It was found that the abundant oxygen-containing functional groups on GONSs surfaces play an important role in metal sorption, which was in agreement with the results of Zhao et al. [111]. It was also reported that Cd(II) and Co(II) sorption on GONSs is strongly dependent on pH and weakly dependent on ionic strength. The presence of humic acid reduced Cd(II) and Co(II) sorption on GONSs at pH < 8. The maximum sorption capacities of Cd(II) and Co(II) on GONSs at pH 6.0 and 303 K were about 106.3 and 68.2 mg g^{-1}, respectively. For Pb(II), the maximum adsorption capacities were about 842, 1150, and 1850 mg g^{-1} at 293, 313, and 333 K, respectively [114], but sorption capacity of U(VI) at pH 5.0, 293 K was 97.5 mg g^{-1} [115].

Modification of GO with organic materials can change the surface functional groups for better adsorption of various metal ion species. A modified GO with thiol (SH) groups by diazonium chemistry was reported to adsorb sixfold higher concentration of Hg(II)ions than GO and AC [116]. When *N*-(trimethoxysilylpropyl) ethylenediaminetriacetic acid (EDTA-silane) was used to obtain a chelating GO for Pb(II) removal, the adsorption was fast and completed within 20 min, with an adsorption capacity of 479 mg g^{-1} at pH 6.8 [117]. Compared to AC and CNTs, GO and GNs present stronger adsorption for many water pollutants.

Metal oxide-based nanomaterials

Metal or metal oxide-based nanomaterials are other inorganic nanomaterials, which are widely used to remove heavy metal ions and dyes. Nanosized metals or metal oxides, including Fe_3O_4 [118], MnO_2 [62], TiO_2 [43], MgO [119], CdO [120] and ZnO [68], provide high surface area and specific affinity. Metal oxides possess minimal environmental impact, low solubility, and are not involved in secondary pollution formation; they have also been adopted as sorbents to remove heavy metals and dyes.

Iron is one of the most widespread elements in the earth. The facileness of resource and ease of synthesis render nanosized ferric oxides to be low-cost adsorbents for toxic metal sorption. Since elemental iron is environmentally friendly, nanosized ferric oxides can be pumped directly to contaminated sites with negligible risks of secondary contamination [121, 122]. Many reports discussed the influence of different parameters on the removal of metal ions by Fe_3O_4 magnetic nanoparticles [47, 123]. For example, the adsorption efficiency of Ni(II), Cu(II), Cd(II) and Cr(VI) ions by Fe_3O_4 nanoparticles was strongly dependent on pH, temperature, amount of the adsorbent and the incubation time [124–127]. Further, a higher removal efficiency of these metal ions at a 3.5 mg mL^{-1} dose of nanoadsorbent with an optimum pH of 4 was obtained. In comparison to bare Fe_3O_4 nanoparticles, surface functionalized Fe_3O_4 nanoparticles have been extensively used for the removal of toxic metal ions [124–127]. Singh et al. [46] reported the removal of toxic metal ions from wastewater using carboxyl-, amine- and thiol-functionalized Fe_3O_4 nanoparticles (succinic acid, ethylenediamine and 2,3-dimercaptosuccinic acid, respectively). Depending upon the surface functionality (COOH, NH_2 or SH), these magnetic nanoadsorbents capture metal ions either by forming chelate complexes, by ion exchange process or else through electrostatic interaction. It has been reported that these surface-engineered Fe_3O_4 nanoparticles have a strong affinity for the simultaneous adsorption of

Table 1 Comparison of different nanomaterials of metal ions and dye removal in view of adsorption capacities and removal rates

Nanomaterials	Adsorbent	Adsorbate	Adsorption capacity (mg g^{-1})	Rate constants (k_1, h^{-1})	References
Carbon-based nanomaterials	AC	Reactive red M-2BE	260.7	1.503	[76]
	PAC	Nitrofurazone	50.8	0.1129	[128]
	SWCNTs	Reactive blue 29 (RB29)	496	–	[92]
		Acid red 18	166.67	21.12	[129]
		Reactive red 120	426.49	–	[130]
		Cr(VI)	1.26	–	[131]
	MWCNTs	Reactive red M-2BE	335.7	2.860	[76]
		Nitrofurazone	59.9	0.2082	[128]
		MB	95.3	–	[132]
		CR	352.1	3.18	[133]
		Maxilon blue	260.7	–	[134]
		Cr(VI)	2.35	0.42	[131]
	Oxidized MWCNTs	Bromothymol blue (BTB)	55	0.042	[88]
	Diethylenetriamine-MWCNTs	Pb(II)	58.26	–	[135]
		Cd(II)	31.45	–	
	GO	MB	714	–	[66]
	rGONSs	Chlorpyrifos	1200	–	[109]
		Endosulfan	1100	–	[109]
		Malathion	800	–	[109]
	Graphene	Cd(II)	106.3	–	[111]
		Co(II)	68.2	–	
	GONSs	Pb(II)	842	–	[114]
	GNS	Ni(II)	3.00	0.0576	[136]
Metal oxide-based nanomaterials	Co_3O_4/SiO_2 nanocomposite	MB	53.87	1.821	[57]
	TiO_2	Cd(II)	16.69	2.244[a]	[67]
		Cu(II)	5.18	0.927[a]	
		MO	85.39	–	
	TiO_2 nanotubes/CNT	Cu(II)	83–124	–	[137]
		Pb(II)	192–588	–	
	Fe_3O_4 magnetic nanoparticles	Cu(II)	61.07	–	[124]
	Modifying Fe_3O_4 microspheres	Hg(II)	37.4 (μmol g^{-1})	–	[126]
	Ethylenediamine-functionalized nano-Fe_3O_4	Cr(VI)	136.98	47.172[a]	[51]
	MgO	Reactive blue 19	166.7	4.2	[138]
		Reactive red 198	123.5	5.4	
	δ-MnO_2	Ni(II)	30.63	0.108	[136]
Carbon and metal oxide hybrid nanomaterials	Graphene oxide–Fe_3O_4 hybrid composite	MB	167.2	–	[65]
		Neutral Red (NR)	171.3	–	
	GNS/δ-MnO_2 composite	Ni(II)	46.55	0.0432	[136]
	RGO/TiO_2	MB	467.6	3.1278	[139]
	Al_2O_3/MWCNTs	Trichloroethylene	19.84	1.1048[a]	[140]
		Cd(II)	27.21	5.7644[a]	
	MnO_2/CNTs	Pb(II)	78.74	0.816	[64]

Table 1 continued

Nanomaterials	Adsorbent	Adsorbate	Adsorption capacity (mg g^{-1})	Rate constants (k_1, h^{-1})	References
	Ni@C composite nanostructures	Pb(II)	21.45	–	[141]
		Cu(II)	14.3	–	
		Cd(II)	6.43	–	
Polymer-based nanomaterials	Polyvinyl alcohol	BTB	276.2	4.266	[56]
		MB	123.3	4.854	
	Polyaniline (PAn)/rice husk nanocomposite	Zn(II)	24.3	–	[142]
	Polypyrrole/Fe_3O_4 magnetic nanocomposite	Cr(VI)	169.4	11.28	[143]
	Polyacrylamide/$Ni_{0.02}Zn_{0.98}O$ nanocomposite	Malachite green (MG)	–	6.12	[144]
		Rhodamine B (RB)	–	8.88	

[a] (k_2, g mg^{-1} h^{-1})

Cr(III), Co(II), Ni(II), Cu(II), Cd(II), Pb(II) and As^{3+} from wastewater [45, 47, 48, 51, 68, 118, 123–126]. In addition, the adsorption process was found to be highly dependent on the amount, surface functionality and pH of the medium, which caused these nanoparticles to selectively adsorb metal ions [125–127]. An almost 100% removal rate of Cr(III), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) ions from water was reported at pH > 8 by these functionalized nanoparticles [124–127].

The removal efficiency of As(III) by carboxyl, amine and thiol-functionalized Fe_3O_4 was found to be 91, 95 and 97%, respectively, at pH 8 [43]. The adsorption–desorption behavior of metal ions on amine-functionalized Fe_3O_4 showed an 85% desorption ratio in the first cycle, which indicates their excellent regeneration capacity for their further use. It was reported that ethylenediaminetetraacetic acid-functionalized (EDTA) Fe_3O_4 nanomagnetic chelators (NMCs), show a strong tendency towards the adsorption of Cr(III), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) from wastewater [67].

Ozmen et al. [124] reported the use of 3-aminopropyltriethoxysilane and glutaraldehyde-modified Fe_3O_4 nanoparticles for the removal of Cu(II) from the water. Ge et al. [125] have studied the effective removal of heavy metal ions [Cd(II), Zn(II), Pb(II)and Cu(II)] from an aqueous solution using a polymer-modified magnetic nanoparticles. They reported a higher removal efficiency of metal ions in acidic pH 5.5 and a lower one in alkaline pH. Based on their results, they have suggested that the polymer-modified Fe_3O_4 was more efficient than bare Fe_3O_4. The reported studies suggest that the functional groups present on the surface of magnetic nanoparticles provide a large number of active sites as well as aqueous stability, which is necessary for the successful adsorption of toxic metals from water. More specifically, these surface-engineered magnetic nanoparticles are highly effective, efficient, economically viable, and reusable magnetic nanoadsorbents for the removal of toxic metal ions from water.

Magnetic nanoparticles were also successfully used as adsorbents of toxic metal ions from different sources. Rhodamine hydrazide modifying Fe_3O_4 microspheres (Fe_3O_4-R6G) has been reported for the selective detection and removal of mercury ions from different environmental samples, such as tap water, lake water and river water [126]. It was found that, 1.5×10^{-7} mol L^{-1} is the detection limit for Hg(II) and that 37.4 μ mol g^{-1} is the maximum adsorption of Hg(II) in 3 mL sample with 5 mg Fe_3O_4-R6G. In addition, the regeneration capability for up to three cycles was studied, and observed that it could reversibly bind with Hg ions repeatedly. Table 1 compares the adsorption capacities and removal rates for some dyes and metal ions on different kinds of nanomaterials. A comparison between the removal of different dyes using MWCNTs and the removal of methylene blue, Cd(II) and Pd(II) by different nanomaterials is displayed in Fig. 5.

Conclusions

The presence of heavy metal ions and dyes in wastewater is a major concern for environment conservation and human health. The removal process of these ions has not reached the optimum conditions. Based on the unique properties of nanomaterials, they have been widely studied for heavy metals and dye removals from wastewater due to their high surface area, low particles size which leads to high numbers of adsorption active centers. Adsorption processes

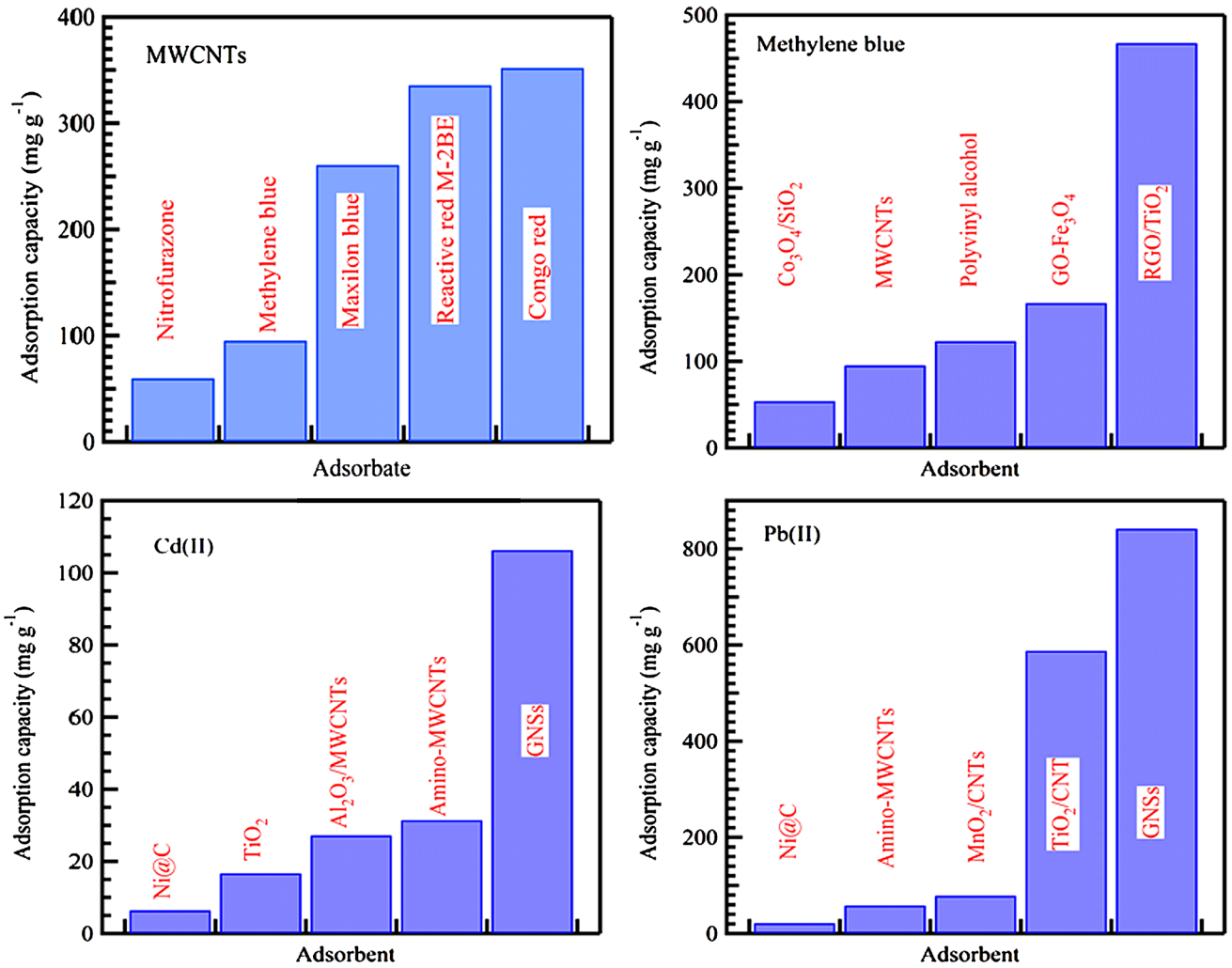

Fig. 5 A comparison of removal of different dyes by MWCNTs; and removal of methylene blue, Cd(II) and Pd(II) by different nanomaterials

using nanomaterials are highly effective, may be easily performed and employed for the removal of organic and inorganic pollutants. It seems very plausible that these types of adsorbents may find wide commercial application in wastewater treatment in the near future.

This article reviews the past, present and future approaches for using nanomaterials as effective adsorbents for the removal of heavy metal ions and dyes from wastewater. The recent trends of using nanomaterials as cost-effective and environmentally acceptable adsorbents for water purification were discussed in this article. This review highlights the promising future applications of nanomaterials as adsorbents because of their unique morphological and structural properties.

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