

Sorption of divalent metal ions from aqueous solution by oxidized carbon nanotubes and nanocages: A review

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ABSTRACT

This is a scientific review defining the technical feasibility of surface oxidized carbon nanotubes (CNTs) for sorption of divalent metal ions (Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}) from aqueous solution. By conducting the detailed literature review it was found that the adsorption capacities of CNTs remarkably increased after conducting their surface oxidation with NaOCl , HNO_3 and KMnO_4 solutions. Unlike many microporous adsorbents, CNTs possess fibrous shape with high aspect ratio, large accessible external surface area, and well developed mesopores, all contribute to the superior removal capacities of these ions. The adsorption mechanisms is majorly contributed by the chemical interactions between the metal ions and the surface functional groups of the CNTs. Larger the surface area greater will be the number of reducing groups hence more attributal to better CNT sorption performances. Effective process parameters defining CNT characterizations such as surface area pore size distribution, sorbent mass, and acidity at surface, solution properties (ionic strength, pH, initial adsorbate concentration and temperature) and competition for sorption sites by multiple metal ions, governs CNTs performances which are detailed in this review. The recovery of metal ions and the regeneration of CNTs can be achieved using acid elution with little effect on the CNT performance. Often during the production of CNTs a by-product is produced known as Carbon Nano Cages. These are hollow graphitic cages similar to fullerene structures having porous morphologies, but can be multilayered and have irregular shapes unlike the traditional fullerene spheres. The adsorption of divalent ions onto the surface of CNCs works as a function of solution pH. The increase in the adsorption of divalent ions with increasing pH for CNCs suggests that an ion exchange mechanism between the H^+ ions and metal ions occurs at the oxygen-containing functional groups on the surface. Process parameters for CNC characterizations mainly elaborates upon zero point charge, dispersibility of sorbent materials in aqueous media, flowability of aqueous media through sorbent materials, variation of pH and agitation time. The kinetics of metal ion adsorption by the nanocages can be very well described by a pseudo-second-order kinetics model (detailed in this paper). The utilization of CNTs & CNCs for the treatment of water and wastewater containing divalent metal ions is gaining more attention as a simple and effective means of pollution control. Copyright © 2013 VBRI press.

Keywords: Adsorption; oxidized CNTs; isotherms; SWCNTs & MWCNTs; dispersibility; CVD; pH sensibility.



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Introduction

Of all the natural resources, water is unarguably the most essential and precious one. There is growing public concern about the condition of fresh water all around the globe¹. The most wide spread concern of all is the heavy metal ion contamination in waste and drinking water and its potential health hazards on human. Heavy metal ions are listed as high priority contaminants by both the 2007 CERCLA Priority List of Hazardous Substances compiled by the US EPA (ATSDR, 2007) and the European Union Restriction of Hazardous Substances Directive (RoHS, 2003) [1,2]. According to UNESCO report a majority of Indian

population has no access to safe drinking water and that about 66 million people rely on un-safe ground water for consumption [3]. Heavy metals basically includes cadmium (Cd), chromium (Cr), copper (Cu), zinc (Zn) and lead (Pb). The main sources of generation of these toxic pollutants are smelting and refining processes, electroplating industry, municipal and industrial wastes. [4] Accumulation of heavy metal ions in the human body can lead to many debilitating effects and numerous other health problems [5-7]. Hence, the need of the hour is to remove these metal ions from the portable or to be specific the drinking water supply. The various conventional methods that are put into action to remove the metal ions include oxidation, reduction, precipitation, seashells, pyrolysis, membrane filtration, ion exchange and adsorption. Among all methods mentioned above, the most promising one is adsorption. However, the major shortcomings of these methods are low adsorption capacities and removal efficiencies of metal ions. Therefore, researchers carried out investigation for new promising adsorbents.

As a new member of the carbon family, carbon nanotubes (CNTs) have exhibited great potentials as an attractive adsorbent in waste water treatment [8-19]. Carbon nanotubes (CNTs) been discovered by Iijima [20], have unique structural, electronic, optoelectronic, semiconductor, mechanical, chemical and physical properties [21]. CNTs have been gaining increasing recognition for their adsorption capabilities primarily due to their extremely small size, uniform pore distribution and large specific surface area. The comparison of CNTs with other adsorbents suggests that the CNTs have great potential applications in environmental protection [22]. The unique properties of carbon nanotubes would allow water molecules to pass through the interior of the cylinders while chemical (heavy metals) contaminants could not.

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure and have been constructed with length-to-diameter ratio of up to 132,000,000:1 [23]. The three main methods that are currently employed for CNTs synthesis are arc-discharge, laser ablation, and chemical vapor deposition (CVD) [24]. The CNTs from the arc discharge are often covered with amorphous carbon, which contains metallic particles in the case of metal-carbon co-evaporation. The yield of CNTs from arc discharge is not very high, whereas with laser vaporization, the yield is much higher, but the quantities are small. With the laser vaporization method, CNTs are very clean i.e. less covered with amorphous carbon.

Carbon nanocages (CNCs) are hollow graphitic cages similar to fullerene structures, these can be multilayered and have irregular shapes unlike the traditional fullerene spheres, and are often produced as a by-product of carbon nanotube (CNT) growth [25,26]. The unique properties of carbon nanotubes would allow water molecules to pass through the interior of the cylinders while chemical and microbial contaminants could not. CNCs can be synthesised by the supercritical deposition of p-xylene over Co/Mo/MgO catalysts, using a method reported by Li *et al.* [27]. CNTs are divided into two types: (1) single-walled CNTs (SWCNTs) and (2) multi-walled CNTs (MWCNTs) [28,29]. Most single-walled nanotubes (SWNT) have a diameter of close to 1 nanometer, with a tube length that

can be many millions of times longer. The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. Multi-walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphite. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 3.4 Å. The experimental history of SWNTs started two years after the discovery of MWNTs. SWNTs were also first produced by arc discharge using a graphite anode containing a metal catalyst (Fe or Co).

Sorption performance

Isotherm equation

The metal ion sorption equilibrium data are commonly correlated with the Langmuir or the Freundlich equations. Many researchers explained that the metal ion sorption onto CNTs can be described by Langmuir and as well as by Freundlich equations [30-32]. After removing the oxidized CNT sheets from solutions, the amount of adsorbed salt can be obtained using the following equation:

$$q_e = (C_0 - C_e)V/w \quad (1)$$

where q_e is the equilibrium adsorption uptake (mg/g), C_0 is the initial salt concentration (mg/l), C_e is the equilibrium salt concentration (mg/l), V is the volume of the solution (l) and w is the mass of the adsorbent (g).

The Langmuir isotherm was used successfully to characterize the monolayer adsorption process. It can be represented by the following equation:

$$q_e = (q_m K_L C_e)/(1 + K_L C_e) \quad (2)$$

where q_e is the equilibrium adsorption uptake of heavy metal ions, in mg/g, C_e is the equilibrium concentration of heavy metal ions, in mg/l, q_m is the maximum adsorption capacity corresponding to the complete monolayer coverage, in mg/g, and K_L is the Langmuir constant which is related to the energy of adsorption. An essential characteristic of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter:

$$C_e/q_e = 1/(K_L q_m) + C_e/q_m \quad (3)$$

where q_e is the equilibrium adsorption uptake of heavy metal ions, in mg/g, C_e is the equilibrium concentration of heavy metal ions, in mg/l, q_m is the maximum adsorption capacity corresponding to the complete monolayer coverage, in mg/g, and K_L is the Langmuir constant which is related to the energy of adsorption. An essential characteristic of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter:

$$R_L = 1/(1 + K_L C_0) \quad (4)$$

where K_L is the Langmuir constant and C_0 is the highest initial heavy metal ions concentration, in mg/l. The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm is a semi-empirical equation based on the adsorption occurred on heterogeneous surface. It can be presented by the following form:

$$q_e = K_F C_e^n \quad (5)$$

Eq. (5) can be expressed in a linear form:

$$\log q_e = n \log C_e + \log K_F \quad (6)$$

where q_e is the equilibrium adsorption uptake of heavy metal ions, in mg/g, C_e is the equilibrium concentration of heavy metal ions, in mg/l, and K_F and n are the Freundlich parameters related to adsorption capacity and adsorption intensity, respectively.

The values of K_F calculated using the Freundlich model are large indicating that the oxidized CNT sheets have high affinity toward heavy metal ions. The n values are smaller than 1, which indicates favourable adsorption of heavy metal ions onto the oxidized CNT sheets.

Sorption capacity

The order of sorption of various metal ions on CNTs roughly follows the order: $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+}$ (discussed later in this literature). The sorption of metal ions by raw CNTs occurred at a very low rate but significantly increased after oxidising it by HNO_3 , $NaOCl$, and $KMnO_4$ solutions because the tips of CNTs were opened and ruptures took place at the location where defects such as pentagons and heptagons existed after oxidation with oxidizing agents. Therefore, oxidation process improved their dispersivity and increased a large amount of oxygen-containing functional groups like $-COOH$, $-OH$, or $-CO$ on the surface site of CNTs [33]. The various oxidation techniques include soaking, refluxing, heating in various temperatures etc. These functional groups caused a rise in negative charge on carbon surface and the oxygen atoms in functional groups donate single pair of electrons to metal ions, consequently increasing their cation exchange capacity [34]. The metal ion adsorption capacity of CNTs strongly depends upon their surface total acidity including functional groups [35]. The SWCNTs have better performance on the Ni^{2+} and Zn^{2+} sorption than the MWCNTs as it contain more surface total acidic sites than the oxidized MWCNTs. High surface area CNCs have been successfully synthesised using a SCF deposition technique providing better adsorption capacities.

Sorption mechanism

As reported in the literature, different acidic functional groups such as carboxyl, lactones and phenols can be formed by nitric acid oxidation. These functional groups induce negative charge on the CNTs surface and oxygen atoms of these functional groups donate their single pair of electrons to the metal ions, and this consequently increases cation exchange capacity of the CNTs. Protons in the functional groups of the CNTs are exchanged with the metal ions. Chemical interaction (bond) between the metal ions and the surface acidic functional groups of the CNTs is mainly responsible for adsorption (Fig. 1). The main sorption mechanisms of metal ions onto CNTs are

electrostatic attraction, sorption–precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs and the most prevalent of them all is chemical interaction.

The analyzation of the adsorption mechanism of heavy metal ions onto the oxidized CNT sheets was explained using three kinetic models - the pseudo-first-order, the pseudo-second-order and the intraparticle diffusion models. The pseudo-first-order kinetic model [36] can be expressed by:

$$Dq_t/dt = k_1(q_e - q_t) \quad (7)$$

Eq. (1) can be expressed in linear form:

$$\log(q_e - q_t) = \log q_e - (k_1 * t)/2.303 \quad (8)$$

The pseudo-second-order kinetic model [40] is expressed by:

$$Dq_t/dt = k_2(q_e - q_t)^2 \quad (9)$$

Eq. (3) can be expressed in linear form:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (10)$$

where k_1 and k_2 are the adsorption rate constants of first and second order kinetic models, in min^{-1} and l/mg.min , respectively; q_e and q_t , in mg/g, are equilibrium adsorption uptake (at time $t = \infty$) and adsorption uptake (at time t), respectively.

At low initial concentration of heavy metal ions, the correlation coefficients (R^2) of the pseudo-second-order kinetics model are higher than those of the pseudo-first-order kinetics model. Further, the experimental and the theoretical values of q_e are quite consistent. This indicates that the adsorption of heavy metal ions onto the oxidized CNT sheets at low initial concentration are controlled by chemisorption involving valence forces through sharing or exchange electrons between sorbate and sorbent. In chemical adsorption, it is assumed that the adsorption capacity is directly proportional to the number of active sites occupied on the adsorbent surface [37-39]. The experimental data of higher initial concentrations is in accordance with pseudo-first-order kinetics, this indicates that adsorption is a diffusion based process as at higher initial concentration, the mass transfer driving force is larger, and hence this results in higher diffusion rates of heavy metal ions within the pores of CNT sheets. The intraparticle diffusion model is expressed by:

$$q_t = k_p t^{1/2} + C \quad (11)$$

where k_p is the intra-particle diffusion rate constant, in $\text{mg/g h}^{1/2}$, and C , in mg/g, is a constant related to the thickness of the boundary layer.

The use of oxidized CNT sheets as adsorbent eliminates problem of agitation and removal of the CNTs with and from water before and after adsorption process, respectively. Also, the use of oxidized CNT sheets as adsorbent helps in economical waste water treatment without CNT leakage into water (Fig. 1).

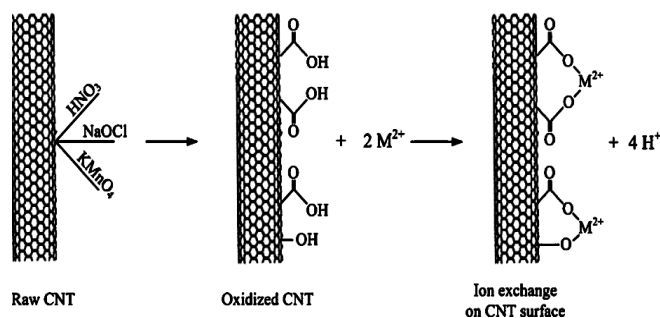


Fig. 1. Schematic diagram showing sorption process on oxidized groups on CNTs where divalent metal gets attached with oxygen and releases protons

Results and discussion

Concerned parameters

CNT & CNC characterization: Characterization of CNTs and CNC play an important key role in influencing adsorption rate of dissolved metal ions. CNT sheets of various morphologies can be synthesized by chemical vapor deposition (CVD) method [43]. Putting our major concern on four kinds of HNO_3 oxidized CNTs i.e. the methane-Ni-CNTs propylene-Ni-CNTs, the xylene-Fe-CNTs, and then the benzene-Fe-CNTs [44]. It can be seen from the **Table 1**; the maximum sorption capacity is of methane-Ni-CNTs which are mainly attributable to their surface defects, which can be easily introduced by functional groups such as carboxyl, lactones & phenols after treatment by HNO_3 solution and thus leading to numerous surface sorption sites. On the other hand, CNCs can be synthesized using a supercritical fluid deposition method [45]. As can be observed (**Fig. 2**), the oxidized CNT sheets exhibit greater heavy metal ions adsorption capacity than the as-synthesized CNT sheets. This can be explained by the fact that the metal ion adsorption capacity of CNTs does not directly related to their specific surface area, pore specific volume and mean pore diameter but strongly depends upon their surface total acidity including functional groups [46]. Various modifications in CNTs structures with specific physicochemical properties can be achieved by chemical treatments to improve CNTs performance for metal ion removal from aqueous solutions.

Certain chemical agents such as HCl , H_2SO_4 , H_2O_2 , O_3 , 30ml HNO_3 +10ml H_2SO_4 , HNO_3 , KMnO_4 and NaOCl have been used to modify the surface property of carbon sorbents for the removal of metal ions from the specific aqueous solution. The Zn^{2+} sorption capacities of different oxidized MWCNTs follow the order: NaOCl , KMnO_4 , HNO_3 , 30ml HNO_3 +10ml H_2SO_4 , O_3 , H_2O_2 , H_2SO_4 , and HCl [47,48,49,50]. The modification of CNTs with strong oxidizing agents such as KMnO_4 , HNO_3 and H_2O_2 solutions suited more efficient for the removal of Cd^{2+} from aqueous solution [47]. The CNTs (KMnO_4) have the best performance on Cd^{2+} sorption, followed by the CNTs(HNO_3), and then the CNTs(H_2O_2). As mentioned in the literature, the metal ion adsorption capacity of CNTs increases with a rise in the amount of surface total acidity (including carboxyls, lactones and phenols) present on the surface site of CNTs. This clearly concludes that the

sorption of metal ions onto CNTs is chemisorption process rather than physisorption process [51,52]. The oxidized CNTs have more surface total basicities, which are responsible for sorption of anions from aqueous solution, than the raw CNTs [53,54].

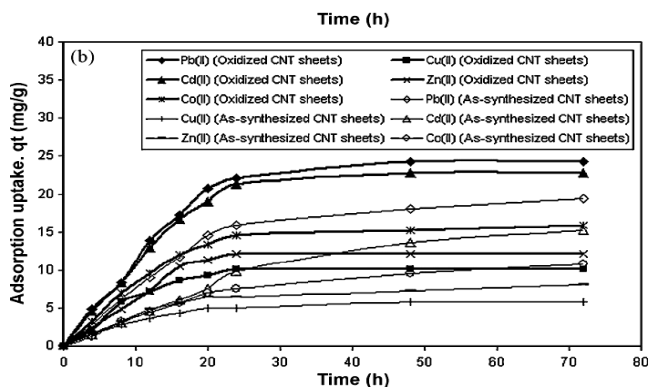


Fig. 2. Graph showing time dependence of adsorption uptake on various types of functionalized CNTs with respect to the raw CNTs.

The surface charge depends on pH of the surrounding electrolyte. There is a pH value, called 'point of zero charge' (PZC), at which the net surface charge is zero [55]. The removal of divalent ions increased with solution pH in the range 1–8, fluctuated little and reached maximum in the range 8–11, and steeply decreased at a pH of 12 [56,57]. A favorable pH range 8–11 can be thus noted for sorption of Ni^{2+} and Zn^{2+} from aqueous solution [58,59]. The effect of solution pH can be explained by considering the surface charge of the CNT and the degree of ionization and speciation of the sorbates. It is known that divalent metal ions (M^{2+}) can be present in deionized water in the forms of M^{2+} , $\text{M}(\text{OH})^{+1}$, $\text{M}(\text{OH})_2^0$, $\text{M}(\text{OH})_3^{-1}$, etc. At a $\text{pH} \leq 8$, the predominant nickel species is always M^{2+} and the M^{2+} removal is mainly accomplished by sorption process. Thus, the fact that more M^{2+} sorption took place at a higher pH could be attributed to a decrease in competition between H^+ and M^{2+} at the same sorption site of CNTs. Furthermore, the surface of CNTs is more negatively charged at a higher pH, which causes a more electrostatic attraction of M^{2+} . In the pH range 8–11, the maximum M^{2+} removal was observed, which might be explained by the formation of hydrolysis ion species [$\text{M}(\text{OH})^{+1}$ and $\text{M}(\text{OH})_2^0$]. Low solubilities of these species contribute in part to maximum M^{2+} removal. At a pH of 12, the predominant nickel species is $\text{M}(\text{OH})_3^{-1}$. Thus, the decrease in M^{2+} removal taking place at a pH of 12 could be attributed in part to a rise in competition between OH^{-1} and $\text{M}(\text{OH})_3^{-1}$ at the same sorption site of CNTs. Additionally, the negatively charged CNT surface may cause an electrostatic repulsion of $\text{M}(\text{OH})_3^{-1}$. The pH_{pzc} of CNCs was close to neutral, i.e. 7.02 and 7.49 respectively. The pH_{pzc} value is dependent on the acid–base relationship of the material is the solution pH where there will be a neutral charge on oxygenated sites which result in a net neutral charge on the surface of the adsorbent [60]. The lower pH_{pzc} value for the CNCs suggests that the material will be a slightly more effective adsorbent at lower pH values, due to the higher density of acid sites.

Table 1. Comparison of amount of different adsorbed divalent metal ions on different types on CNTs.

Sorbents	q_m					Conditions	Ref.
	Cd^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}		
CNTs				1.00		pH: 7.0, T: room, S/L: 0.05/100, $C_0 = 2-14$ mg/L	[40]
CNTs (HNO ₃)				49.95			
SWCNTs			9.22			pH: 7.0, T: 25, S/L: 0.05/100	[41]
SWCNTs (NaOCl)			47.85				
MWCNTs			7.53				
MWCNTs (NaOCl)			38.46				
CNTs (HNO ₃)a						pH: 5.0, T: room, S/L: 0.02/100, $C_0 = 10-60$ mg/L	[42]
Xylene-Fe				14.8			
Benzene-Fe				11.2			
Propylene-Ni				59.8			
Methane-Ni				82.6			

The adsorption of Pb^{2+} ions onto the surface of CNCs works as a function of solution pH. The increase in the adsorption of Pb^{2+} ions with increasing pH for CNC samples suggests that an ion exchange mechanism between the H^+ ions and metal ions occurs at the oxygen-containing functional groups on the surface of the adsorbent. Below a pH of approximately 6, Pb^{2+} will exist as free ions in solution, making their interaction with the surface unhindered [61,62]. At pH values above 6, Pb hydroxide complexes form, e.g. $Pb(OH)^+$, $[Pb(OH)_2]$ and $[Pb(OH)_3]$, which can precipitate from solution. Additionally, an unfavourable interaction of these Pb hydroxide complexes with the surface of both the carbon adsorbent materials was also noticed [62,63,64].

Ionic strength

Ionic strength, which is a general property of the solution affecting the affinity between the solute and the aqueous phase, has a negative effect on the metal ion sorption onto CNTs.

It was found that the Ni^{2+} sorption decreases with increasing solution ionic strength [58]. However, the effect became small for solution ionic strength >0.05 mol/L as $NaClO_4$. Hence it clearly reflects that the sorption capacities of Pb^{2+} , Cu^{2+} and Cd^{2+} ions by CNTs decreases with an increase in solution ionic strength [59]. The decrease in sorption capacity of metal ions by CNTs can be mainly attributed to the increase in activity coefficients of

these metal ions, which retards their transfer to the surface site of CNTs & CNCs.

CNT mass

The amount of divalent metal ions adsorbed per unit mass of CNTs & CNCs at a given C_0 decreased with a rise in CNT mass. However, the sorption percentage of Ni^{2+} , Pb^{2+} , Cu^{2+} and Cd^{2+} increased with an increase in CNT mass, which could be due to the availability of more sorption sites [58,59]. Up to a certain value, no further increase in percent sorption of metal ion occurred as an increase in CNT mass.

Temperature and sorption kinetics

The temperature at which a sorption process is carried out will influence both the sorption rate and the degree to which sorption takes place. The sorption capacity of Pb^{2+} and Zn^{2+} ions remarkably increased with a rise in temperature indicating an endothermic reaction [65,66]. The time required to uptake 50% of the maximum Zn^{2+} sorption capacity (t_{50}) would be reached faster at a higher temperature. The kinetic sorption process of Pb^{2+} and Zn^{2+} ions onto CNTs could be well described by the pseudo-second-order rate law and the rate constants increased with a rise in temperature [65,66]. This could be explained by the fact that increasing temperature results in a rise in diffusion rate of metal ions across the external boundary

layer and within the pores of CNTs due to the result of decreasing solution viscosity.

Activation energy of sorption (E_a) is the free energy required for metal ions adsorbed onto CNTs. The faster the rate of sorption process, the lower the E_a . It was determined that the E_a for Zn^{2+} sorption onto CNTs and found that the E_a is less for the SWCNTs than for the MWCNTs, which could be explained by the fact that a SWCNT has no multiple atomic layers structure like a MWCNT requiring more energy for the diffusion of Zn^{2+} ions. The E_a is also less with a higher C_0 [65]. This could be explained by the fact that the diffusion driving force would be greater at a higher C_0 , which causes a faster diffusion rate of Zn^{2+} ions and thus requires less energy for the progress of the sorption process.

Competition

Competitive sorption is important in water and wastewater treatment because most metal ions to be sorbed exist in solution with other sorbable metal ions. By the concerned literature the competitive sorption of Pb^{2+} , Cu^{2+} and Cd^{2+} ions onto HNO_3 oxidized CNTs was studied [65]. The sorption capacities of CNTs for the three metal ions are in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$ and the competitive adsorption of metal ions also follows the same order. The sorption capabilities of CNTs without competition are much better than those with competition because the CNT surface is utilized by competing metal ions.

Thermodynamics

The thermodynamic parameters for Pb^{2+} , Zn^{2+} , and Ni^{2+} ions onto CNTs, which provide useful information concerning the inherent energetic changes of sorption process, revealed that the enthalpy change ($-H^\circ$) is positive indicating the endothermic nature of the sorption process. The negative free energy change ($-G^\circ$) suggests that the sorption process is spontaneous with a high preference of Pb^{2+} , Zn^{2+} and Ni^{2+} ions for the CNTs [65,66,67]. The positive entropy change ($-S^\circ$), which may be due to the release of water molecules produced by ion-exchange reaction between the metal ions and the surface functional groups of CNTs, reflects the affinity of the CNTs for the Pb^{2+} , Zn^{2+} and Ni^{2+} ions and the increase of randomness at the solid/liquid interface during the sorption process.

Desorption: Desorption of these metal ions from CNTs surface depends on pH of the regeneration solution. By experimental studies it was found that Zn^{2+} recovery from SWCNTs and MWCNTs using different pH values of regeneration solution ranging from 1 to 5 can be easily formulated and the results showed the Zn^{2+} recovery from SWCNTs and MWCNTs, respectively, reached 91.1 and 90.7% at a solution pH of 1 and decreased to 62.3 and 43.3% at a solution pH of 5 [69]. The sorption capacity was maintained after 10 cycles of sorption/desorption process. It was also reported that the Cd^{2+} , Mn^{2+} and Ni^{2+} ions could be effectively desorbed from the MWCNTs by a 1.0 mol/L HNO_3 solution and the performance was stable up to 50 adsorption–elution cycles without obvious decrease in the recoveries for the studied ions [65,66,68]. The desorption of the Pb^{2+} increased with

decreasing pH of the regeneration solution and reached 100%

Pb^{2+} desorption from CNTs using HCl or HNO_3 solutions at a pH of 2.0. Further it was also found that the Ni^{2+} desorption was 9% at $pH > 5.5$, then sharply increased with decreasing pH of the regeneration solution and ultimately reached 93% at $pH < 2.0$. The above results demonstrate that the CNTs are regenerable sorbents for the removal of divalent metal ions in water and wastewater treatment.

Drawbacks and future prospects

No doubt that CNTs & CNCs possess great potential as superior adsorbents for removing divalent metal ions from aqueous solution, but the relatively high unit cost restricts their practical use at the present time. In addition to it, the raw CNTs may possess some degree of toxicity due to the presence of metal catalysts while chemically functionalized CNTs have not demonstrated any toxicity so far [70]. As a result, the practical use of CNTs as sorbents in water and wastewater treatment depend upon the continuation of research into the development of a cost-effective way of CNT production and the toxicity of CNTs and CNT related materials such as CNCs.

A very new generation of carbon nano particles is dealing with the fabrication of carbon nano scrolls (CNC) [71,72,74]. Carbon nanoscrolls (CNSs) belong to the same class of carbon-based nanomaterials as carbon nanotubes but are much less studied in spite of their great potential for applications in nanotechnology and bioengineering [73,75]. Perturbations of the surface energy, which can be controlled by an electric field, will cause a CNS to undergo breathing oscillatory motion as well as translational rolling motion on a substrate [76]. The tunable core size of CNS also enables it to serve potentially as transmembrane water channels in biological systems. The equilibrium core size of CNS is controlled by the surface energy of CNS, the bending modulus of graphene, the interlayer space and the basal graphene length. Changing any of these parameters would lead to variations, or tuning, of the core size of CNS. Beside applications as water channels, the tunable CNS channel model can also serve as ion channels across cellular membrane or controllable nanofilters to prevent the passing of heavy metal ions or nanoparticles [77]. Fundamental description, understanding and regulation of such materials will ultimately lead to a new generation of integrated systems that utilize their unique properties.

Conclusion

This review summarized the removal of divalent metal ions (Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}) from aqueous solution using various kinds of CNTs. Most sorption works adopted either the Langmuir isotherm or the Freundlich isotherm (or both) for equilibrium sorption data correlation. The sorption capacities of metal ions to different CNTs follow roughly the order: $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+}$. Oxidation of CNTs with acid solution can considerably improve the sorption capacity of metal ions. The sorption mechanism appears mainly attributable to chemical interaction between the metal ions and the surface functional groups. Process parameters such as surface total acidity, pH and

temperature play a key role in determining sorption rate of metal ion onto CNTs. Sorption/desorption study elucidated the possibility to reuse the spent CNTs for the removal of divalent metal ions in water and wastewater treatment. The oxidized CNT sheets are promising materials for pre-concentration and solidification of heavy metal ions from large volume of solutions. Further research works on developing a cost-effective way of CNT production and testing toxicity of CNTs and CNT-related materials are recommended.

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