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Removal of Heavy Metal Ions from Wastewater by Carbon Nanotubes (CNTs)

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Abstract

Advent of nanotechnology has introduced us with new generation of adsorbents such as carbon nanotubes (CNTs) which have aroused widespread attention due to their outstanding ability for the removal of various inorganic and organic pollutants from large volumes of water. This article reviews the practical feasibility of various kinds of raw and surface modified carbon nanotubes for adsorption of heavy metal ions from wastewater. Further, properties of CNTs (adsorption sites), characterization of CNTs (pore volume, BET surface area, surface total acidity, surface total basicity) and solution properties (ionic strength, effect of pH) are explained very well. The adsorption mechanisms are mainly attributable to chemical interactions between metal ions and surface functional groups of the CNTs. The adsorption capacity increases to greater extent after functionalization i.e. surface oxidation of CNTs. Future work on developing cost effective ways of production of CNTs and analyzing its toxicity are recommended.

Keywords: Carbon Nanotubes, Heavy Metal Ions, Adsorption.

Introduction

Extensive industrialization and improper disposal are attributed to be a prime factor responsible for the release of heavy metals into the ecosystems. In India, it has been reported that, only 60% of industrial waste water, mostly large scale industries, is treated (1). Almost all heavy metals are toxic to living beings and excessive levels are known to cause both acute and chronic toxicity (2) e.g. cadmium exposure may cause nausea, salivation, cancer (3), lead causes gastrointestinal disorder, constipation, abdominal pain and central nervous system (CNS) effects (4, 5), exposure to nickel causes cancer of lungs, nose and bones, extreme weakness, dermatitis, headache, dizziness and respiratory distress (6). Heavy metals cannot be degraded or destroyed. Therefore removal of heavy metal is best accompanied by immobilization on suitable adsorbent.

Many adsorbents have been studied for removal of heavy metals such as activated carbon (7), modified activated carbon (8-10), husk of Lathyrus sativus (11), olive stone waste (12), bagasse (13), mordenite (14), crab shells (15) Novel e-waste-derived material (16). However, because of their low adsorption capacities, further applications of these adsorbents are restricted. Therefore, researchers are still making great efforts to investigate new

adsorbents with high adsorption capacities and efficiencies.

With the emergence of nano science and technology in the last decade, research has been initiated to exploit the unusual and unique properties of carbon nanomaterials (CNMs). CNMs may exist in several forms, such as, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), carbon beads, carbon fibres and nanoporous carbon. CNMs have been studied widely for potential applications in catalyst supports, optical devices, quantum computer, and biochips. However, their sorption potential has not been studied extensively. CNMs are engineered materials targeted to exhibit unique surface morphologies, hence, they may prove to be good sorbents (17). Carbon nanotubes (CNTs) have attracted special attention because of their unique properties, such as electrical conductivity, optical activity, and mechanical strength. This fascinating new class of materials has shown promising application in many areas since its discovery. However, CNTs are being spread quickly in the environment because of their growing use (18, 19).

Synthesis methods are quickly improved year to year, to produce large amount of size-controlled CNTs for commercial applications. CNTs

could be visualized as a sheet of graphite that has been warped to a tube.

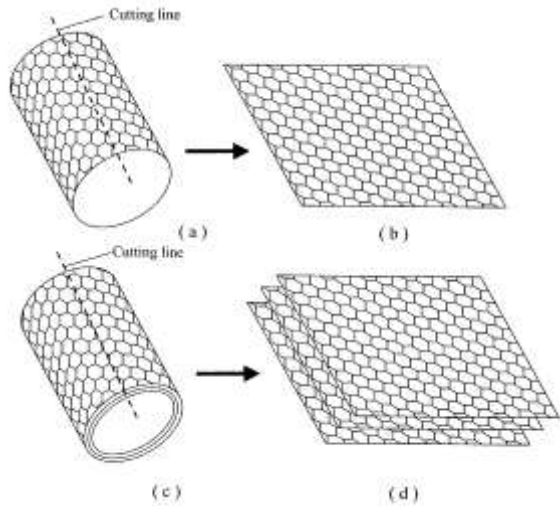


Figure 1. Sketch of carbon nanotubes unrolling to form graphene sheets. (20)

Presently, there are three main methods for CNTs synthesis: i. Arc Discharge method (21) ii. Laser ablation method (22) iii. Chemical vapor deposition (23).

Carbon nanotubes are of two types: i. Single walled carbon nanotubes (SWCNTs) (22) ii. Multi walled carbon nanotubes (MWCNTs) (23).

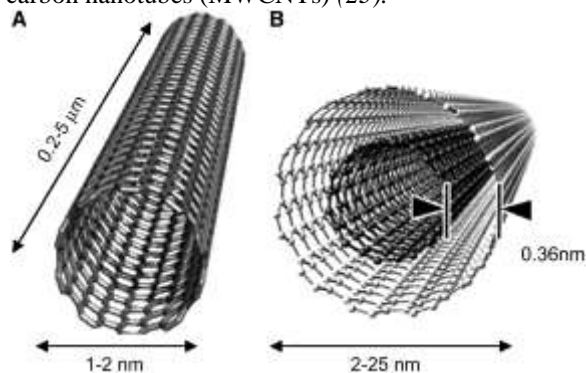


Figure 2. Conceptual diagram of (A) single-walled carbon nanotube (SWCNT) and (B) multi-walled carbon nanotube (MWCNT) (49).

Adsorption Properties of CNTs

Due to CNTs highly porous and hollow structure, large specific surface area, light mass density and strong interaction between CNTs and pollutant molecules (43), their applicability for removal of hazardous pollutants from gas (76, 77) as well as aqueous (58, 78, 79) streams have been studying extensively. A number of experiments have been carried out on adsorption of small molecules, heavy metal ions, organic chemicals on various types

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of CNTs. The study of adsorption properties of CNTs plays an important role in both fundamental and practical point of view.

Adsorption properties of any adsorbent are mainly depend adsorption sites. There are four possible adsorption sites (as shown in fig. 3) present in CNT bundles (34, 35).

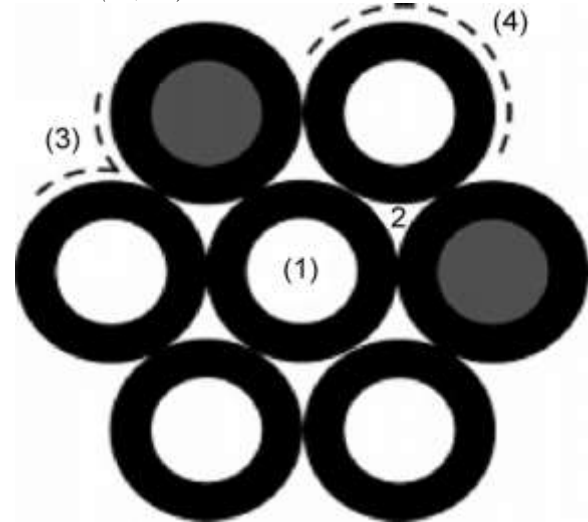


Figure 3. Different adsorption sites on a homogeneous bundle of partially open-ended SWCNTs: 1. internal, 2. interstitial channel, 3. external groove site, and 4. external surface (36)

“internal sites” – the hollow interior of individual nanotubes (accessible only if the caps are removed and the open ends are unblocked)

“interstitial channels (ICs)” – the interstitial channels between individual nanotubes in the bundles

“grooves” – the grooves present on the periphery of a nanotube bundle and the exterior surface of the outermost nanotubes, where two adjacent parallel tubes meet

“outside surface” – the curved surface of individual nanotubes on the outside of the nanotube bundles.

Considerable experimentation and analysis have been carried out to determine the occupied sites by adsorbate molecules after adsorption (66-72). It is depicted that the adsorption reaches equilibrium much faster on external sites than on internal sites under same conditions of temperature and pressure (73, 74). Further, it has been seen that fraction of opened and unblocked nanotubes can considerably influence the overall adsorption capacity. The opened CNTs provide more adsorption sites than closed ones (75).

Functionalization

Functionalisation plays very important role in adsorption properties of CNTs. CNTs possibly

contain functional groups such as -OH, -C=O, and -COOH depending on the synthetic procedure and purification process. Functional groups can also be intentionally added by oxidation (24). Functionalization of CNTs is aimed for easy processing, but at the same time, their adsorption properties with organic chemicals can be altered greatly as shown in figure 4.

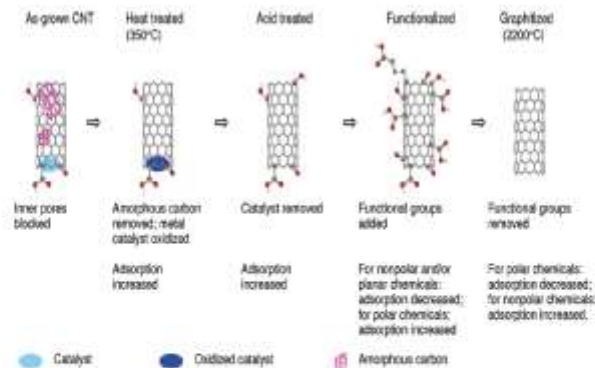


Figure 4. Adsorption properties as affected by functional groups (37)

Fig. 4 clearly shows that CNT is oxidized and further functionalized with the help of catalyst (Ni, Pt, Pd etc). These functional groups can be removed by heat treatment of CNT at 2200°C. Functionalisation changes CNTs properties drastically. Before functionalization CNTs have strong preference to hydrophobic groups (e.g. hexane, cyclohexane, benzene) over hydrophilic (e.g. alcohol) which gets reversed after functionalisation. Functional groups can change the wettability of CNT surfaces, and consequently make CNT more hydrophilic and suitable for the adsorption of relatively low molecular weight and polar compounds (25, 26, 27). CNTs have attracted great attention in latent applications such as nanodevices (28), field emission (29), gas adsorption (30), composite reinforcement (31), metal (ion) nanocomposites (32) and as catalyst supports (33) as they possess exceptional mechanical properties, unique electrical properties, high chemical and thermal stability and a large specific surface area.

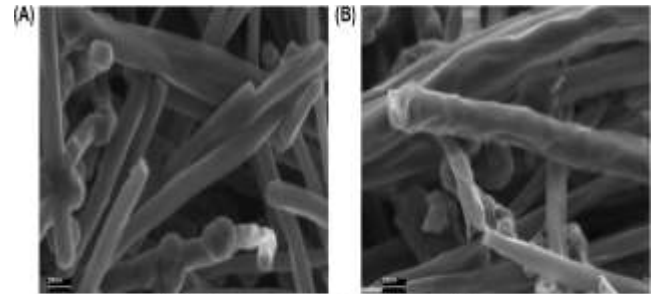


Figure 5. SEM images of (A) non functionalized CNTs (B) functionalized CNTs (50)

CNTs Characterization

CNT characterization plays a key role in adsorption mechanism.

Surface Area, Porous Volume, Surface Acidity and Basicity

Table 1 shows the comparisons of CNT characterization and their adsorption capacity of various heavy metal ions. Even though it is claimed that increase in BET surface area leads to increase adsorption potential (58), it is clearly shown that there is no direct correlation between metal ion adsorption capacity of CNTs and their specific area, pore specific volume and mean pore diameter. But their surface total acidity influences adsorption capacity to large extend. The metal ion adsorption capacity of CNTs increases with rise in the amount of surface total acidity present on surface site of CNTs. From this, it is easily depicted that adsorption of metal ions on CNTs is chemisorptions process rather than physisorption process. It is suggested by some researchers that the adsorption of heavy metals onto the CNTs are mainly controlled by the strong interactions between the metal ions and hydrophilic surface functional groups, especially carboxyl and hydroxyl groups (56,57).

Table 1. Comparisons of CNT characterization and maximum adsorption capacity of various heavy metal ions

Metal ions	Adsorbents	SA	PV	MPD	STA	STB	q _{max}	Ref.
Pb(II)	CNTs/MnO ₂	275	0.576	2.6			78.74	58
	CNTs/HNO ₃							59
	Xylene-Fe	47	0.18	3.4	1.63		14.8	
	Benzene-Fe	62	0.26	2.4-3.2	1.65		11.2	
	Propylene-Ni	154	0.58	3.6	4.04		59.8	
	Methane-Ni	145	0.54	3.6	4.31		82.6	
Ni(II)	SWCNTs	577	1.15	7.98	0.54	0.23	9.22	47
	SWCNTs/NaOCl	397	0.46	4.62	4.42	0.35	47.85	
	MWCNTs	448	1.1	8.26	0.44	0.19	7.53	
	MWCNTs/NaOCl	307	0.39	5.21	3.06	0.31	38.46	
Cd(II)	As-grown CNTs	122	0.28	3.6			1.1	60
	CNTs/H ₂ O ₂	130	0.36	3.6	2.52		2.6	
	CNTs/KMnO ₄	128	0.32	3.6	3.36		11	
	CNTs/HNO ₃	154	0.58	3.6	4.04		5.1	
	Ag-MWCNTs	101.47	0.27	10.98	4.69	0.1	16.95	62
Zn(II)	SWCNTs	590	1.12	7.6			11.23	41
	SWCNTs/NaOCl	423	0.43	4.12			43.66	
	MWCNTs	435	0.91	8.35			10.21	
	MWCNTs/NaOCl	297	0.38	5.17			32.68	

SA = BET surface area (m²/g), PV = pore volume (cm³/g), MPD= mean pore diameter (nm), STA= surface total acidity (mmol/g), STB = surface total basicity (mmol/g), q_{max} = maximum adsorption capacity (mg/g).

Water Content, Ion Exchange Capacity (IEC)

It has been observed that water content increases with increase in CNT loading. The inner diameter of carbon nanotubes provides enough space to accommodate water molecules. Moreover, increase of membrane heterogeneity by the additive loading enhances the amount of water content in modified membranes. But water content decreases with extensive loading of CNTs which can be explained with respect to pore filling phenomenon by CNTs particles at high additive content which reduces water capacity (79).

Further, S.M. Hosseini et. al. observed that ion exchange capacity (IEC) decreases with increase in CNTs concentration in modified membranes which is because of resin particle isolation surrounding by CNTs (79).

Adsorption Performance**Adsorption Isotherm of CNTs**

The metal ion adsorption equilibrium are commonly correlated with the Langmuir or the Freundlich equations where the Langmuir equation is valid for dynamic equilibrium adsorption process on completely homogenous surfaces while the Freundlich equation is applicable to heterogeneous surface. Several researchers depicted that metal ion adsorption on CNTs can be well described by Langmuir equation (39-44) whereas some researchers reported that sorption of heavy metals on CNTs can be correlated with both Langmuir and Freundlich equations (38, 46, 47, 48). Li et al. mentioned that the metal ion (Pb^{2+}) sorption onto CNTs follows the Freundlich equation (45). The maximum adsorption capacities of several heavy metal ions on CNTs compared to other adsorbents are listed in Table 2.

Adsorption Mechanism

The mechanisms of heavy metal ion adsorption on CNTs are very complicated and appear attributable to physical adsorption, electrostatic attraction, precipitation and chemical interaction between the heavy metal ions and the surface functional groups of CNTs. Among all these, chemical interaction between heavy metal ions and the surface functional groups of CNTs is the major adsorption mechanism (see Fig. 6) (47, 51). Hydrogen atoms i.e. protons from carboxylic and phenolic groups of CNTs exchange with metal ions which results in drop in pH of solution as more protons are released into solution.

Effect of pH

The value of pH plays very vital role with respect to adsorption of metal ions on CNT surface. When the solution pH is higher than pH_{PZC} (a pH value, called 'point of zero charge', at which the net surface charge is zero), the negative surface charge provides electrostatic interactions that are favourable for adsorbing cation ions. The decrease of pH leads to neutralization of surface charge, thus, the adsorption of cation ions should decrease. pH also affects metal ion species and competing complexation reactions, and influences adsorption capacity of MWCNTs for heavy metal ions (41, 55).

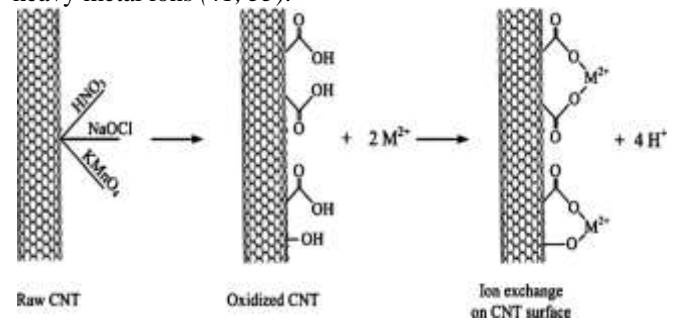
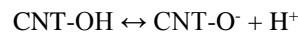
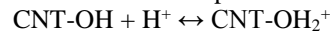


Fig. 6 Schematic diagram of the major mechanism for sorption of divalent metal ions onto CNT surface. (53)

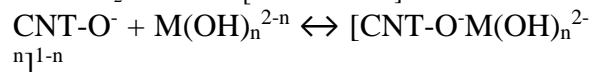
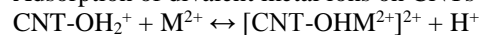
These can be explained by following reactions (52).

Step I

Protonation and deprotonation of CNTs:

**Step II**

Adsorption of divalent metal ions on CNTs



When the solution pH is lower than pH_{PZC} , the surface charge of CNTs is positive and M^{2+} is generally the predominant species in solution. The adsorption of divalent metal ions that takes place in this pH region is attributed partly to the competition between H^+ and M^{2+} on the surface sites ($CNT-OH$) (54). When the solution pH is higher than pH_{PZC} , the surface charge of CNTs is negative and the divalent metal ions exist predominantly in $M(OH)_n^{2-n}$ species. The removal of divalent metal ions is possibly accomplished by simultaneous adsorption and precipitation reactions at high pH values.

Table 2. The maximum adsorption capacity (q_{\max} , mg/g) of several heavy metal ions on CNTs.

Adsorbate	Adsorbent	Parameters	Initial Conc. of metal soln	q_{\max} (mg/g)	Ref.
Pb(II)	Amino modified MWCNTs	pH=6-7, T=318K	5 ppm	58.26	61
	Dispersed MWCNTs	pH=5.6	10 ppm	92.3	39
	Undispersed MWCNTs	pH=5.6	10 ppm	74.5	39
	CNTs/MnO ₂	pH=7, Contact Time= 2h	30 ppm	78.74	58
	CNTs/HNO ₃	pH=5, T=298K	10-80 ppm	35.6	45
Cu(II)	Dispersed MWCNTs	pH=5.6	10 ppm	67.8	39
	Undispersed MWCNTs	pH=5.6	10 ppm	51.3	39
	Ag-MWCNTs	pH=6-7, contact time= 2h, T= 293-313K	50 ppm	16.21	62
Cd(II)	amino modified MWCNTs	pH=6-7, T= 318K	5 ppm	31.45	61
	Activated alumona-CNT nanoclusters	pH=7.5 contact time= 4h	250 ppm	229.9	38
	Ag-MWCNTs	pH=6-7, contact time= 2h, T= 293-313K	50 ppm	16.94	62
	MnO ₂ /o-MWCNTs	pH=5, contact time= 150 min.	30 ppm	41.6	63
Cr(VI)	MnO ₂ /Fe ₃ O ₄ /o-MWCNTs	pH=2 Contact time: 150 min. T= 335K	300 ppm	186.9	82
	SWCNTs	pH=4	0.5 ppm	20.3	64
	Activated carbon supported CNTs	pH= 4 Contact time= 60min.	0.5 ppm	9	81
	Activated alumona-CNT nanoclusters	pH=2 Contact time= 4h	250 ppm	264.5	38
Ni(II)	SWCNTs/NaClO	T=298K	60 ppm	47.86	65
	MWCNTs/NaClO	T=298K	60 ppm	38.46	65
	MWCNTs	pH=5.4, T=293K	10 ppm	3.72	42

Future Work

Much progress has been made over the last few years in adsorption applications of CNTs. In spite of high costs, using CNTs as adsorbents may be advantageous in future because the high adsorption capacities of CNTs compared to other media may offset their high cost. In addition, many researchers are branching out with the modification of CNTs by innovative processing techniques. However, there are still a lot of works to do to enhance CNT adsorption properties in future. The aggregation of CNTs in aqueous solution limits the available sites for binding with pollutants. The surface modification to enhance the dispersion property of CNTs in solution can greatly increase the interaction of CNTs with pollutants, and thereby can increase the removal capacity of CNTs in the preconcentration of pollutants. Although conventional chemical methods can modify the surface properties of CNTs, large amounts of chemicals are used in the process, which causes environmental pollution.

Furthermore, 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. 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 (83).

Conclusion

The report presents the adsorption applications of CNTs in the removal of metal ions from large volumes of aqueous solutions. CNTs show considerable adsorption capacity for heavy metal ions. CNTs have a range of unique properties, not the least of which is their adsorption properties and their sizes. CNTs provide a large specific surface area and a strong van der Waals binding energy for ion adsorbates on well-defined adsorption sites such as interior sites, groove sites, exterior sites and interstitial sites. According to experimental and theoretical research, the binding energy of the interior sites is the highest, followed by the one of the groove sites on the outside of CNT bundles, and the one of the exterior sites on the convex outer surface is the lowest. The interstitial sites appear to be inaccessible to the adsorbate ions. Further, 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 threw light on the possibility to reuse the spent CNTs for the removal of metal ions in water and wastewater treatment. 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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