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Carbon Nanomaterials – A New Form of Ion Exchangers

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1. Introduction

Carbon nanomaterials are a new form of carbon based materials which have been receiving much attention for their interesting properties over the past three decades. The materials were initially discovered in 1952 [1] but were only scientifically recognized in 1991 when Iijima submitted a report [2]. An interesting feature of these allotropes of carbon has been the different forms in which they can exist. These include single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). These structures are depicted in **Figure 1**. The fundamental difference between these unique forms of carbon lies in their structural properties. SWCNTs and MWCNTs differ with respect to number of graphene carbon sheets.

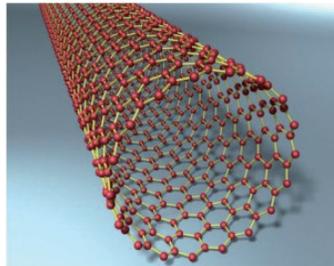
Nevertheless, these carbon based materials have demonstrated a vast array of physical and chemical properties. Such properties include outstanding mechanical properties, electrical properties, chemical and thermal stability and large specific surface areas [4]. Consequently, much emphasis has been placed on synthesizing these materials and using them in a number of applications which include nanodevices [5], field emissions [6], plasma apheresis [7], catalyst supports [8], biosensors [9] and chemosensors [10,11]. However, one application of much interest has been their use in environmental remediation. Such an application has arisen from their well-defined porosity and functionality [12]. This property has enabled them to demonstrate superior adsorption capabilities to that of conventional adsorbents like activated carbon [12]. Among, the numerous adsorption applications examined, metal ion uptake by these materials has featured quite prominently. However, the actual mechanism of metal ion adsorption by these materials has been poorly understood.

This chapter therefore serves to examine the ion-exchange properties of carbon nanomaterials. The ability of wide range of nanomaterials namely carbon nanotubes to act as anion and cation exchangers are discussed. Such a discussion includes potential

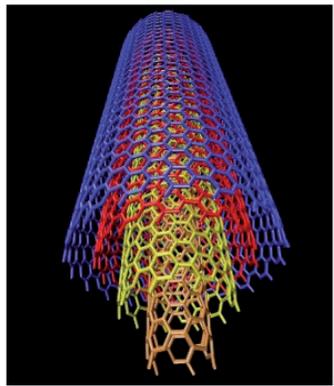
modifications to these materials improve the ion exchange capacities. Such modifications include heteroatom doping and functionalisation of the surfaces of these materials.

With regards to functionalisation acid-base treatment is discussed. The focus in this section of the chapter is mainly on the how the introduction of functional groups alters the surface of the nanomaterials thereby improving the ion exchange capacities. The influence of various functional groups on the point of zero charge is examined. Such effects are then extended to the effect of heteroatom doping such as sulphur-doping and acid-base treatment.

Lastly, the ability of carbon nanomaterials to act as selective ion-exchangers is reviewed. This includes a discussion on how these materials can function as ion-exchangers in complex matrices. The use of these materials as ion-exchangers in real industrial effluents is also discussed. The way forward with respect to using carbon nanomaterials in analytical ion-exchange applications is discussed with some conclusions and recommendations for future research.



A)



B)

Figure 1. The two main types of carbon nanotubes a) Single –walled carbon nanotubes (b) Multi-walled carbon nanotubes (from: <http://www.cnano-rhone-alpes.org/spip.php?article57&lang=en> [3] Courtesy of Alain Rochefort, Polytechnique Montreal

2. Problem statement

Both SWCNTs and MWCNTs have been extensively used in a number of environmental applications. These include the removal of both organic and inorganic contaminants by

adsorption. However, as far as the uptake of ions (especially metal ions) is concerned, ion-exchange has been identified as one of the key mechanisms governing this process. The key question to be addressed here is how can these carbon nanotubes act as ion-exchangers? What properties of these materials enable them to possess ion-exchange characteristics? A number of researchers have attempted addressing these questions and the findings of the research conducted to date are reviewed below.

3. Carbon nanomaterials as anion and cation exchangers

In some recent studies conducted it has been shown that surface modifications to carbon nanotubes have played a key role influencing their ion exchange properties. It has been said that oxidized CNT's show a better potential for cation uptake than unoxidised CNTs [4]. Conversely, it has also been shown that unoxidised MWCNTs are more effective for uptake of anions such as dichromate than oxidized MWCNTs [13]. In such observations it has been argued that oxidation has an impact on the point of zero charge (pH_{PZC}) of these materials which ultimately governs the overall surface charge [4,13,14].

Typically, oxidation lowers the pH_{PZC} of these materials thereby resulting in a predominantly negatively charged surface which is more favorable for cation uptake. Likewise, unmodified or unoxidised CNTs have a higher pH_{PZC} which results in a predominantly positively charged surface which is more favorable for anion uptake. This is supported conclusively by experimental evidence where Rao et al. [4] have reported that oxidized SWCNTs showed a better uptake for Ni(II) and Zn(II) ions than unmodified MWCNTs. Further, Pillay et al. [13] have also shown conclusively that unmodified MWCNTs were more effective for removal of Cr(VI) than oxidized MWCNTs due to a higher (pH_{PZC}).

The question of how these surface modifications can be achieved so as to control the ion-exchange properties of these materials has thus arisen. This can be achieved in two ways. One way includes the addition of surface functional groups and the other is via heteroatom doping. These methods are discussed below.

4. Functionalisation of carbon nanotubes

A number of functional groups have been added to the surface of CNTs. These have included mostly oxygen-containing functional groups which take on the form of both $-OH$ and carboxyl groups. This type of functionalisation has been primarily via oxidation of the CNTs in acid which results in the introduction of carboxyl groups. Consequently, these types of CNTs have been extensively used in the uptake of a number cations. These studies are summarized in **Table 1**.

Most of the above results conclusively support the fact that interaction between the functional groups and the cations are the primary means by which the cations are retained. The fact that an ion exchange mechanism predominates is also supported by the fact the

uptake of cations has been pH dependent in some cases. In general it has been observed that cation uptake is low at low pH and high at high pH. This suggests that electrostatic repulsions between the cations and excess H^+ ions at low pH hinder the uptake of cations whereas electrostatic attractions between the cations and excess OH^- ion at high pH enhances the uptake of the cations.

TYPE OF NANOTUBE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
SWCNTs and MWCNTs purified with a sodium hypochlorite solution	Zn(II).	<ol style="list-style-type: none"> 1. This purification method rendered the CNTs more favourable for the uptake of Zn(II) by making the CNTs more hydrophilic. 2. The adsorption was also pH dependent. 3. Both types of CNTs were better adsorbents than powdered activated carbon (PAC) 	1. The concentration range studied was 10-80 mg L ⁻¹ .	Lu and Chiu[12]
Oxidised MWCNTs	Ni(II)	<ol style="list-style-type: none"> 1. Up to 93% Ni(II) could be desorbed from the oxidised MWCNTs at pH < 2 using distilled water as the desorbing agent. 2. Lack of dependence on ionic strength. 3. Equilibrium is attained within 40 min of contact time 		Chen and Wang[15]
As grown and oxidised MWCNTs	Ni(II)	<ol style="list-style-type: none"> 1. Adsorption capacity of oxidised MWCNTs was superior. 2. A short time was required to attain equilibrium and noted that the adsorption capability 	These workers also neglected to study the effect of competing cations and did not conduct any desorption experiments.	Kandeh and Meunier[16]

TYPE OF NANOTUBE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
		of this material was also superior to that of peanut shell		
NaOCl oxidised SWCNTs and MWCNTs	Ni(II)	1. More efficient at adsorbing and desorbing over 10 cycles than granular activated carbon.	None	Lu et al. [17]
Oxidised MWCNTs	Cd(II)	1. MWCNTs oxidised with KMnO ₄ gave the best results. 2. Oxidation also lowered the p _H pzc of these materials and increased the quantity of surface functional groups.	Did not examine the effects of competing anions or determine the regenerability of these materials.	Li et. al[18]
Acid-treated MWCNTs	Pb(II).	1. The adsorption capacity reported was 85 mg g ⁻¹ which is higher than that reported for unmodified MWCNTs and activated carbon. 2. The equilibrium adsorption time was shortened to 20 minutes. 3. Provided experimental evidence that chemical interactions between Pb(II) and oxygen containing functional groups accounts for 75,3% of the Pb(II).	The adsorbed Pb(II) aggregates occur mainly on the ends and defect sites of the MWCNTs.	Wang et. al [19]
Oxidised MWCNTs	Ni(II)	1. The presence of polyacrylic acid	The strength of the complexes of Ni(II)	Yang et. al.[20]

TYPE OF NANOTUBE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
		(PAA) enhanced the uptake at low pH. 2. That the adsorption was independent of the addition sequence of PAA and Ni(II). 3. The presence of foreign ions had no effect at low pH.	with PAA adsorbed onto the MWCNTs was higher than the strength between Ni(II) and oxygen containing functional groups.	
MWCNTs	Cu(II)	Adsorption was positively affected by the presence of humic and fulvic acids at pH>7.5	Adversely affected at pH < 7.5.	Sheng et. al [21]
Activated carbon, carbon nanotubes and carbon encapsulated nanoparticles	Co(II) and Cu(II).	Both types of carbon nanomaterials had a superior adsorption capability to that of activated carbon.	The carbon nanomaterials only lost 5-11% of their adsorption efficiency in saline environments where competing ions exist while activated carbon lost 30-50% of its adsorption efficiency.	Pyrzynska and Bystrzejewski[22]

Table 1. Some Cation Uptake Studies by Oxidised CNTs (from Pillay [14])

Another interesting feature of the above results has been the general observation that surface modified CNTs show superior adsorption capabilities than that of conventional adsorbents like activated carbon and other low cost adsorbents. Furthermore, the methods of functional group introduction have varied from acid-treatment to purification with sodium hypochlorite. The primary atom that seems to be governing the surface charge hence the pH_{pzc} seems to be the oxygen atom. Such an electron rich atom would impart a negative surface charge to these materials. However, it is by no means the only atom which can achieve this.

Recently Cech et al. [23] showed that sidewall thiolation of MWCNTs can be achieved by treatment with P_2S_5 and Pillay et. al [24] modified this method to produce sulphur containing MWCNTs which showed improved and selective uptake of Hg(II). Thus, both functional group and heteroatom introduction can be controlled by well-defined chemical

treatment of CNTs. Such a method has been identified as acid and base treatment of the CNTs.

5. Acid and base treatment of carbon nanotubes

As discussed above acid treatment of CNTs leads primarily to the introduction of oxygen containing functional groups such as hydroxyl and carboxyl groups. The introduction of these functional groups subsequently leads to a negative surface charge which favours cation uptake. However, very little knowledge on the effect of base treatment is available. Pillay [14] attempted studying the effect of strong and weak acid mixtures on the uptake of both cations and anions. Here it was observed that treatment in both strong acid and base mixtures resulted in the introduction of oxygen-containing functional groups which favoured cation uptake by lowering the pH_{PZC} of these materials. Conversely, treatment in a weak base like NH_3 resulted in the introduction of nitrogen-containing functional groups which favoured anion uptake by increasing the pH_{PZC} . Thus treatment in acid and base depends on the strength of the acid or base and the types of heterotoms which can be introduced. The ion exchange properties of the CNTs have therefore become dependent ultimately on heteroatom doping. The methods of heteroatom include functional group addition but the effects of individual heteroatoms depends on the individual atoms added the method of introduction.

6. The effect of heteroatom doping on the ion exchange properties of carbon nanotubes

Thus far it has been noted that the addition of oxygen-containing functional groups and oxygen as a heteroatom favours cation uptake by lowering the pH_{PZC} . Likewise sulphur-containing functional groups and sulphur as a heteroatom have been shown to have a similar effect for the uptake of $Hg(II)$ [24]. However, the effect of other heterotoms such as the nitrogen atom have been poorly understood. Nitrogen –doped carbon nanotubes (N-CNTs) have been receiving much attention recently. Although the properties such as the semi-conducting properties of these materials are well understood [25] little is known about their function in metal ion exchange. Although Perez-Aguilar et al. [26] showed that oxidized nitrogen-doped carbon nanotubes were more effective for the uptake of $Cd(II)$ and $Pb(II)$ than undoped unoxidised MWCNTs the actual role played by the introduction of nitrogen as a heteroatom in this study was not clear. Pillay [14] investigated this further and found that the role played by the nitrogen atom depends largely on the form in which nitrogen occurs on the carbon nanotubes, For instance if quaternary nitrogen is present this can result in positively charged nitrogen centres which increase the pH_{PZC} and favour anion uptake. On the other hand if nitrogen is occurring in conjunction with oxygen this can lower the pH_{PZC} thereby favouring cation uptake.

Some emphasis has therefore been placed on the introduction of heteroatoms such as oxygen, sulphur and nitrogen atoms. The question of whether the introduction of other

heteroatoms particularly less electronegative atoms can also influence the ion-exchange properties of CNTs has arisen. Again this is an area which has not been extensively explored. Although Aguiar et al [27] showed the SWCNTs doped with iron were effective for the removal of benzonitrile, the question of how this would affect metal ion exchange still needs to be investigated. Furthermore the introduction of other electronegative atoms such as the halogens needs to be explored. Tan et al [28] also showed the introduction of surfactants to these materials also influence the ion-exchange properties where such a system provided a counterion system for the uptake of Ni(II). The issue of whether the introduction of such atoms or groups of atoms can also impact on the selectivity of CNTs for specific target pollutants also needs to be addressed.

7. Carbon nanotubes as selective ion exchangers

Carbon nanotubes are therefore a new form of ion-exchangers which have demonstrated potential to extract a number of cations and anions based on the functional groups and heteroatoms which are present. However, the selectivity of these materials for specific pollutants is still questionable and limited studies in this area have been conducted. Li et al. [29] attempted addressing this issue by showing that MWCNTs are able to adsorb Pb(II) more efficiently in the presence of other competing cations such as Cd(II) and Cu(II). However, complete selectivity was not achieved. Pillay et al. [13] also showed that unfunctionalised MWCNTs were not selective to the uptake of Cr(VI) in the presence of competing anions such as chloride and sulphate ions. This also applied to industrial effluents where sulphites are present [14]. In fact, the only study to date which been the study in which sulphur-doped MWCNTs showed selectivity for Hg(II) in the presence of competing ions [24]. Thus the selectivity of these ion-exchangers needs improvement.

8. Conclusion

From the information reviewed in this chapter it is evident that carbon nanomaterials are a new form of ion-exchangers based on the diverse number of metal ion uptake studies which have been conducted using these materials. An interesting feature of these materials has been the fact that they can be modified to function as both cation and anion exchangers. This is carefully controlled by both the introduction of functional groups and heteroatoms which ultimately impact on the surface charge. However, the selectivity of these materials for specific ions still needs improvement. Furthermore, the heteroatoms introduced have been restricted to oxygen, sulphur and nitrogen. The effect of other heteroatoms also need to be explored. Even acid and base treatments contribute mainly to the introduction of oxygen and nitrogen atoms. Such topics now lend themselves to future research perspectives.

Nomenclature:

CNTs	Carbon Nanotubes
SWCNTs	Single-walled Carbon Nanotubes

MWCNTs	Multi-walled Carbon Nanotubes
S-MWCNTs	Sulphur-containing Multi-walled Carbon Nanotubes
N-MWCNTs	Nitrogen-doped Multi-walled Carbon Nanotubes

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