



**CARBON NANOMATERIALS FOR THE REMOVAL AND RECOVERY OF
METAL IONS FROM AQUEOUS SOLUTIONS**

by

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DECLARATION

I hereby declare that this thesis, which I herewith submit for the research qualification

DOCTOR OF PHILOSOPHY IN CHEMISTRY

to the University of the Witwatersrand, School of Chemistry, is, apart from the recognised assistance of my supervisors, my own work and has not previously been submitted by me to another institution to obtain a research diploma or degree.

_____ on this ____ day of _____

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(Supervisor)

_____ on this ____ day of _____

(Co-supervisor)

DEDICATION

In loving memory of my late parents and brother

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ABSTRACT

Carbon nanomaterials are a group of materials which have been gaining increasing recognition for their applications in environmental remediation. Studies on the use of single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) for the remediation of various contaminants including metal ions like Cr(VI) and Hg(II) have already been undertaken. However, these studies have mostly focussed on the uptake of parts per million (ppm) levels of contaminants. The uptake of parts per billion (ppb) levels of such contaminants have not been extensively examined. Studies on the effect of sulphur doping on the uptake of Hg have not been undertaken. Competitive adsorption studies in which competing cations and anions are present have also been scarce. The effect of surface modifications such as acid and base-treatment and the effect of nitrogen doping have not been extensively studied.

This study was therefore undertaken to address the above issues. It was found that unfunctionalised MWCNTs could adsorb 98% of a 100 ppb Cr(VI) solution. These materials had superior adsorption capabilities to that of activated carbon and functionalised MWCNTs. The difference in adsorption capabilities of these materials was attributed to the differences in points of zero charge (pHpzc). The Langmuir and Freundlich adsorption isotherm models were also used to describe the adsorption process.

Sulphur-containing MWCNTs (S-MWCNTs) showed the highest uptake capacities for both 100 ppb solutions of Hg(II) and organic forms of mercury respectively. This was attributed mainly due to mercury's high affinity for sulphur and evidence of a chemisorption process was presented. The uptake capacity of sulphur-containing activated carbon (S-AC) was inferior to that of the S-MWCNTs but this was attributed mainly to a difference in sulphur content. The only advantage that S-MWCNTs presented over S-AC was a greater selectivity in the presence of SO₂. The S-MWCNTs were also highly selective to the uptake of Hg in the presence of competing cations and in a chlor-alkali effluent where a complex

chemical matrix was noted. The Freundlich adsorption isotherm model best described the uptake of Hg.

Both Cr(VI) and Hg were efficiently desorbed in 0,1 M NaOH and 0,5% thiourea in 0,05 M HCl solutions respectively. This implied that the MWCNTs could be reused and regenerated and this could address cost issues.

Results from the surface modification studies showed that acid-treatment (both strong and weak) resulted in oxygen-containing functional groups which lowered the point of zero charge of the MWCNTs thereby rendering these suitable for cation uptake. The effect of base-treatment depended on the type of base used. The strong base KOH had a similar effect to that of the acid-treated MWCNTs. The weak base NH_3 on the other hand resulted in the presence of quaternary nitrogen which increased the point of zero charge and made the MWCNTs more suitable for anion uptake. Similar observations were made for nitrogen-doped multi-walled carbon nanotubes (N-MWCNTs) and nitrogen doped carbon spheres (N-CSs) . The effect of nitrogen doping does however depend on the form in which nitrogen is present. In this case the predominant form of nitrogen was quaternary nitrogen.

Carbon nanomaterials have therefore demonstrated a great ability to extract a variety of anions and cations from aqueous solution and thus show potential for industrial applications especially since they show superior adsorption capabilities to that of activated carbon. The selectivity of the unfunctionalised MWCNTs and MWCNTs treated with acid and base was however, poor when competing anions and cations were present. This suggested that the selectivity of these materials needs to be improved upon in further studies before these are used in industrial applications.

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LIST OF ABBREVIATIONS

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
CSs	Carbon Spheres
N-CSs	Nitrogen-doped Carbon Spheres
S-AC	Sulphur-containing Activated Carbon
pH_{Pzc}	Point of Zero Charge
COPR	Chromite Ore Processing Residue
AAS	Atomic Absorption Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
XPS	X-ray Photo Electron Spectroscopy
BET	Brunauer-Emmett-Teller
DTPA	Diethylenetriamine pentaacetate
HBIG	2-nitrobenzaldiminoglycine
ppm	parts per million
ppb	parts per billion

CHAPTER 1

INTRODUCTION

1.1 Overview and Scope

The literature survey conducted in Chapter 2 has indicated that carbon nanotubes and other forms of carbon such as carbon spheres have been gaining increasing recognition for applications in environmental remediation studies. Both single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) have been used for the adsorption of a number of organic and inorganic pollutants. In comparative studies these adsorbents have demonstrated superior adsorption capacities to that of activated carbon. MWCNTs in particular have been effective due to their high chemical stability and purity. Thus, such adsorbents could replace activated carbon as an adsorbent for the treatment of industrial wastes that are rich in heavy metals and other contaminants.

Although, the use of carbon nanotubes for the uptake of various metal ions including Cr(VI) and Hg(II) have been well documented, most of the studies conducted to date have focussed only on the uptake of parts per million (ppm) levels of these ions. Studies on the ability of these materials to adsorb organic forms of mercury have also been scarce. There have been no literature reports on the uptake of ppb levels of metal ions by carbon nanotubes. Studies on the ability of MWCNTs to selectively extract metal ions from a complex chemical matrix have also been limited. The practical use of carbon nanotubes has not been explored simply because these have are deemed to be too expensive to synthesise. Although cheaper methods of synthesising these materials are essential, the possibility of embedding the carbon nanotubes or carbon spheres into an inert support and regenerating the material by desorption of the metal ions has not been considered.

Further to these shortcomings of the research conducted to date, the surface modifications of carbon nanotubes which influence metal ion uptake such as the role played by nitrogen-doping and the effect of microwave-induced acid-base treatment have not been extensively explored and are still not properly understood. Although studies on the applications of carbon nanotubes in the trace analysis of various organic and inorganic contaminants have been rather extensive, studies on the selective solid phase extraction and pre-concentration of oxyanions and oxycations have been limited.

1.2 Objectives of the study

This study was therefore undertaken to investigate the following aspects of using carbon nanotubes for the uptake of metal ions.

- (i) Evaluating the capacity of MWCNTs to extract ppb levels of metal ions from pure aqueous solutions. (The emphasis is placed on Cr(VI) and Hg which are two extremely toxic heavy metals and present problems in industrial effluents.)
- (ii) Examining the most effective method of using MWCNTs for practical use.
- (iii) Studying the effect of nitrogen doping and microwave induced acid and base treatment on both anion and cation uptake using MWCNTs and carbon spheres (CSs).
- (iv) Exploiting the adsorption capacities of MWCNTs for the selective solid phase extraction and pre-concentration of oxyanions and oxycations from binary and ternary mixtures.

1.3 Outline of the Thesis

The thesis begins with a detailed literature review (Chapter 2) in which the chemistry of chromium and mercury are reviewed. The speciation, toxicity, occurrences and distribution of these elements in the environment are discussed. The various treatment technologies that have been utilised for treatment of industrial wastes containing Cr(VI) and Hg (Hg(II) and organic forms namely monomethyl mercury (CH_3Hg^+) and dimethyl mercury ($(\text{CH}_3)_2\text{Hg}^+$)) are reviewed and their advantages and drawbacks are highlighted. The current knowledge on carbon nanotubes and carbon spheres is reviewed with special emphasis on their environmental applications and the chapter concludes with a rationale for the current study.

Chapter 3 presents and discusses the results obtained on the uptake of ppb levels of Cr(VI). The adsorption capabilities of both functionalised and unfunctionalised MWCNTs as well as activated carbon are compared. The influence of key parameters e.g. contact time, solution pH etc. are discussed. Adsorption isotherm models are used to describe the adsorption process and the mechanism of Cr(VI) adsorption is also discussed. The ability of Cr(VI) to desorb from these carbons is also examined.

Chapter 4 highlights a case study in which the ability of MWCNTs to selectively adsorb Cr(VI) from a metal plating effluent is examined. Herein, the influence of the chemical composition of the effluent and the matrix effects are discussed. The results from continuous flow studies in which the MWCNTs were embedded into silicon carbide (used as an inert support) are also discussed. The extent of regeneration after six successive adsorption-desorption cycles is examined and recommendations for industrial practice are made.

In Chapter 5 the results on the uptake of ppb levels of Hg(II) and organic forms of mercury (dimethyl and monomethyl mercury) are discussed. The uptake capacities of sulphur-containing MWCNTs (S-MWCNTs) and activated carbon (S-AC) are compared. Control studies on the unmodified MWCNTs and activated carbon are also presented. The influence of critical parameters such as the

sulphur content of the adsorbents are highlighted. Adsorption isotherm models are used to evaluate the maximum uptake capacities of the S-MWCNTs and S-AC. A mechanism for the uptake of mercury by these sulphur-containing adsorbents is also proposed.

Chapter 6 presents another case study in which the ability of sulphur-doped MWCNTs (S-MWCNTs) to selectively extract mercury from a chlor-alkali effluent is discussed. The results from continuous flow studies in which the S-MWCNTs are embedded into silicon carbide are discussed and recommendations for the best industrial practice are made.

Chapter 7 examines some of the key surface modifications of carbon nanotubes which influence the uptake of anions and cations. Such modifications include the effect of nitrogen doping and the dopant content, the effect of microwave – induced acid and base treatment and point zero charge, the effect of the physical morphology of the carbons and lastly the effect of impurities in the nanotubes.

Chapter 8 presents a study on the ability of acid-treated and NH_3 -treated MWCNTs to selectively extract chromates from a ternary mixture containing arsenates and selenates. The influence of different eluents is examined. The ability of MWCNTs to sequentially extract chromates, arsenates and selenates from multicomponent systems is also evaluated and discussed. Lastly, a method for the sequential extraction of the oxyanions is developed and this is also applied to the extraction of oxycations from multi-component systems.

Chapter 9 is the concluding chapter and highlights the major findings of the study undertaken and the extent of fulfilment of the objectives of the study and concludes with some recommendations for further studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter aims at reviewing the chemistry, speciation, toxicity and industrial uses of chromium and mercury. Emphasis is placed on these elements as these are extremely toxic and present major problems when released into the environment. The treatment technologies which are currently employed for the removal of these metals from solution are also critically discussed and the advantages and disadvantages of each method is highlighted. A critical discussion on the chemistry of carbon nanotubes with a special emphasis on the environmental applications of these materials is also provided. The chapter concludes with a discussion as to the motivation for the current study.

2.2 Chromium

Chromium was discovered by the scientist, Louis Nicholas Vacquelin in 1797¹. Its name originates from the Greek word for colour “chroma”. It has the chemical symbol, Cr and atomic number, 24. It is situated in the d-block of the Periodic Table and is considered to be one of the transition elements or heavy metals.

2.2.1 The Occurrence of Chromium

Chromium is the 21st most abundant element on Earth.¹ Its existence in the environment is a result of both natural and anthropogenic activities. It is distributed in rocks, seawater, rivers and lakes² In South Africa, it is found as chromite ore and constitutes two-fifths of the chromite ore concentrates in the world.³

2.2.2 The Physical Properties of Chromium

Chromium is noted for its high resistance to corrosion and discolouration which warrants its use in industrial applications such as stainless steel production and electroplating.⁴

2.2.3 The Chemical Properties and Speciation of Chromium

Chromium, like most transition elements can exist in a variety of oxidation states ranging from the -2 to +6.⁵ However, under environmental conditions the +3 and +6 oxidation states predominate.⁶ The speciation is high pH dependent.

Figure 2-1 shows the Pourbaix diagram of chromium.¹

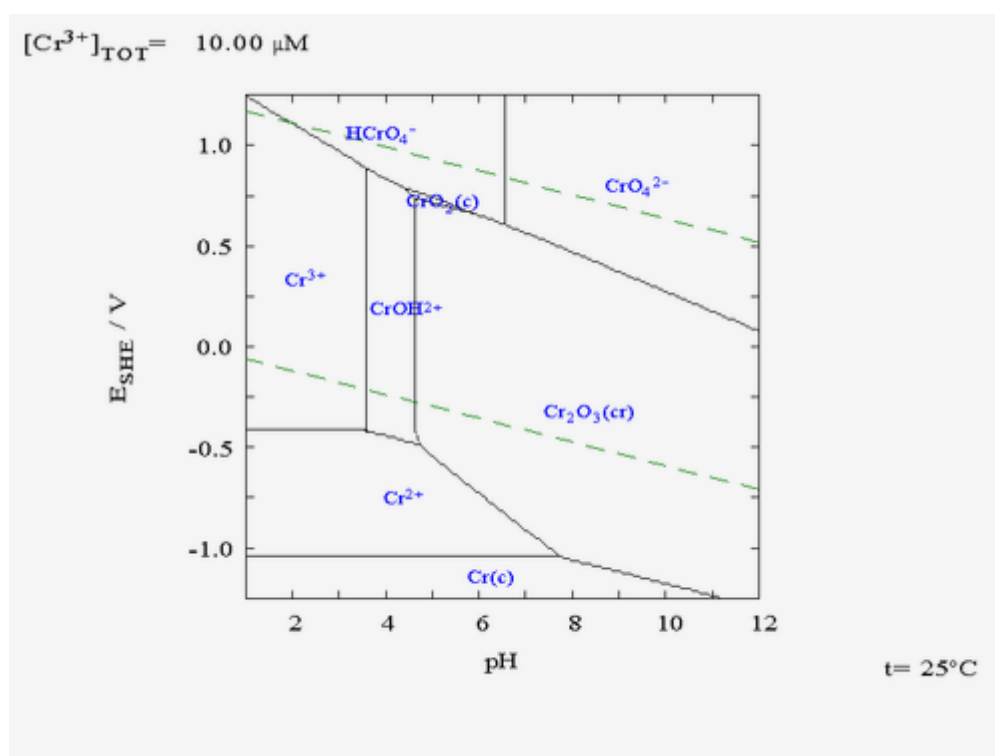


Figure 2-1: The Pourbaix diagram of chromium (from: www.wikipedia.org¹, Kotas and Stasicka⁵ and Ignasi⁷)

From this diagram, it is seen that the predominant form of chromium at low pH is Cr(III) which can take the form of the free Cr^{3+} ion or $CrOH^{2+}$. Only a small amount of Cr(VI) in the form of $HCrO_4^-$ is observed at low pH but this form tends to

predominate at high pH as the chromate (CrO_4^-) ion. This aspect of the chemistry of Cr(III) and Cr(VI) is important when considering the effect of pH on the uptake of Cr(VI) and is discussed further in Chapter 3.

2.2.4 The Toxicity of Chromium

Both the trivalent (Cr(III)) and hexavalent (Cr(VI)) forms differ with respect to their properties and toxicities. Cr(III) is known to be a less toxic and a less mobile form of chromium. As a result only small amounts of Cr(III) can enter cells¹ but high concentrations of Cr(III) in cells can lead to DNA damage.⁸ However, Cr(III) is also considered as an important dietary supplement.⁸

By contrast, Cr(VI) is a highly toxic and mobile form of chromium whose acute oral toxicity is known to range between 50-150 μg per kg.⁹ One of its most notable toxic effects is as a carcinogen where it can cause a multitude of cancers.¹⁰ Its role as a carcinogen dates back to 1890 where the cancer risks of the employees of a chromate dye company were reported.^{11,12}

Cr(VI) is also known to cause chronic dermatitis and mucousal ulcerations.^{13,14} Workers in the electroplating, tanning and chrome-producing industries face the greatest risk of suffering from these toxic effects.¹⁵

The toxic action of Cr(VI) stems from its properties as an oxidant.⁹ It is known to cause damage to the kidneys, liver and blood cells due to its ability to act as a strong oxidant thereby leading to conditions such as haemolysis, kidney and liver failure.

Since the toxic effects of Cr(VI) can be lethal, organisations such as the World Health Organisation (WHO) have restricted its maximum allowable intake to 0.05 milligrams per litre.¹

2.2.5 The Industrial Uses of Chromium

Chromium is a useful element in the metallurgical industry where it is used for electroplating.¹ Another metallurgical application is in the stainless steel industry where about 18% chromium is incorporated into stainless steel.⁴

Chromium is also used in the dye and pigment industry in the form of PbCrO_4 which is commonly known as chrome-yellow.¹ Other chromium compounds that are of use to the dye industry include $\text{PbCrO}_4 \cdot \text{Pb(OH)}_2$ (chrome red) and Cr_2O_3 (chrome oxide green).¹⁶

The tanning industry also makes use of chrome alum and chromium(III) sulphate for the tanning of leather where Cr(III) helps to stabilise the leather by crosslinking collagen fibres.¹⁷ Chromium normally comprises 4-5% in leather and is bound to proteins.¹⁸

Another important industrial application of chromium is in the refractory industry where chromite and chromium(III) oxide are used in blast furnaces, cement kilns etc.¹ However, this use has been phased out due to a possible formation of Cr(VI) and its toxicity.¹⁹

2.3 Mercury

Mercury was discovered by the Chinese²⁰ and also by Egyptians where it was used in ancient Egyptian tombs.²¹ It has the chemical symbol Hg and an atomic number of 80. It has a characteristic, silvery appearance, is one of six elements which exists as a liquid at room temperature and is also one of the d-block (transition) elements.^{22,23}

2.3.1 The Occurrence of Mercury

Mercury is mostly distributed throughout the world as cinnabar (mercury(II) sulphide).²⁴ The most common natural source of mercury is from volcanic eruptions which result in about 50% of the atmospheric mercury emissions.

However, anthropogenic activities have also led to elevated levels of mercury in the environment. The distribution of mercury from the various anthropogenic sources is given in **Figure 2-2**.

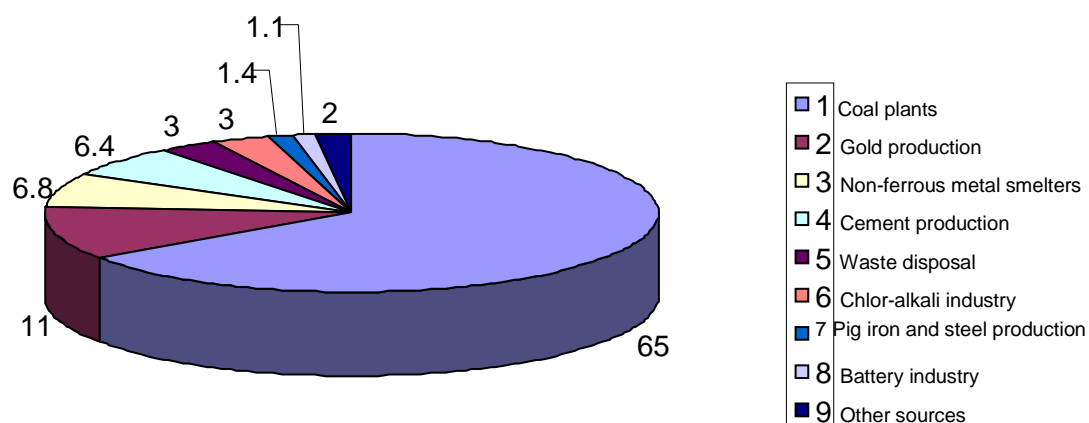


Figure 2-2: The distribution of mercury from various anthropogenic sources (Compiled from information given in Pacyna et. al.²⁵ and Solnit²⁶)

It is seen from **Figure 2-2** that most of the mercury released into the environment as a result of anthropogenic activities is via mercury emissions from coal plants. This releases mercury vapour into the atmosphere which can undergo interconversions into other forms of mercury (See Section 2.3.3)

2.3.2 The Physical Properties of Mercury

The physical appearance of elemental mercury is usually silvery.²⁷ Like chromium, mercury is also one of the transition metals but is a poor conductor of heat and conducts a fair amount of electricity. It also has an unusually low melting point of $-38,83^{\circ}\text{C}$, a boiling point of $356,73^{\circ}\text{C}$ and a density of $13,534\text{ g cm}^{-3}$.²⁸

2.3.3 The Chemical Properties and Speciation of Mercury

Mercury can form amalgams with most metals except for iron, tantalum, tungsten and platinum.²⁴ One of the most common reactions of mercury is its reaction with oxygen to form mercury oxide.²⁹ However, the reactivity of mercury under environmental conditions depends largely on its speciation. The predominant forms of mercury which exist under environmental conditions include elemental mercury, (Hg^0), monovalent mercury, (Hg^{1+}), divalent mercury (Hg^{2+}), methyl mercury (CH_3Hg^+) and dimethyl mercury ($(\text{CH}_3)_2\text{Hg}^+$).³⁰ **Figure 2-3** shows how both the inorganic and organic forms of mercury can interconvert under environmental conditions.

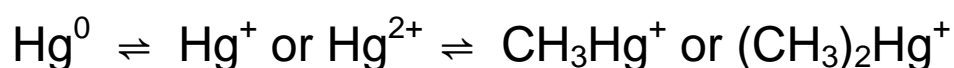


Figure 2-3: The interconversions of the different forms of mercury under environmental conditions (from: Okoronkwo et. al.³⁰)

Essentially elemental, monovalent and dimethyl mercury can be interconverted by oxidation-reduction reactions. This can happen in the presence of oxidising and reducing agents which can exist under environmental conditions. These include sulfites (from atmospheric SO_2) which can reduce divalent and monovalent mercury to elemental mercury and aqueous bromine which oxidises elemental mercury in aqueous environments.^{31,32}

The ionic inorganic forms can also interconvert to the organic forms by methylation processes. Sulphate-reducing bacteria, methylcobalamin, methyl iodide and methyl tin compounds are primarily responsible for methylation of inorganic mercury and exposure to sunlight can result in the demethylation of organic mercury.^{21,30}

As in the case of chromium the predominant species of mercury is highly pH dependent. **Figure 2-4** shows the Eh-pH diagram of mercury.

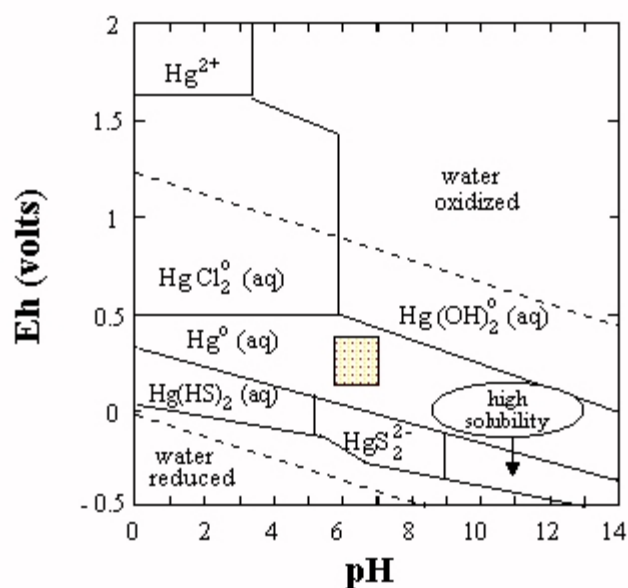


Figure 2-4: The Eh-pH diagram of mercury (From: Baeyens et.al.³³)

Figure 2-4 clearly shows that divalent mercury predominates at low pH. This is primarily in the form of HgCl_2 and Hg-S complexes. The predominance of the Hg-S complexes stems from mercury's high affinity for sulphur which is based on hard and soft acid-base (HSAB) theory where Hg(II) is a hard acid and tends to bond readily with soft bases like sulphides and sulfhydryls^{30,34,35} Other sulphur-containing species such as $\text{Hg}_2(\text{SH})_2$ are also known to exist.³⁶

$\text{Hg}(\text{OH})_2$ predominates at high pH. Other hydroxy species of mercury such as $\text{Hg}(\text{OH})_3^+$, HgOH^+ are believed to exist at very high pH.^{37,38,39,40} This is again critical in understanding the effect of solution pH on the uptake of mercury ions.

2.3.4 The Toxicity of Mercury

An interesting aspect of the toxicity of mercury is that each form of mercury has its own toxicity. The organic forms of mercury (methyl mercury and dimethyl mercury) are by far the most toxic forms.^{24,41} This is due to their ability to bioconcentrate and biomagnify in living organisms especially in fish where methyl mercury bioconcentrates. This led to the notorious Minamata disease in Minamata, Japan where a number of the local occupants suffered from symptoms such as ataxia,

numbness of the limbs, impaired vision, hearing and speech, insanity, paralysis, coma and even death as a result of consuming too much fish that had been contaminated with methyl mercury.²⁴ A similar incident occurred in Cato Ridge, South Africa in April 1990 where the workers of a local chemical company suffered severe symptoms of mercury poisoning due to occupational exposure to organic mercury.⁴²

However, elemental mercury, particularly mercury vapour is also toxic. Case studies have reported incidents where workers have suffered from symptoms such as tremors, impaired cognitive skills, sleep disturbances, interstitial pneumonitis and psychotic reactions as a result of occupational exposure to mercury vapour in concentrations ranging from 0.7 - 42 $\mu\text{g}/\text{m}^3$ and 1.1 - 44 mg/m^3 .^{43,44,45,46} The ingestion or inhalation of the dusts of inorganic mercury compounds such as cinnabar can also lead to toxic effects.⁴⁷ Mercury(II) salts are also more toxic than mercury(I) salts since these salts are more soluble in water and can therefore be adsorbed from the gastrointestinal tract more easily.⁴⁸

The toxic action of mercury results from its high affinity for sulphur. Inorganic mercury(II) salts can readily bind to the thiol groups of amino acids such as cysteine thereby leading to protein damage.⁴⁸ Unlike the organic forms of mercury, these salts are not lipid soluble and therefore cannot cross the blood-brain barrier. The ability of the organic forms to cross the blood-brain barrier renders these forms more toxic than inorganic mercury.

The severe toxic effects of mercury has therefore led organisations like USEPA to impose a nil concentration of mercury in drinking water.³⁷ Thus, the complete removal of mercury from industrial effluents and contaminated water bodies is essential.

2.3.5 The Industrial Uses of Mercury

Mercury is a useful element in a number of industrial sectors. These include the medical industry where its most common use is as amalgam in dentistry.³⁷ Other medical uses include the use of thimerosal as a preservative for vaccines but this use has declined due to the toxicity of mercury.⁴⁹

The most common industrial use of mercury is in the chlor-alkali industry where sodium hydroxide and chlorine are produced by redox processes and mercury acts as the cathode in these processes.^{50,51} This includes the Castner–Kellner process which employs the use of a sodium-mercury amalgam as the cathode.^{51,52} Other industrial applications of mercury include the mining of metals such as copper, zinc, gold and silver, oil refining, paint, rubber-processing, metal-plating, tanning, production of fertilisers and waste incineration.^{37,52,53,54} It is these industrial uses of mercury which contribute to anthropogenic sources of mercury in the environment. Hence, the need to remediate wastes generated by these industries has arisen.

2.4 Treatment Technologies Employed for the Removal of Chromium and Mercury

The most common methods that have been used for the treatment of wastes containing chromium and mercury include reduction/chemical precipitation, reverse osmosis, ion-exchange and adsorption by activated carbon and other low cost adsorbents. These are discussed in detail below.

2.4.1 Reduction/chemical Precipitation

Since Cr(III) is deemed to be a less toxic form of chromium, a common method of eliminating Cr(VI) from industrial wastes is to reduce Cr(VI) to Cr(III) and to precipitate the chromium as $\text{Cr}(\text{OH})_3$, which is subsequently disposed of in a landfill. The four primary steps in this process therefore involve⁵⁵;

1. The reduction of Cr(VI) to Cr(III)

2. The precipitation of Cr(III) as Cr(OH)₃ at high pH.
3. The settling of the insoluble precipitate
4. Disposal of the dewatered sludge into a landfill.

However, this process presents a number of disadvantages: namely the incomplete removal of chromium, high costs of chemicals and the production of undesirable sludges.^{56,57,58,59,60,61,62,63,64,65} Concerns have also been expressed about the safety of the disposal of the Cr(III) sludge especially since there is enough evidence in the literature to reveal that Cr(III) can reoxidise to Cr(VI) upon exposure to manganese oxides..^{66,67,68,69}

In a similar manner mercury has been eliminated from industrial wastes by sulphide precipitation. A common method that is used is the Sulphur Polymerisation Stabilization/Solidification Method (SPSS) method.⁷⁰ In this method, elemental mercury is reacted with a sulphur polymer cement to produce cinnabar, HgS with reduced leachability and vapour pressure.^{34,38,71,72,73,74,75,76,77} The cinnabar is subsequently disposed of in a landfill.

This process again presents disadvantages such as incomplete removal, high costs of chemicals and the production of an undesirable sludge. As discussed earlier, the inhalation of cinnabar dust can lead to toxic effects.⁴⁷

2.4.2 Reverse Osmosis

Reverse osmosis is a separation technique whereby pressure is used to force a solution through a membrane such that the solute is retained on one side and the solvent passes through the other side of the membrane.⁷⁸ This is therefore the opposite of normal osmosis where the solvent moves from an area of low solute concentration to an area of high solute concentration through a selectively permeable membrane and no external pressure is applied.⁷⁹

Reverse osmosis has been employed for the removal of Cr(VI)^{80,81} and Hg.⁸² Although recent studies have shown that up to 99% chromium can be removed by reverse osmosis and that this method is more efficient than biological and conventional chemical methods⁸¹, reverse osmosis is still disadvantageous in that it is a technology which can allow contaminants of small size to easily pass through the membrane, it sometimes eliminates essential minerals like calcium and magnesium from drinking water, the membrane filters are expensive, the running costs are high and the membrane filters are bulky and consume a lot of storage space.⁸³

2.4.3 Ion Exchange

Ion exchange is a method of water treatment whereby cations and anions can be extracted from water using an ion-exchange resin.⁸⁴ Since both cations and anions can co-exist in water supplies, both cationic and anionic exchange resins are used to treat water.⁸⁵ The cation exchangers are used to remove anionic contaminants by electrostatic interactions. Likewise, the anionic exchangers are used to remove cationic contaminants.⁸⁵

There have been reports in the literature on the removal of chromium and mercury by ion-exchange.^{86,87,88,89,90,91} However, ion-exchange presents disadvantages such as lack of selectivity and high costs since the ion-exchange resins are expensive.^{65,85} Other disadvantages of this process are outlined in **Table 2-18**.⁶⁵

2.4.4 Adsorption by Activated Carbon

Activated carbon is an impure form of graphite which is amorphous and highly porous in nature⁶⁵ Both the porosity and the large surface area of activated carbon have rendered it suitable for adsorption applications.⁹² The extent of porosity is defined largely by the method of activation.⁶⁵

In the sections that follow, the use of activated carbon as an adsorbent (particularly for Cr(VI) and Hg remediation) is critically reviewed. The mechanisms of removal are also discussed and the limitations of activated carbon as an adsorbent are discussed to motivate why the focus has shifted towards other low cost adsorbents and nanosorbents.

2.4.4.1 Adsorption of Cr(VI)

Activated carbon has been widely used for the uptake of various contaminants from water including Cr(VI). It has even been shown that synthetic high performance activated carbons perform better at removing Cr(VI) than activated carbons derived from coconut shells where over 97% adsorption was achieved.^{93,94} Rana et. al.⁹⁵ also showed that carbon aerogel (a high surface carbon) can remove up to 98% Cr(VI) but this involves an electrochemical process which is expensive.

Some studies have shown that activated alumina is a better adsorbent for Cr(VI) removal when compared to activated charcoal⁶ and activated rice husk carbon⁹⁶ Furthermore, since high quality activated carbon (HAC) is expensive⁶⁵ current studies have focused more on using activated carbons that have been derived from cheaper and readily available materials. Such studies are summarised in **Table 2-1**.

The data in **Table 2-1** shows that the use of low cost activated carbons have been successful in the sense that good uptake capacities have been observed in most cases. However, it is evident from the studies conducted to date that the extents of desorption observed were less than 100%. Chemical affinity competition studies have also been scarce. In some cases the uptake capacities have also been inferior to that of high quality activated carbon (HAC).

Table 2-1: A Summary of the Studies Undertaken for the Removal of Cr(VI) by Activated Carbons Derived from Low Cost and Readily Available Materials

Type of activated Carbon	Key observations	Shortcomings	Reference
Coconut tree sawdust	Maximum uptake capacity of 3,6 mg per gram activated carbon observed.	1. Effect of competing anions was not studied. 2. Impure form of activated carbon was used. 3. Mechanism of adsorption not clearly elucidated.	Selvi et.al. ⁶²
Granular and powdered activated carbons derived from different materials and different activation methods	1. The porosity of the activated carbons did play a key role in the uptake of Cr(VI). 2. Physically activated carbons were more suitable for this purpose . 3. Oxygen surface groups could play role in the uptake process.	No experimental evidence for the role played by functional groups.	Perez-Candela et. al. ⁹⁷
<i>Terminalia arjuna</i> nuts	1. Activation with ZnCl ₂ imparted porosity to the material which rendered this suitable for the uptake of Cr(VI). 2. Kinetic studies showed that the adsorption process was a first order process.	The results contradict those of Perez-Candela et.al. ⁹⁷ where adsorption occurred without functional groups.	Mohanty et. al. ⁹⁸

Type of activated Carbon	Key observations	Shortcomings	Reference
<i>Casurina Equisetifolia</i> leaves	<ol style="list-style-type: none"> 1. High adsorption efficiencies. 2. Materials could be regenerated and reused without a loss in adsorption efficiency. 	Only about 80% desorption of Cr(VI) was achieved.	Ranganathan ⁹⁹
Activated cow dung carbon	<ol style="list-style-type: none"> 1. Sufficient evidence for a chemisorption process presented. 2. First order kinetics for the adsorption process. 	<ol style="list-style-type: none"> 1. Concentrations in ppm scale. 2. Only 90% removal observed. 	Das et.al. ¹⁰⁰
Reed black liquor	Uptake capacity of 53,71 mg/g	Did not report on the effect of competing anions.	Sun et. al. ¹⁰¹
Almond shell	<ol style="list-style-type: none"> 1. 99,99% Cr(VI) removal was attained. 2. Material compared well with other adsorbents. 3. The adsorption process was highly pH dependent and the optimum pH was 1. 	Focus was only on the uptake of ppm levels of Cr(VI).	Demirbas et.al. ^{102, 103}
Olive bagasse	<ol style="list-style-type: none"> 1. The adsorption process was highly pH dependent and the primary species of Cr(VI) that was adsorbed was HCrO_4^-. 2. The extent of adsorption increased with temperature. 	The maximum uptake of Cr(VI) observed was only 54%.	Demiral et. al. ¹⁰⁴
Hazelnut shell	1. Highest adsorption capacity (170 mg/g).	Only effective for ppm levels	Kobyas ¹⁰⁵

Type of activated Carbon	Key observations	Shortcomings	Reference
Fertiliser waste material	Good uptake capacity of 16.18 mg/g.	Lower uptake capacity than HAC.	Srivastava et. al. ¹⁰⁶
Rice-husk based activated carbon	Effective adsorption of Cr(VI).	Only worked with a concentration range of 5-60 mg/l.	Guo et. al. ¹⁰⁷
<i>Tamarind wood</i>	Up to 99% adsorption of Cr(VI) from wastewater could be achieved.	Worked with ppm concentrations of Cr(VI).	Acharya et. al. ¹⁰⁸

2.4.4.2 The Effect of Surface Functional Groups on the Uptake of Cr(VI) by Activated Carbon

Different reports and postulates on the effect of surface functional groups on the uptake of Cr(VI) have been presented in the literature. These reports are outlined in **Table 2-2**.

The information presented in **Table 2-2** alludes to the fact that surface treatment and chemical modification of activated carbon favours Cr(VI) uptake. There are some contradictions in the studies by Aggrawal et. al.¹⁰⁹ and Park and Jung¹²⁰ which indicate that the introduction of oxygen-containing functional groups and surface modification by copper plating did not favour the uptake of Cr(VI). In both cases, the authors account for this in terms of a negative surface charge imparted by both the functional groups and copper plating but have not supported their postulates with the relevant point of zero charge (pH_{pzc}) data.

Table 2-2: Reports on the Effect of Surface Functional Groups on the Uptake of Cr(VI) by Activated Carbon

Reference	Main Observations
Aggrawal et. al. ¹⁰⁹	Oxygen-containing functional groups introduced by acid-treatment impart a negative surface charge which favours the uptake of Cr(III) and hinders the uptake of Cr(VI).
Park and Kim ^{110,111} and Liu et. al. ¹¹²	The introduction of acid surface functional groups via anodic surface treatment of activated carbons with HCl and oxidative acid and base treatment enhanced the uptake of Cr(VI).
Park and Jang ¹¹³ , Ghosh ¹¹⁴ , and Liu et. al. ¹¹⁵	Acid and base-treated activated carbons favoured the uptake of Cr(VI) by introduction of surface oxygen groups.
Zhao et. al. ¹¹⁶	Chemically modified activated carbons performed better at the uptake of Cr(VI) especially when lactone groups were added by treatment with Fe(NO ₃) ₂ .
Giraldo-Gutierrez and Moreno-Pirajan ¹¹⁷	The uptake of both Pb(II) and Cr(VI) by activated carbons derived from sawdust and sugar cane husk was favoured by the presence of carboxylic acid groups.
Lach et. al. ¹¹⁸	The inclusion of acid functional groups onto activated carbon by oxidation with CO ₂ favoured both the uptake of Cr(III) and Cr(VI).
Park et.al. ¹¹⁹	The introduction of oxygen-containing functional groups by anodic oxidation of activated carbon enhanced Cr(VI) adsorption.

Reference	Main Observations
Park and Jung ¹²⁰	Copper plating was unfavourable for Cr(VI) removal.
Valix et. al. ¹²¹	Heteroatoms such as nitrogen and sulphur imparted basic properties to activated carbon and favoured the uptake of Cr(VI).
Harry et. al. ¹²²	Both electrochemically oxidised and reduced activated carbon cloth worked well for the uptake of Cr(VI).
Ko et. al. ¹²³	Ozone treatment of activated carbon fibres enhanced the uptake of Cr(VI).

2.4.4.3 Selectivity Studies on Cr(VI) removal

Some studies have also demonstrated that activated carbon is not very selective to the uptake of Cr(VI) in the presence of other species. These are highlighted in **Table 2-3**.

Table 2-3: The Selectivity Studies on Cr(VI) removal Conducted to Date

REFERENCE	MAIN OBSERVATIONS
Yavuz et. al. ¹²⁴	The adsorption of Cr(VI) decreased by about 10-25% when organic matter is present in wastewater.
Monser and Adhoum ¹²⁵	The selectivity of modified activated carbons for chromium uptake was poor in the presence of copper and zinc.
Di Natale et. al. ¹²⁶	Competing anions such as hydroxyl and chloride ions inhibited the uptake of Cr(VI).
Bautisto-Toledo et. al. ¹²⁷	The uptake of Cr(VI) by activated carbon can be hindered by the presence of humic acid.

The studies conducted to date have revealed that the selectivity of activated carbon for Cr(VI) removal is poor in the presence of other organic and inorganic pollutants. Monser and Adhoum¹²⁵ attempted overcoming this problem by modifying the surface of activated carbon with tetrabutyl ammonium and sodium diethyl dithiocarbamate to improve the selectivity for inorganic pollutants such as cyanide, copper, zinc and chromium. This proved to be successful in the sense that better uptake capacities were observed for all inorganic pollutants when activated carbon was modified. The authors, however, did not demonstrate that this applied even when organic pollutants are present. Furthermore, the authors were also only able to reduce the concentrations of the metals to acceptable effluent levels. Thus, complete metal removal was not achieved.

There are also studies which have demonstrated that activated carbons can adsorb a variety of organic and inorganic pollutants but have not evaluated the selectivity of activated carbon for a specific pollutant. These studies are summarised in **Table 2-4**.

The literature analysis in **Table 2-4** has revealed that activated carbon can adsorb a range of organic and inorganic pollutants in single component systems but the selectivity for a specific pollutant in multi-component systems has not been demonstrated.. As an example, Namasivayam and Sangeetha¹²⁸ showed that oxyanions such as nitrates, phosphates, sulfates, molybdates and Cr(VI) could be successfully adsorbed in isolation but failed to consider possible chemical affinity competition between these ions due to their chemical similarity. This was in fact only achieved by Fang et.al.¹²⁹ who showed that there was a slight reduction in Cr(VI) uptake by an activated carbon quarternised with 4-vinyl pyridine in the presence of phosphates, sulfates and nitrates.

Table 2-4: Studies on the Adsorption Performances of Activated Carbon for a Variety of Pollutants

REFERENCE	MAIN OBSERVATION	SHORTCOMING
Namasivayam and Sangeetha ¹²⁸	ZnCl ₂ activated coir pith carbon was effective at adsorbing a variety of inorganic anions and cations as well as a variety of organic contaminants including dyes. Uptake capacities in the range of 90-100% were observed.	The adsorption performance of this type of activated carbon in multi-component systems was not examined.
Gonzalez-Serreno et. al. ¹³⁰	Activated carbons produced by H ₃ PO ₄ activation were effective for the removal of phenol, 2,3,4 trichloro-phenol and Cr(VI).	Did not study the competitive adsorption of the ion that may have occurred in a ternary system containing all of these components.
Duman et.al. ¹³¹	Activated carbon derived from pine cone was better at adsorbing phenol, methylene blue and Cr(VI) when activated with ZnCl ₂ .	Did not report on the relative selectivities of this adsorbent for all three contaminants.
Giraldo-Gutierrez and Moreno-Pirajan ¹¹⁷	Studied the uptake of Pb(II) and Cr(VI) by activated carbons derived from sugar cane husk and sawdust	Did not study the chemical affinity competition between these ions for active adsorption sites in a binary system.
Hasar and Cuci ¹³²	Report high removal rates for Cr(VI) , Cd(II) and Cu(II)	Did not examine the selectivity in a ternary system.

Other studies in multi-component systems have been attempted but few have been successful at the selective uptake of Cr(VI). These are outlined in **Table 2-5**

Table 2-5: Selectivity Studies on Cr(VI) Removal in Multi-component Systems

Reference	Study Undertaken	Result
Wu et.al. ¹³³	The uptake of Cr(VI) and As(III) in a binary system.	The uptake of both metal ions was synergistic where the uptake of As(III) was enhanced in the presence of Cr(VI) but did not show any selective uptake of either metal ion.
Di Natale et. al. ¹³⁴	Presented a model which predicted that activated carbon shows a greater affinity towards metal ions with higher charges.	More selectivity to the uptake of As(V) than for Cr(VI), Cr(III) and Cd(II).
Choi et. al. ^{135,136}	Improved uptake capacity of activated carbon for Cr(VI) by modifying the surface with a cationic surfactant and increasing the number of positively charged surface sites for the adsorption of anionic Cr(VI).	Did not evaluate the ability of the modified activated carbons to adsorb Cr(VI) in the presence of competing anions and therefore did not show any selectivity of these materials for Cr(VI) adsorption

The studies reported thus far therefore show the selectivity for Cr(VI) in the presence of other pollutants is either poor or has not been established. The work of Hong et. al.¹³⁷ also shows that the efforts of Choi et.al.^{135,136} were not appropriate since chemical affinity competition among anionic contaminants can occur in a ternary system in surfactant modified activated carbons.

It is only the work of El Nemr et. al.¹³⁸ which conclusively showed any selectivity of activated carbon for a metal ion. These workers showed that the adsorption capacity of activated carbons derived from date palm seed (for Cr(VI)) did not decrease when sodium chloride was added to the chemical matrix and noted that the uptake capacity did not change even when Cr(VI) was removed from real wastewater. The authors did, however, acknowledge that the concentrations of other pollutants in the wastewater may have been too low to present any significant competition to the uptake of Cr(VI). The studies did not examine the effect of competing oxyanions. In a subsequent study El Nemr¹³⁹ also demonstrated that the uptake of Cr(VI) onto activated carbon derived from pomegranate husk is hindered by the presence of NaCl. Thus the type of carbon used for adsorption studies can influence the uptake capacities.

2.4.4.4 The Uptake of Hg by Activated Carbon

Similar studies on the uptake of mercury particularly Hg(II) by activated carbon originating from low cost materials have also been initiated. These are summarised in **Table 2-6**.

The data presented in **Table 2-6** has shown that the uptake of Hg(II) by activated carbons derived from low cost materials has been successful in some cases where 100% removal has been achieved. However, the major problems seem to arise with desorption and regeneration where a 100% desorption has yet to be achieved. This problem is highlighted in studies undertaken by Ekinci et. al.¹⁴⁰ and Budinova et. al.¹⁴¹ who observed low extents of desorption of Hg(II) from activated carbons derived from furfural and low rank Turkish coals respectively. These authors explained the low extents of desorption as due to a chemisorption process. The possibility of using another desorption medium which could reverse the chemisorption was not considered.

Namasivayam and Periasamy¹⁴² observed only 47% desorption of Hg(II) from peanut hull activated carbon using 0,6 M HCl and 87% desorption in 0,6 M HCl

and 1% KI. Similar results were again achieved by Namasivayam and Kadirvelu¹⁴³ who observed 63% desorption in 0,5 M HCl and 84% desorption in 2% KI from an activated carbon derived from coirpith. Thus, the studies conducted to date seem to indicate that a higher desorption is achieved in KI than in HCl but the desorption in KI is still not 100%.

Table 2-6: A Summary of the Studies Undertaken on the Uptake of Hg(II) by Activated Carbon Derived from Low Cost Materials

TYPE OF ACTIVATED CARBON	MAIN RESULTS	SHORTCOMINGS	REFERENCE
Antibiotic Waste	1. Uptake capacity of 129 mg/g. 2. Uptake capacity was higher than that of granular activated carbon and activated carbon derived from peanut hull.	Uptake capacity was still lower than that of activated carbon derived from coir pith and furfural.	Budinova et. al. ¹⁴⁴
Various types of activated carbon	100% uptake of Hg(II).	The observation for the influence of pH was contrary to that of other workers.	Huang and Blankenship ¹⁴⁵
Sewage sludge	Recovered Hg(II) as Hg (0) by modification with TiO ₂ .	Only recovered 40-65% mercury.	Zhang et. al. ¹⁴⁶
Walnut shell	Reported an uptake capacity of 151.5 mg/g.	Did not examine the selectivity of the adsorbent for Hg(II).	Zabihi et. al. ¹⁴⁷
<i>Terminallia catappa</i>	100% removal of Hg(II).	Achieved incomplete desorption.	Inbaraj and Sulochana ¹⁴⁸

Furfural	Uptake capacity of 174 mg/g.	Only 4-6% desorption in hot water	Yardim et. al. ¹⁴⁹
Agricultural waste	Desorption increased with increase in HCl conc.	Only 79% desorption achieved.	Rao et. al. ¹⁵⁰

Studies on the uptake of Hg(II) by sulphur modified activated carbons have also been undertaken. These are summarised in **Table 2-7**.

Table 2-7: Studies on the Uptake of Hg(II) by Sulphur Modified Activated Carbons

REFERENCE	MAIN OBSERVATIONS
Mohan et. al. ¹⁵¹	Treating an activated carbon derived from fertilizer waste with sulphur significantly enhanced the mercury uptake rates.
Krishnan and Anirudhan ¹⁵²	Sulfurised activated carbons adsorbed Hg(II) to a better extent than unmodified steam activated carbon and observed that the uptake capacity increased with increasing sulphur content
Cai and Jia ¹⁵³	The mercury uptake capacities of sulphur impregnated activated carbons derived from oil sands fluid coke by KOH-SO ₂ activation were comparable to the commercial analogues and indicate that the predominate forms of sulphur that are effective in Hg(II) removal are elemental sulphur, disulfide and thiophene.
Mullet et .al. ¹⁵⁴	Removed Hg(II) from digestion condensate using silver and sulphur impregnated activated carbons.but noted that these materials were highly unstable in digestion condensate.

The studies reported in **Table 2-7** reveal that incorporating sulphur into activated carbon enhances the uptake of Hg(II) which is not surprising since mercury does have a high affinity for sulphur. However Krishnan and Anirudhan¹⁵² also indicate that some adsorption could have also been due to carboxylic acid groups present on the activated carbon and the study by Mullet et. al.¹⁵⁴ also indicated that sulphur impregnated activated carbons are unstable in a digestion condensate.

2.4.4.5 The Uptake of Hg Vapour by Activated Carbons

Studies using both low cost activated carbons and sulphur impregnated activated carbons have also been extended to the uptake of mercury vapour. These studies are outlined in **Table 2-8**.

Table 2-8: Studies on the Uptake of Mercury Vapour by Low Cost and Sulphur Impregnated Activated Carbons

TYPE OF ACTIVATED CARBON	MAIN RESULTS	DISADVANTAGE	REFERENCE
Powdered and granulated activated carbons impregnated with sulphur	Achieved up to 99% removal of mercury vapour.	The adsorption process was highly exothermic and the extent of adsorption was hindered at higher temperatures.	Yan et. al. ¹⁵⁵
KOH activated carbon derived from olive seeds	Showed the best results for the uptake of mercury vapour.	The amount of KOH required for activation could increase production costs.	Skodras et. al. ¹⁵⁶
Activated carbon modified with 3% CeO ₂	Improved mercury vapour uptake capacities.	This adsorbent has poor anti-temperature performance.	Tian et. al. ¹⁵⁷

TYPE OF ACTIVATED CARBON	MAIN RESULTS	DISADVANTAGE	REFERENCE
Range of activated carbons	The uptake of mercury vapour was enhanced by the presence of sulphur.	Showed variable adsorption performance in the presence of competing gases.	Yan et. al. ¹⁵⁸

The studies conducted on the uptake of mercury vapour have therefore also been successful in the sense that high uptake capacities have been observed. However, the disadvantages observed range from poor performance at high temperatures to poor selectivities in the presence of competing gases. In some cases, solutions to the problems have been proposed. For example, Skodras et. al.¹⁵⁶ stated that regeneration and reusability should solve the problem of production costs but they did not present any data to support this proposal. In other cases further problems have been highlighted. Yaji et. al.¹⁵⁹ for instance explored the possibility of using activated carbon derived from CO₂ which is generated from chicken waste but indicated that this is not suitable for injection into flue gas containing mercury due to poor mass transfer properties.

The effect of a range of gases on the uptake of mercury vapour has been extensively studied and different reports have been presented. In a recent study Diamantopoulou et. al.¹⁶⁰ showed that mercury uptake was enhanced in the presence of HCl, O₂ and SO₂ and accounted for this in terms of the presence of these gases promoting the chemisorption of mercury. These authors also presented experimental evidence for the inhibition of mercury uptake by CO₂. Zhang and Bishop.¹⁶¹ also showed that reactivating powdered activated carbon in CS₂ enhanced mercury uptake capacities.

The above observations were however contradicted by studies by O' Dowd et. al.¹⁶² who showed that sulphur-modified activated carbons did not significantly

enhance the uptake of mercury vapour. Presto and Granite¹⁶³ also made contrary observations where it was shown that sulphur introduction via H_2SO_4 hindered the uptake of mercury vapour. These authors noted that the uptake of mercury vapour was reduced by about 80% in the presence of SO_2 and SO_3 due to competition for active sites on activated carbon. They have also verified these findings in a subsequent study¹⁶⁴. This is supported by the studies of Olson et. al.¹⁶⁵ who observed that acidic gases hinder the uptake of mercury vapour by activated carbon. Recently, Ochiai et. al.¹⁶⁶ also noted that the presence of SO_2 suppresses the uptake of mercury vapour onto activated carbon. Sjostrom et. al.¹⁶⁷ attempted to improve the mercury removal capacity in the presence of SO_3 by injecting the activated carbon upstream but were still only able to achieve 58% mercury removal with a SO_3 injection system.

Nabais et. al.⁵³ on the other hand found that it was the method of sulphur introduction and the accessibility of sulphur functional groups to mercury rather than the actual sulphur content which influenced the uptake of both mercury(II) and mercury vapour by activated carbon fibres. These workers observed that sulphur introduction via a method involving the bubbling of H_2S onto the activated carbon fibres gave better results for the uptake of mercury than the introduction of sulphur via heating in elemental sulphur simply because the functional groups introduced by the H_2S method were more accessible to the mercury. This was in spite of the fact that the H_2S method resulted in a lower sulphur content (0.7% as opposed to 6%). The observations of these authors especially the accessibility and types of sulphur-binding sites was also reiterated by Korpiel and Vidic.¹⁶⁸, Liu et. al.¹⁶⁹ and Lee and Park¹⁷⁰. They all noted that commercial activated carbon containing oxygen functional groups had a superior adsorption capability to commercial activated carbon containing sulphur. Additionally Liu et.al.¹⁶⁹ noted that the sulphur impregnation temperature significantly influenced the mercury uptake capacity.

In a separate study, Skodras et. al.¹⁷¹ made an interesting observation that the removal of inorganic matter from activated carbon favoured the uptake of mercury

vapour by releasing lactone groups and supported this in another study.¹⁷² They attributed the uptake of mercury vapour by activated carbon to the presence of functional groups such as lactone groups but also indicated that other functional groups like phenolic groups can act as inhibitors. These authors also reported high uptake capacities by activated carbon impregnated with sulphur via chemisorption but did not report on the regeneration and reuse of these materials. Vitolo and Seggiani¹⁷³ made similar observations for the uptake of mercury vapour from a geothermal exhaust gas but again did not explore the possibility of regeneration and reuse. Pavlish et. al.¹⁷⁴ also indicated that activation is a necessary step by showing that unactivated sorbents were not very efficient at the uptake of mercury vapour. Feng et. al.¹⁷⁵ noted that the uptake of mercury vapour increased with increasing sulphur content but were unable to work out which form of sulphur gave the best results. Similar observations were made by Hsi et. al.¹⁷⁶ who also observed high mercury uptake capacities for activated carbon fibres impregnated with sulphur but could not conclude whether organic sulphur played a role in the adsorption process.

Lee et. al.¹⁷⁷ made similar observations for the uptake of mercury vapour by iodine-impregnated granular activated carbon where they noted that the adsorption capacity was not proportional to the iodine concentration. Additionally, these authors noted that while the uptake capacity of iodine impregnated activated carbons was independent of temperature the adsorption efficiency of chlorine-impregnated activated carbons decreased with increasing temperature.

In summary the findings suggest that the uptake of mercury vapour by the various forms of activated carbon depend largely on the type of activated carbon used. There have been some debates and contradictions involving the role played by heteroatoms particularly sulphur. Another important observation made is that competing gases can have different effects. In some cases these enhanced the uptake of mercury while in other cases some gases have inhibited the adsorption of mercury vapour.

2.4.4.6 Studies on the Uptake of Organic Forms of Mercury

The studies on the uptake of the organic forms of mercury have been more limited. These are summarised in **Table 2-9**.

Table 2-9: Limited Studies on the Uptake of Organic forms of Mercury

TYPE OF ACTIVATED CARBON	MAIN RESULTS	DISADVANTAGE	REFERENCE
Granular activated carbon	Observed up to 97% adsorption of thimerosal from industrial wastewater.	The adsorption was favoured by low pH but below pH 3 precipitation occurred and the authors could not identify the precipitate or the cause of precipitation.	Velicu et. al. ¹⁷⁸
Granular activated carbon	Developed a treatment process for the removal of thimerosal, Hg(II) and even copper and phenol from pharmaceutical waste.	The cost calculations of these workers showed that the process is expensive.	Cyr et. al. ¹⁷⁹
Sulphur impregnated activated carbons	Could remove up to 100% Hg in the form of mercury vapour and organomercury from gas condensate.	Did not report on the regenerability of these activated carbons.	Shafawi et.al. ¹⁸⁰

The studies on the uptake of organic forms of mercury have been successful. However, some inherent disadvantages such as undesirable precipitation at low pH have also been noted. Velicu et. al.¹⁷⁸ impregnated the activated carbons with sulphur but as per the findings of O'Dowd et.al.¹⁶² did not observe any appreciable

enhancement in the adsorption after the introduction of sulphur. The authors also indicated that the pre-acidification of the wastewater prior to remediation and pH neutralization after remediation could result in additional costs and the disposal of sludge.

2.4.4.7 Selectivity studies on Hg removal.

Studies on the effect of competing ions and other chemicals on the uptake of Hg have also been conducted. These are highlighted in **Table 2-10**.

Table 2-10: Chemical affinity competition studies on Hg removal by activated carbon

TYPE OF ACTIVATED CARBON	OBSERVATIONS	REFERENCE
Activated carbon derived from sago waste	The uptake of Hg(II) by is hindered in the presence of NaCl where Na ⁺ ions compete with Hg ²⁺ ions for active adsorption sites.	Kadirvelu et. al. ¹⁸¹
Granular activated carbon	Background chemicals in wastewater can interfere with the uptake of thimerosal by activated carbon and that pre-treatment may be necessary to ensure complete removal.	Velicu et. al. ¹⁷⁸
Sulphur impregnated activated carbons	The uptake of Hg(II) was hindered in the presence of NaCl even when activated carbon was sulfurised.	Krishnan and Anirudhan ¹⁵²
Sulphur-impregnated activated carbons.	The presence of both humic acid and chloride ions suppressed the uptake of Hg(II).	Wang et. al. ¹⁸²

TYPE OF ACTIVATED CARBON	OBSERVATIONS	REFERENCE
Carbon aerogel (a new form of activated carbon)	Had a higher uptake capacity for Pb(II) than Hg(II).	Goel et. al. ¹⁸³
Carbon aerogel	Selectively adsorbed Cd(II) over Hg(II) and Pb(II) in a ternary system.	Kadirvelu et. al. ¹⁸⁴
Carbon aerogel	Higher uptake capacity for Cd(II) and Cu(II) than for Hg(II) using the Langmuir model and a higher uptake capacity for Cd(II), Cu(II) and Ni(II) using the Freundlich model.	Meena et. al. ¹⁸⁵
Wood-based granular activated carbon	<p>1. More selective to the uptake of Cd(II) than the uptake of Hg(II).</p> <p>2. An ion exchange resin had a better uptake capacity for these divalent ions than this form of activated carbon.</p>	Rangel-mendez and Streat. ¹⁸⁶
Activated carbon derived from flax shive	The uptake of Hg(II) by was hindered by the presence of Na ⁺ , K ⁺ , Mg ²⁺ and Ca ²⁺ .	Cox et. al. ¹⁸⁷

Selectivity studies involving the uptake of mercury have generally failed to demonstrate any selectivity for this ion even when sulphur is incorporated into activated carbon. Some workers have neglected to examine the competitive effects of other ions in binary and ternary systems. For example, Baghel et. al.¹⁸⁸ showed that activated carbon can adsorb up to 99% Pb(II), Cu(II), Hg(II) and Mn(II) but did not evaluate the selectivity of this adsorbent in a multi-component system. Yusof et. al.¹⁸⁹ report that zirconium modified activated carbon is effective for the pre-concentration of As(V), Hg(II) and Cr(VI) by adsorbing reduced

forms of these metal ions but it is unclear whether this adsorbent preferentially adsorbs one ion over the other. El-Shafey¹⁹⁰ showed that an activated carbon derived from rice husk was more effective at adsorbing Hg(II) than Zn(II) but did not provide any experimental evidence of this for a binary system in which both ions co-exist. This author also indicated that even though the adsorption efficiency is higher for Hg(II) the adsorption kinetics for the uptake of Zn(II) are faster.

Some studies have also proposed ways of eliminating the effects of competing ions. For instance Zhang and Bishop¹⁶¹ showed that interference from chloride ions can be reduced by solidifying reactivated carbon in Portland cement but this is yet to be extended to interferences from competing divalent cations.

The work of Starvin and Rao¹⁹¹ however showed high selectivity for Hg(II) removal by activated carbon functionalised with 1-(2-thiazolylazo)-2-naphthol in the presence of competing divalent alkaline-earth cations and even from complex chemical matrices like brine sludge and a chloralkali effluent. These authors did not report on the regenerability of the adsorbent. Srinivasen and Sathiya¹⁹² have shown that an activated carbon derived from cotton seed was effective at simultaneously removing Pb(II) and Hg(II) from aqueous solution. The uptake capacity of Hg(II) was only slightly better than that of Pb(II) and up to 99% of both metal ions could be removed when the carbon dosage was 100 mg. At the same time these authors also showed the uptake capacity of Hg(II) dropped from 99% to 95% when the ratio of Hg(II) to Pb(II) was increased from 2:1 to 4:1.

2.4.5 Mechanisms for Removal by Activated Carbon

2.4.5.1 Removal of Cr(VI)

Studies that have shed some light on the mechanism of Cr(VI) uptake by activated carbon are highlighted in **Table 2-11**.

Table 2-11: Studies on the Mechanism of Cr(VI) Removal by Activated Carbon

REFERENCE	PROPOSED MECHANISM
Selomulya et. al. ¹⁹³ ; Di Natale et. al. ¹²⁶	Direct adsorption of Cr(VI) followed by the reduction of Cr(VI) to Cr(III) on the activated carbon surface.
Mohan et. al. ¹⁹⁴	Electrostatic interactions between the ion and the adsorbent surface.
Bello et. al. ¹⁹⁵	Diffusion of the metal ions into micropores on the activated carbon surfaces.

Table 2-11 reveals that three different mechanisms of Cr(VI) adsorption on activated carbon can occur.

2.4.5.2 Removal of Hg

Studies on the mechanism of Hg uptake by activated carbon have indicated that a chemisorption process in which mercury interacts with heteroatoms such as sulphur, oxygen and chlorine predominates.¹⁷¹ As stated above this is supported by observations that the uptake of mercury is in some cases enhanced when sulphur is incorporated into activated carbon and the fact that better desorption is achieved in KI due to the formation of mercury iodide complexes.¹⁷¹ Further evidence is provided in the paper by Li et. al.¹⁹⁶ who showed that the presence of moisture on activated carbon is closely associated with oxygen complexes which provide more active sites for mercury uptake. This is to some extent supported by the findings of Kwon et. al.¹⁹⁷ who noted that the presence of moisture enhanced the uptake of mercury by both physisorption and chemisorption onto activated carbon. However, these workers also noted that oxygen-containing functional groups did not play a role in the chemisorption of mercury onto activated carbon. Zhu et. al.¹⁹⁸ noted that the introduction of functional groups containing nitrogen, sulphur and chlorine enhanced the mercury uptake capacity of activated carbon

by lowering the point of zero charge of the carbon surface and improving its cation exchange capacity.

Felsvang et. al.¹⁹⁹ also showed that iodine and sulphur impregnated activated carbons showed a superior uptake capacity for mercury vapour thereby suggesting an interaction between mercury and heteroatoms. Zeng et. al.²⁰⁰ proposed that the adsorption of mercury vapour onto ZnCl₂ activated carbon occurs by the formation of mercury chloro complexes which are created by the introduction of chlorine atoms. Further to these findings Mei et. al.²⁰¹ showed that a nitrogen-doped metal oxide loaded onto activated carbon enhanced the uptake of mercury vapour. Cui et.al.²⁰² observed high uptake rates for the removal of mercury vapour by activated carbons derived from chicken waste and coal. These authors have attributed this to the release of heteroatoms such as chlorine from chicken waste which can provide active binding sites for mercury. They did not provide experimental evidence for this proposal.

Morimoto et.al.²⁰³ made some interesting observations about the mechanism of the uptake of mercury vapour by activated carbon. These workers noted that the uptake of mercury vapour was enhanced both in the presence of H₂S and SO₂ at low temperatures. Another important observation included the fact the adsorption was independent of the presence of O₂. These authors were able to propose a mechanism involving the Claus reaction in which H₂S was partially oxidised to elemental sulphur in the presence of SO₂ and reaction of Hg(II) with sulphur gave HgS. This mechanism was validated by a visual observation of the formation of elemental sulphur on activated carbon but as discussed earlier, there are other studies which showed that SO₂ can suppress the uptake of mercury vapour.

Lee et. al.²⁰⁴ have also proposed a different mechanism for the uptake of mercury vapour by CuCl₂ impregnated activated carbons. These authors indicated that the mercury vapour, upon contact with the activated carbon surface, is oxidised to Hg(II) which is subsequently readsorbed onto the activated carbon surface. In

another study²⁰⁵ these authors showed that this process was dependent on the CuCl_2 injection rate. An increase in CuCl_2 injection increased the $\text{Hg}(0)$ oxidation but did not significantly increase the readsorption of $\text{Hg}(\text{II})$ and reduced the amount of CuCl_2 active sites for $\text{Hg}(\text{II})$ readsorption.

2.5 The Limitations of Using Activated Carbon as an Adsorbent

The studies conducted on the uptake of Hg and $\text{Cr}(\text{VI})$ by activated carbon have in some cases shown good uptake capacities but have also highlighted some of the limitations of using this adsorbent. One of these limitations include poor selectivity especially in the presence other metal ions and contaminants.

The lack of selectivity of activated carbon for heavy metals is also reiterated by Mohan and Pittman⁶⁵ in their review article where they pointed out that the adsorption of heavy metal ions is more complex than the removal of organic pollutants. This arises since the charges on these ions affect the removal kinetics from solution. Other disadvantages of activated carbon reported in this review article include the incomplete removal of metal ions (milligrams of metal ions per gram adsorbent), problems with the regeneration process and the high cost of activated carbon which clearly does not favour its use in developing countries.

The incomplete removal of metal ions by activated carbon is proposed to relate mainly to its hygroscopic nature where it adsorbs moisture with time thereby losing its adsorption effectiveness.²⁰⁶ This can present problems with the uptake of hydrophilic substances⁶⁵ particularly $\text{Cr}(\text{VI})$ and $\text{Hg}(\text{II})$ which are highly hydrophilic and mobile. However, there are some contradictions to this proposal as the effect depends largely on type of species undergoing adsorption and the mechanism of adsorption. As stated earlier, the work of Li et. al.¹⁹⁶ and Kwon et. al.¹⁹⁷ showed that the presence of moisture on the surface of activated carbon

promotes the uptake of mercury vapour due to a close association with oxygen complexes.

Activated carbon is also not known to be an effective adsorbent for the uptake of trace or ppb levels of contaminants.²⁰⁷ Indeed most studies on the uptake of various contaminants including Cr(VI) by activated carbon have focussed on the uptake of ppm levels. There have thus been only a few reports on the uptake of ppb levels of these contaminants by activated carbon. These include the work of Starvin and Rao¹⁹¹ who reported >99% removal of 5 µg Hg(II). Gajghate et. al.²⁰⁸ showed that up to 100% Cr(VI) could be adsorbed as a diphenyl carbazide complex onto activated carbon when using concentrations ranging from 700-2600 ppb. Dobrowolski and Stefaniak²⁰⁹ also reported good uptake capacities of a 500 ppb solution of Cr(VI) by activated carbon.

Besides the limitations presented by the high cost of high quality activated carbon, poor selectivity to inorganic contaminants and its hygroscopic nature other disadvantages such as poor regeneration capacities and house-keeping problems have also been noted. Mei et.al.²¹⁰ were able to solve this problem for the uptake of gaseous mercury by loading an oxide of cobalt onto activated carbon and regenerating this adsorbent by heating in a nitrogen atmosphere. Ho et. al.²¹¹ also showed that elevated temperatures and fluidised bed conditions can enhance the desorption of mercury vapour from powdered activated carbon. However, this is yet to be achieved for the uptake of aqueous metal ions. Hamdaoui et. al.²¹² improved the desorption rates of selected metal ions from activated carbon by using ultrasound. Although the presence of ultrasound did enhance the desorption rates of all metal ions, this favoured the desorption of divalent cations such as Mn(II) over anions such as Cr(VI). The maximum desorption observed was only 43% for Mn(II). The lowest desorption rates were observed for Cr(VI) and Hg(II). Zhang et. al.²¹³ achieved better results by desorbing Hg(II) adsorbed onto an activated carbon from organic sewage sludge under sonication but even here only a maximum desorption of 80% was achieved. Thus, the desorption of these

specific metal ions from the surface of activated carbon was not optimized by the presence of ultrasound.

Hu et. al.²¹⁴, on the other hand showed that the extent of desorption of Cr(VI) from coconut shell activated carbon was favoured by mesoporosity. Contrary to these findings, Han et. al.²¹⁵ and Huang et. al.²¹⁶ showed that regenerated carbons could be reused for the uptake of Cr(VI) without presenting any serious problems. Graydon et. al.²¹⁷ presented experimental evidence that mercury that is sorbed on sulphur impregnated carbons is very stable and not easily released back into the environment and therefore proposed that these sorbents can be disposed of as landfill in the environment once the mercury has been sorbed. However, the toxic effects of activated carbon and the cost implications of resynthesising these materials were not considered.

The main disadvantages of using activated carbon are highlighted in **Table 2-18**. The studies conducted on the uptake of Cr(VI) and Hg by activated carbon have therefore revealed that although most forms of activated carbons have shown high uptake capacities for both metals, selectivity, re-use and regenerability remain a problem. There have been few reports on a type of activated carbon which demonstrates any selectivity for Cr(VI) and only one report on selectivity studies for mercury. The maximum extent of desorption that has been achieved is only about 86%. This has therefore led to an investigation into the use of other types of low cost adsorbents where the selectivity and regeneration of the adsorbents can be improved.

2.6 Adsorption by Low Cost Adsorbents (including Biosorbents)

A number of low cost adsorbents have been employed for the uptake of Cr(VI) and mercury. These can be broadly divided into three categories: adsorbents derived from industrial, agricultural wastes and natural materials, adsorbents

derived from plant material (phytoremediation) and biosorbents (bioremediation). Details of such studies are discussed below.

2.6.1 Adsorption by Industrial, Agricultural and Natural Materials

2.6.1.1 Removal of Cr(VI)

Some studies that have been conducted on removal of Cr(VI) by low cost materials derived industrial, agricultural and natural materials are summarised in **Tables 2-12**.

The studies, conducted on the uptake of Cr(VI) by low cost materials derived from industrial, natural and waste materials, have successfully achieved 100% removal. The studies on the different types of sawdust in particular have been very successful in this regard. However, these adsorbents also show disadvantages such as incomplete desorption and difficulties in regenerating the materials. This is not critical if the materials have a low cost. There are even a few cases where good extents of desorption have been achieved. For example, Unnithan and Anirudhan²⁴⁷ observed that about 95,5% of the adsorbed Cr(VI) could also be desorbed in 0,1 M NaOH from an iron(III) complex of a grafted copolymer sawdust.

Another issue that is evident upon examining the data in **Table 2-12** is the lack of reports on the selectivity of these materials for Cr(VI) removal. There are few papers which report high selectivity for Cr(VI). One example is that of Unnithan et. al.²¹⁸ who showed that polyacryl-amide grafted coconut coir pith was effective for the removal of Cr(VI) (99,4% removal) due to positively charged centers which are favourable for anion exchange. The spent adsorbent can also be regenerated and reused using 0,1 M NaOH and good removal rates from an electroplating effluent were also observed. Dahbi et. al.²¹⁹. on the other hand showed that bone charcoal had a good affinity for Cr(VI) even in a complex matrix,

Table 2-12: A Summary of Reports on the Uptake of Cr(VI) by Low Cost Materials Derived from Industrial, Agricultural and Natural Materials

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Carbon slurry (a low cost fertiliser waste material)	Good regeneration capacities where a column loaded with this adsorbent could be regenerated and reused for 5 cycles, losing only up to 15% of its capacity.	Maximum adsorption capacity of 15,24 mg/g Cr(VI) was lower than those observed for activated carbon.	Gupta et. al. ⁵⁵
Waste Fe(III)/Cr(III) hydroxide from the fertiliser industry	Effective adsorption of Cr(VI) and reuse and regenerability of adsorbent.	Waste material can also adsorb other metal ions such as Pb and Hg. No report on selectivity for Cr(VI).	Namasivayam and Ranganathan ²²⁰
Tea factory waste	Maximum uptake capacity 43,67 mg g ⁻¹ when the concentration was increased to 200 mgL ⁻¹ .	Did not report on the regenerability and the selectivity of this adsorbent.	Malkoc and Nuhoglu ²²¹
Raw rice husk bran	Some uptake of Ni(II) and Cr(VI) due to strong interactions	The adsorption of Ni(II) and Cr(VI) was non-spontaneous	Oliviera et. al. ²²²

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Raw bagasse and flyash	Removal capacities were higher for Ni(II) than that for Cr(VI)	Inferior adsorption capacities and selectivities for these ions than powdered activated carbon.	Rao et. al. ²²³
Distillery sludge	1. Adsorption capacities 5.7 and 3,9 mg/g from the Langmuir and Freundlich Isotherms respectively. 2. 91% Cr(VI) removal from a chrome-plating effluent which contained competing ions such as chloride ions and sodium ions.	1.The uptake capacities are lower when compared to other low costs adsorbents. 2. Only 86% of Cr(VI) can be desorbed in NaOH.	Selvaraj et. al. ²²⁴ .
Flyash pellets	Cr(VI) could be effectively adsorbed without leaching back.	Adsorption was suppressed by competing anions.	Dasmahaptra et. al. ²²⁵
Silico-aluminous flyashes and sulfo-calcic flyashes	Reasonable adsorption for cations such as Pb ²⁺ .	The uptake capacity for Cr(VI) was very poor and ranged from 5-9%.	Rio et. al. ²²⁶
Coir pith	99,99% Cr(VI) removal.	Mostly Cr(III) that was bound.	Suksabye et. al. ²²⁷

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Soya bean hulls, sugar bagasse and corn stover modified with dimethyloldihydroxyethyleneurea (DMDHEU) and choline chloride	<p>1. Uptake capacities of 1.97, 1.61 and 1.12 mmol/g for each adsorbent respectively.</p> <p>2. Preferential adsorption of chromates over arsenates and selenates.</p>	<p>1. The uptake capacities are still lower than that of other low cost adsorbents.</p> <p>2. Other aspects such as sorbent regeneration and the ultimate fate of the chromate ion after adsorption still need to be investigated.</p>	Wartelle and Marshall ²²⁸
Activated red mud	The adsorption process was temperature dependent where the adsorption capacity decreased with increasing temperature.	Poor selectivity to the removal of Cr(VI) especially in the presence of sulphate and phosphate ions.	Pradhan et. al. ²²⁹ ; Danis ²³⁰
Layered double hydroxides (LDH) containing Mg-Al and Zn-Cr.	<p>1. Calcined Mg-Al LDH with a higher Al³⁺ content was the most effective for Cr(VI) removal.</p> <p>2. The adsorbed Cr(VI) could be desorbed provided that the right competing anion (CO₃²⁻) was present.</p>	Calcinations of the Cr(VI) adsorbed phases did not result in any Cr-immobilised phases.	Goswamee et. al. ²³¹ .

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Palygorskite clay	Effective removal lead, chromium, nickel and copper from aqueous solution.	Did not examine chemical affinity competition between these metals in a multi-component systems.	Potgieter et. al. ²³²
Impregnated fireclay	Effective for the removal of Cr(VI).	No report on its selectivity for Cr(VI) removal.	Bajpai ²³³
Wollanstanite	First order kinetics where intraparticle diffusion occurs.	Adsorption was highly dependent on concentration.	Sharma et. al. ²³⁴
Natural clays	These materials had good potential for Cr(III) removal,	Retention of Cr(VI) was very poor.	Ribeiro and Labrincha ²³⁵
Uncalcined hydrocalcite	Greater than 95% removal of Cr(VI) and proposed an ion exchange mechanism.	Did not report on regeneration and reusability or selectivity.	Terry ²³⁶
Kaolinite, vermiculite and mica	Kaolinite and mica preferentially adsorbed Cr(VI)	Did not clearly state whether these materials can be regenerated and reused.or what the environmental fate of these materials is once Cr(VI) is adsorbed.	Covelo et. al., ²³⁷

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Iron-bearing solids	Best results were achieved with fine-grained iron	Did not discuss the fate of the oxyhydroxide	Blowes et. al. ²³⁸ .
Bentonite	The uptake of the cations was exothermic, the uptake of anionic Cr(VI) was endothermic.	Selectivity was not reported	Khan et.al. ²³⁹
Akaganeite	Showed an uptake capacity of 80 mg g ⁻¹	The adsorbent may be regenerated by flotation which is an expensive process.	Lazaridis et. al. ²⁴⁰
Hydrocalumite and ettringite	These materials preferentially adsorbed borates and selenates over chromates.	Chemical affinity competition from other oxyanions such as phosphates and carbonates is not considered.	Zhang and Reardon ²⁴¹
Hydrotalcite	Report an uptake capacity of 120 mg g ⁻¹	Kinetically controlled process.	Lazaridis and Asouhidou ²⁴²
Treated sawdust	Rapid uptake within a 3 hour equilibration time.	Maximum uptake capacity of 9,95 mg/g was somewhat lower than that of other low cost sorbents.	Baral et.al. ²⁴³

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Sawdust coated with polyaniline	Doping the polyaniline with acid worked best for Cr(VI) remediation since the process was highly pH dependent	The adsorbent is difficult to regenerate as some of it is lost by reaction and only 10-70% desorption of Cr(VI) is thus reported.	Ansari ²⁴⁴
Phosphate treated sawdust	100% removal even from electroplating waste where competing ions such as Ni(II) and Zn(II) are present.	Only able to desorb 87% Cr(VI) using 0,01 M NaOH	Ajmal et. al. ²⁴⁵
Beech (<i>Fagus orientalis</i> L.) sawdust	100% removal of Cr(VI) by at pH 1,0	The percentage removal decreased with increasing concentrations of Cr(VI).	Acar and Malkoc ²⁴⁶
Iron(III) complex of a grafted co-polymer sawdust	Could remove up to 99% Cr(VI) from both aqueous solutions and even from an electroplating effluent.	The uptake of Cr(VI) was reduced when the ionic strength of salts such as NaNO ₃ was increased.	Unnithan and Anirudhan ²⁴⁷
Acid-modified oak sawdust	The removal efficiency of was better for Cu(II) than for Cr(VI).	93% removal of Cu(II) was reported as opposed to 84% for Cr(VI).	Argun et. al. ²⁴⁸

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Natural zeolite clinoptilolite	> 95% Pb(II) and Cd(II) could be removed under acidic conditions.	Cr(VI) was not successfully adsorbed but rather tended to form anionic complexes with Cd(II) and Pb(II) thereby suppressing the retention of these ions.	Mier et. al. ²⁴⁹
Synthetic granulated goethite	This adsorbent was more efficient for the uptake of Cr(VI) than for the uptake of Zn(II).	The adsorption of Cr(VI) was hindered in the presence of EDTA while that of Zn(II)	Lehmann et. al. ²⁵⁰
Condensed tannin gels from natural polymers	Can effectively adsorb Cr(VI) (287 mg g ⁻¹).	There was no report on regeneration and reuse.	Nokano et. al. ²⁵¹ .
Amorphous aluminium oxide	< 90% Cr(VI) removal	The uptake capacity for Cr(VI) was significantly suppressed in the presence of sulphate ions.	Alvarez-Ayuso et. al. ²⁵²
Treated bauxite	Could remove up to 98% Cr(VI) from synthetic solutions.	Did not report on the selectivity and regenerability.	Baral et. al. ²⁵³

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Heat-treated bauxite	Reported a maximum adsorption yield of only 64,9%.	Very weak adsorbent for Cr(VI) removal.	Erdem et. al. ²⁵⁴
Mesoporous and amorphous silica modified with 2-mercaptopyridine	Uptake capacities of 1,83 mmol g ⁻¹ and 0.86 mmol g ⁻¹ .	Did not report on chemical selectivity.	Perez-Quintanilla et. al. ²⁵⁵ .
Cement paste	Report an adsorption capacity of 0,165 mmol g ⁻¹ .	Did not report on the selectivity of this material for Cr(VI) uptake.	Park et. al. ²⁵⁶
Aminated polyacrylo nitrile fibres from cheap polymer materials	96% removal of Cr(VI) with complete desorption.	Did not examine the selectivity of th for Cr(VI) removal.	Deng and Bai ²⁵⁷
Granular ferric hydroxide	Report a maximum adsorption capacity of 0,788 mg/g.	Competing anions did not suppress the uptake of Cr(VI).	Asgari et. al. ²⁵⁸
Calcium polysulphide	Were able to reduce Cr(VI) concentrations to levels that were acceptable to regulatory standards.	The removal was still incomplete with only 62% Cr(VI) being extracted.	Wazne et. al. ²⁵⁹
Ground shell of coconut	Could act as an efficient adsorbent for the removal of Cd(II), Cr(III) and Cr(VI).	The removal percentage of Cd(II) was higher than that of Cr(VI) and no selectivity report.	Pino and co-workers ²⁶⁰

In some cases, inferior adsorption capacities relative to other low cost adsorbents and activated carbon have been reported. Gallios and Vaclavikova²⁶¹ explored the possibility of using synthetic magnetite as an adsorbent for Cr(VI) removal but found that this material only had average adsorption efficiency. In **Table 2-12** it is also shown that Rao et. al.²²³ observed that raw bagasse and flyash has an inferior adsorption capacity and selectivity relative to that of powdered activated carbon. Nevertheless, these authors state that both waste materials offer an advantage over powdered activated carbon with respect to reuse and regeneration. Powdered activated carbon is difficult to reuse and regenerate whereas these low cost waste materials can simply be dried, burned and disposed off. However, the environmental impacts of disposing such materials must also be assessed. Further to these reports the well-known adsorbent, clinoptilolite, has shown no retention capacity for Cr(VI) in the presence of cations.²⁴⁹

Other adsorbents have presented their own limitations. As an example, Unnithan and Anirudhan²⁴⁷ report an excellent removal capacity for Cr(VI) by a sawdust containing an iron(III) hydroxide. However, it is also stated that the use of this adsorbent could increase iron concentrations in water. The authors also indicated that the regeneration of this adsorbent is expensive so the exhausted adsorbent would require disposal in a landfill.

In other cases like in the study by Wazne et. al.²⁵⁹ incomplete removal capacities have been reported. The authors stated that more studies on alkaline digestion are needed in order to determine whether this method gives a true reflection of the residual Cr(VI) concentration in chromite ore processing residue (COPR).

Other studies have also proposed possible solutions to the inherent problem of Cr desorption. Wang et. al.²⁶² have reported on the use of an anionic clay (a Li/ Al double hydroxide which contains positive charges which provide binding sites for anions) for the adsorption of Cr(VI). These authors indicated that a disadvantage

of using this adsorbent is the deintercalation of Li^+ at high temperatures which leads to the release of adsorbed Cr(VI) . A possible solution to this problem is to adsorb Cr(VI) at low temperatures and desorb Cr(VI) by deintercalation of Li^+ at high temperatures. Tzou et. al.²⁶³ confirmed that this can indeed be achieved.. These authors state the deintercalation can be conducted simply by using hot water; 95% deintercalation then occurs. These workers also proposed that the residual Gibbsite can be used to resynthesise the double hydroxide and the desorbed chromium solution can be used to recover chromium. However, the positively charged binding sites of this adsorbent can also adsorb other anions and the possibility of chemical affinity competition from sulphates and phosphates was not considered.

2.6.1.2 Removal of Hg

Similar studies on the uptake of Hg have also been reported. These are outlined in **Table 2-13**.

Table 2-13: Studies on the Uptake of Hg by Low Cost Materials Derived from Natural, Industrial and Waste Materials

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
A yellow tuff, a char and a pozzoloan	The only low cost material that had an uptake capacity close enough to that of activated carbon was pozzoloan.	Did not examine the selectivity of this adsorbent for mercury removal.	Di-Natale et. al. ²⁶⁴
A range of minerals and zeolites	Mangenite, zeolites and vermiculite gave the best adsorption and desorption efficiencies.	Did not examine the selectivity for mercury removal.	Melamed and de Luz ²⁶⁵

The use of low cost adsorbents has been extended to studies on the uptake of mercury vapour. For instance, O'Dowd et. al.²⁶⁶ examined a range of novel adsorbents for the uptake of mercury vapour and compared their adsorption performances to that of commercial activated carbons. These included a treated zeolite, a range of carbons derived from flyash and granular alumina. However, apart from the treated zeolite all other low cost adsorbents showed a negligible uptake of mercury vapour even after modification with sulphur.

Examination of **Table 2-13** also reveals that for mercury removal the selectivity of these materials and their uptake capacities is inferior to that of activated carbon. In contrast the adsorption performance of sulphur modified activated carbons has been shown to give up to 80% adsorption.

2.6.2 Phytoremediation

The use of readily available plant materials as adsorbents for metal ion uptake has been explored. The studies undertaken for the removal of Cr(VI) are outlined in **Table 2-14**.

Regeneration and desorption are noted to be problematic when using plant materials as adsorbents for Cr(VI). According to Sharma and Forster²⁶⁷ further research is required to improve regeneration capacities. Other workers have however, shown that desorption can be achieved provided that a suitable desorbing medium is used. For example, Salwalha et. al.²⁷⁶ reported that both Cd(II) and Cr(VI) can be easily desorbed from the surface of a plant based material using sodium citrate and HCl.

Once again, selectivity studies are lacking. The few selectivity studies conducted have shown poor selectivity for Cr(VI)

Table 2-14: Studies conducted on the removal of Cr(VI) by readily available plant materials

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Sphagnum Moss Peat	Reported a higher uptake capacity by Irish peat as opposed to Chinese peat.	40% regeneration efficiency of the peat could be achieved in 1 M NaOH	Sharma and Foster ²⁶⁷
Natural moss and copper coated moss	1. Natural moss worked better for the uptake of Cr(III) and copper coated moss worked better for the uptake of Cr(VI) 2. Reported uptake capacities of 18,9 and 7,1 mg/g for Cr(III) and Cr(VI) respectively.	1. While the removal of Cr(III) was efficient, the removal of Cr(VI) was incomplete. 2. The selectivity of both adsorbents for these ions in the presence of competing cations and anions was not studied and the uptake capacities were still lower than that of other low cost adsorbents and activated carbon.	Lee et. al. ²⁶⁸
The leaves of a 34 conifer species	Reported that the Cr(VI) concentration in the effluent studied could only be reduced 1,6 mg L ⁻¹	Incomplete removal of Cr(VI).	Cho et.al. ²⁶⁹
<i>Platanus orientalis</i> leaves and their ash	Reported > 85% removal with the dried ash giving better results.	The adsorption was hindered by the presence of competing light metal cations with Ca ²⁺ and Mg ²⁺ having the most influence.	Mahavi et. al. ²⁷⁰

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
<i>Limnanthemum cristatum</i> Griseb	The uptake capacity for chromium was higher (960 µg per g dry wt. versus 520 µg per g dry wt for Cd).	Did not present any data on the selectivity of this material for chromium and cadmium in a binary system and show that both metals had toxic effects on the plant where high concentrations of chromium led to a reduction in chlorophyll in the roots and Cd resulted in leaf and root decay.	Chandra and Garg ²⁷¹
Aquatic macrophytes	High removal capacities	The extents of removal were species dependent.	Rai et.al. ²⁷²
Aquatic plants. <i>Salvinia</i> and <i>Spirodela</i>	Reported high removal rates for both chromium and nickel	Removal capacities of both metals were reduced in a binary system containing both metals	Srivastav et. al. ²⁷³
<i>Salvinia minima</i> BAKER (a floating aquatic plant)	Reported the highest bioconcentration factor of 784 for Cr(VI)	The removal percentage of Cr(VI) was minimal when compared to those of the other metals (Cd and Pb) (81-97%).	Olguin et. al. ²⁷⁴
Floating macrophyte <i>Elodea canadensis</i> Michx.	More selective to the uptake of Ni than Cr	The uptake of Ni was 25-40 times higher than that of chromium at the same initial concentration.	Kahkonen and Manninen ²⁷⁵

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Saltbush (<i>Atriplex canescens</i>)	Identified carboxyl functional groups on which could effectively bind Cr(VI) and Cd(II).	FTIR studies suggest that different functional groups are involved in the binding of Cr(VI) and these authors did not report any data on the desorption of Cr(VI).	Sawalha et. al. ²⁷⁶
Modified tree barks	More than 95% uptake of Cr(VI) from aqueous solutions and 90% uptake from wastewaters	The adsorbed Cr(VI) can be regenerated from the barks by incineration which led to 50% recovery of chromium.	Gaballah and co-workers ²⁷⁷
Eucalyptus bark	99% removal; adsorption capacity of 45 mg g ⁻¹)	<ol style="list-style-type: none"> 1. Highest removal efficiency for Cr(VI) (when compared to other low cost adsorbents such as bagasse, charred rice husk and activated charcoal. 2. Satisfactory removal rates from industrial effluents 3. Neglected to examine the selectivity of this adsorbent for Cr(VI) removal especially in the presence of competing anions. 	Sarin and Pant ²⁷⁸

There is also some uncertainty in the literature as to what functional groups are responsible for the binding of Cr(VI) to the plant material. As shown in **Table 2-14** Salwalha et. al.²⁷⁶ postulated that carboxyl groups were involved but the FTIR results showed that other functional groups were involved. Further to these findings Mohanty et.al.²⁷⁹ were also able to show that the non-living biomass of *Eichhornia crassipes* was able to adsorb Cr(VI) by attachment to hydroxyl groups on this biomass.

Another prominent feature in these studies is that the extent of adsorption is species dependent. Espinoza et. al.²⁸⁰ noted that extent of adsorption of metal ions varied among different species of plant. These workers observed that the living biomass of *Eichhornia crassipes* had the highest removal capacity for Cr(III) while the living biomass *Salvinia auriculata* had the highest removal capacity for Cr(VI).

The studies conducted on the removal of mercury by plant materials are summarised in **Table 2-15**

The limitations associated with the phytoremediation of mercury include low adsorption capacities, environmental problems and poor selectivity for mercury removal. Chemical affinity competition was evident in column studies reported by Deskar et. al.²⁸³ where other divalent metal ions such as Pb(II), Zn(II), Cd(II) and Cu(II) out-competed Hg(II) for active adsorption sites. Thus, the treated bark was not very selective to the removal of Hg(II).

Table 2-15: Studies on the uptake of mercury by plant materials

ADSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
<i>Coriandum sativum</i>	Showed an ability to remove both inorganic mercury and methyl mercury efficiently and even report high recoveries of both forms of mercury from synthetic water samples containing competing cations such as Ca(II).	The maximum uptake capacities are again lower than that of other low cost adsorbents and activated carbon (24 mg/g and 7 mg/g for Hg ²⁺ and CH ₃ Hg ⁺ respectively)	Karunasagar et. al. ²⁸¹
<i>Brassica juncea</i> (an Indian Mustard plant)	Could bioaccumulate and volatilise mercury from base mine tailings.	Although these workers indicate that the release of mercury vapour is unlikely to harm the local and regional environment, this release is still not very environmentally friendly and this process is clearly not feasible from an environmental perspective.	Moreno et. al. ²⁸²
<i>Hardwickia Binata</i> bark	The uptake of Hg(II) onto treated was pH dependent and required an optimal contact time of 2h	The uptake of Hg(II) was however, hindered in the presence of light metal ions especially Mg(II).	Deskar et.al. ²⁸³

2.6.3 Bioremediation

The major bioremediation studies conducted for Cr(VI) removal are presented in **Table 2-16**.

Table 2-16: Bioremediation studies for Cr(VI) removal

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Waste biomass of Cassava	Reported an uptake capacity of 61,79 mg g ⁻¹ for the uptake of Cr(VI) and even indicate that this material can be regenerated in 1 M H ₂ SO ₄ .	Did not compare the uptake capacities of this adsorbent for other metal ions to that of Cr(VI) even though they stated that this is a well known metal ion sorbent.	Horsfall et. al. ²⁸⁴
<i>Agave Leuchugilla</i> biomass	<ol style="list-style-type: none"> 1. A greater removal percentage for Cr(III) than for Cr(VI) (95% versus only 36%). 2. Cr(III) was more easily recovered from the spent sorbent than Cr(VI). 	This material was more suitable for cation uptake than anion uptake.	Romero-Gonzalez et. al. ²⁸⁵
Brown seaweed (<i>Sargassum</i> biomass)	Metal ion uptake was dependent on ionic strength.	None	Tsui et.al. ²⁸⁶

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
<i>Sargassum wightii</i>	83% Cr(VI) was adsorbed and improved uptake was observed when this seaweed was treated with sulphuric acid, calcium chloride and magnesium chloride.	1. Inhibition in the presence of high concentrations of salts and incomplete removal	Aravindhan et. al., ²⁸⁷
Activated sludge flocs	The removal efficiency of Cr(VI) improved from 9% to 41% upon addition of powdered activated carbon to the activated sludge system.	The removal efficiency of Cr(VI) did not exceed 41%	Lee et. al. ²⁸⁸
Aerobic sludge bacteria	Up to 100% Cr(VI) could be removed by once these have acclimatized to the inlet Cr(VI) concentrations.	This was independent of powdered activated carbon addition.	Chen and Gu ²⁸⁹
Dried activated sludge	Effective at adsorbing Ni(II) and Cr(VI) in single component systems.	1. The uptake capacity was pH dependent where Ni(II) was selectively adsorbed at pH 4,5 and Cr(VI) was selectively adsorbed at pH 1,0. 2. The adsorption of both ions decreased in a binary system due to the antagonistic effects of both ions	Aksu et. al. ²⁹⁰

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Micro-organisms	Over 55% Cr(III) was removed but less than 60% Cr(VI) could be removed.	Oxidation state of chromium influenced its uptake capacity	Imai and Gloyna ²⁹¹
<i>Chlorella vulgaris</i>	Developed a model for the competitive sorption of Fe(III) and Cr(VI) in a binary system	The sorption was highly dependent on the ratio of the volume of the solution to the amount of biosorbent	Aksu and Acikel ²⁹²
<i>Pseudomonas auriginosa</i>	Proposed a biosorption and bioreduction for Cr(VI) removal	Also presented evidence that Cr(III) binds to carboxyl and amine groups on this organism.	Kang et.al. ²⁹³
Bio flocs	Metals such as copper, chromium, lead and zinc acted as strong competitors to organics for active adsorption sites even when present at sub-lethal concentrations	The uptake capacity for copper was the highest but did not report on the relative selectivities for each metal ion in a multi-component system containing all four metals.	Chua et. al. ²⁹⁴
41 strains of actinomycetes	Reported that the highest removal percentage (40%) was achieved by a strain isolated from a sugar cane plant and the highest uptake capacity (75,5 mg.g ⁻¹) for a strain isolated from a copper filter plant.	Although this study showed some promise for Cr(VI) bioremediation, the removal percentages and uptake capacities still need to be improved upon.	Polti et. al. ²⁹⁵

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
A gram negative bacterium, <i>Pantoea</i> sp. TEM18	<p>1. Showed good biosorption capacities for chromium(VI), cadmium(II) and copper(II) and reports a higher adsorption capacity for Cr(VI) than for the other two metal ions.</p> <p>2. The uptake capacity of Cr(VI) was also higher when compared to other biosorbents.</p>	The selectivity of this microorganism for Cr(VI) uptake was uncertain and the authors also indicated that much more work is required before bacterial biosorption is practically implemented.	Ozdemir et. al. ²⁹⁶
Agar immobilised cells of <i>Anacytis nidulans</i> (a cyanobacterium)	Observed 86% Cr(VI) removal efficiency.	The adsorption process was highly dependent on flowrates.	Khattar et.al. ²⁹⁷
Algal biomass of <i>Clorella Vulgaris</i>	Only observed a maximum removal capacity of 75% .	The uptake capacity was reduced to between 55-49% in the presence of a sodium/magnesium chloride matrix and reported that this biosorbent can only be regenerated and reused for four cycles after which its adsorption capacity reduces to 40% and 34% respectively.	Pappas et. al. ²⁹⁸

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
High biomass producing algal strains	Accumulated large amounts of toxic heavy metals from effluents with the highest accumulation of Cr(VI).	Although this study formed the basis of further studies into the uptake of Cr(VI) from tannery effluent, no further investigation into this was conducted.	Rai et. al. ²⁹⁹ .
Biomass of filamentous green algae (<i>Spirogyra</i> sp.)	Good potential for Cr(VI) removal and reported a maximum uptake capacity of $14,3 \times 10^3 \text{ kg}^{-1}$.	Did not report on the selectivity of this adsorbent for Cr(VI) removal.	Gupta et. al. ³⁰⁰
Biomass of the microalgae, <i>Chalmydomonas reinhardtii</i>	<p>1. Heat-treated biomass performed better at the uptake of Cr(VI) than the native adsorbents and acid-treated adsorbents</p> <p>2. Reported uptake capacities of 18,2, 25,6 and 21,2 mg/g for the native-, heat- and acid treated biomasses respectively.</p> <p>3. These adsorbents could also be regenerated using 0,1 M NaOH with 96% recovery.</p>	No data on the selectivity of these adsorbents for Cr(VI) removal was reported.	Arica et. al. ³⁰¹
Two strains of <i>Dunaliella</i> algae	Uptake capacities of 58,3 and 45,5 mg g ⁻¹ .	Chemical affinity competition occurred.	Donmez and Aksu ³⁰²

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Autoclaved mycelial biomass of <i>Aspergillus Flavus</i>	Reported a maximum uptake capacity of 0,335 mg g ⁻¹ which was somewhat lower when compared to those other low cost adsorbents and activated carbon.	No reports on the regeneration capacity of this biosorbent and its selectivity for Cr(VI) removal.	Deepa et. al. ³⁰³
<i>Aspergillus carbonarius</i>	The uptake of both metals increased with lower biomass concentrations and increasing concentrations of the metals.	The selectivity of this adsorbent for chromium and copper in a binary mixture was not examined.	Al-Asheh and Duvnjak ³⁰⁴
Dead fungal biomass of <i>Aspergillus Niger</i>	<ol style="list-style-type: none"> 1. Pre-treatment of the biomass with cetyl trimethyl ammonium bromide resulted in the maximum chromium removal 2. 90% chromium could be desorbed by using NaOH as the desorbing medium 3. Over 70% removal. from a soil microcosm 4. The biosorption was governed by the reduction of Cr(VI) to Cr(III) and the retention of solid Cr(III) onto the dead fungal biomass. 	<ol style="list-style-type: none"> 1. Maximum uptake capacity of 11,6 mg/g which was still somewhat lower when compared to those other low cost adsorbents and activated carbon 2. The selectivity of this adsorbent for Cr(VI) removal was not reported on. 	Mungsavalli et.al. ³⁰⁵ ; Srivastava and Thakur ³⁰⁶ . Park et. al. ³⁰⁷

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
<i>Sargassum</i> sp. and <i>Padina</i> sp (brown algae)	The uptake of the cations was much faster than that of the anionic chromates.	Proposed that a bioreduction of Cr(VI) to Cr(III) occur simultaneously.	Sheng et. al. ³⁰⁸
Dried vegetative cells and the spore crystal mixture of <i>Bacillus thuringiensis</i>	18% removal by the vegetative cells and 24,1% removal by <i>B. thuringiensis</i> .	Poor removal capacities.	Shahin and Ozturk ³⁰⁹
Two strains of <i>Bacillus</i> viz. <i>B. megatarium</i> and <i>B.coagulans</i>	1. Uptake capacities of Cr(VI) ranging from 15,7 – 39,9 mg g ⁻¹ 2. The dead cells of these bacteria adsorbed Cr(VI) to a higher extent than the living cells.	The authors attributed this to poor pH conditioning of the dead cells so better pH conditioning is needed to verify these results.	Srinath et. al. ³¹⁰
<i>Bacillus laterosporus</i> and <i>Bacillus licheniformis</i>	Higher uptake capacities for Cd(II) (159,5 mg g ⁻¹ for <i>B.laterosporus</i> and 142,7 mg g ⁻¹ for <i>B. Licheniformis</i>) than for Cr(VI) (72,6 mg g ⁻¹ for <i>B.laterosporus</i> and 62 mg g ⁻¹ for <i>B. Licheniformis</i>).	Selectivity in a binary system was not examined.	Zouboulis et. al. ³¹¹
<i>Ochrobacterium</i> sp., <i>Salmonella enterica</i> and <i>Pseudomonas aeruginosa</i>	90-99% removal of Cr(VI) and 80% removal of the dye Reactive BLACK B	Did not report on chemical affinity between both contaminants for active adsorption sites on the bacteria	Kilic et.al. ³¹²

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
<i>Staphylococcus xylosus</i> and <i>Pseudomonas</i> sp.	Both strains were more selective to the uptake of Cd(II) even in a binary system	Selectivity for Cr(VI) was only achieved if this was the dominant ion in a binary system.	Ziagova et. al. ³¹³
Microbial biomasses from molasses and NaCl media	90-95% removal of Cr(VI) but the uptake capacity reported in the absence of NaCl was about 80% higher than the uptake capacity observed in NaCl media (109,45 mg g ⁻¹ versus 26,2 mg g ⁻¹ in the highest NaCl concentrations	NaCl presented some competition to the uptake of Cr(VI).	Donmez and Kocberber ^{314, 315}
A range of biosorbents from the non-living biomass of selected fungal and bacterial species	Concluded that these can selectively extract this metal ion from solution.	Did not provide experimental evidence which shows that the biomasses are indeed selective to the removal of Cr(VI).	Nourbakhsh et. al. ³¹⁶
Biomass of <i>Streptomyces rimosus</i>	Can adsorb Cu(II), Zn(II) and Cr(VI) but report the lowest biosorption capacity for Cr(VI) removal	The study was only preliminary and other investigations such as the desorption of the metal ions, the regenerability of the biosorbent and chemical affinity competition need to be conducted before the complete viability of this biosorbent is assessed.	Chergui et. al. ³¹⁷

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Waste dead fungal biomass from a solid-state fermentation industry	The uptake of Cr(VI) was the least affected by co-ions in solution	Still observed the lowest adsorption capacity for Cr(VI).	Shekar et. al. ³¹⁸
Algae, <i>Lyngbya putealis</i>	Up to 94,8% removal was observed	The removal percentage was reduced to 90,1% in the presence of 0,2% salts which suggested that some chemical affinity competition occurred and the selectivity of this biosorbent for Cr(VI) removal is not very high.	Kiran et. al. ³¹⁹
<i>Nostoc calcicola</i> and <i>Chroococcus</i> sp.	<i>Chroococcus</i> sp was more favourable for Cr(VI) uptake in the sense that it gave a higher adsorption capacity.	Studies which aim at characterising adapted strains at the molecular level for selective metal ion uptake are still needed.	Anjana et. al. ³²⁰
<i>Sacchromyces cerevisiae</i>	A fairly low uptake capacity of 6,3 mg/g (60% saturation).; 2-6.7 mg/g reported.	These authors also experienced difficulties in desorbing Cr(VI) both in salt and alkali media where only 5,2% desorption was observed.	Zhao and Duncan ³²¹ ; Kaszcycski et.al. ³²²
<i>Micrococcus</i> sp. and <i>Aspergillus</i> sp.	Good bioaccumulation high concentrations of chromium and nickel.	No selectivity and regeneration report.	Congeevaram et.al. ³²³

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Immobilised biomass of <i>Rhizopus nigricans</i>	Immobilisation with polysulfone gave the best results with an uptake capacity of 101,5 mg g ⁻¹ .	This was however still lowerer than that of the free biomass (119,2 mg g ⁻¹). Furthermore even though these authors show that this biosorbent could be regenerated over 25 cycles the removal efficiency for Cr(VI) was only 75-78%.	Bai and Abraham ³²⁴
<i>Rhizopus arrhizus</i>	The uptake of Cr(VI) by was higher than most of the other biosorbents studied thus far (78 mg g ⁻¹).	This uptake capacity was reduced at increasing salt concentrations which suggested that chemical affinity competition occurred.	Aksu and Balibek ³²⁵
Cross-linked quaternary chitosan salt	Reported a maximum adsorption capacity of 1,31 mmol/g and observed 95% desorption of Cr(VI).	Selectivity in the presence of competing anions was not examined.	Spinelli et. al. ³²⁶
Cross-linked chitosan	Not favourable for cation exchange and report a maximum uptake capacity of 215 mg/g for Cr(VI).	These workers did not report on the effect of competing anions.	Rojas et. al. ³²⁷
Crosslinked chitosan synthesised by gamma radiation	The adsorbent could be regenerated and reused after Cr(VI) loading.	The selectivity of this adsorbent for Cr(VI) removal was not examined.	Ramnani and Sabharwal ³²⁸

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Chitosan coated onto oil palm shell charcoal	<p>1. Uptake of capacity of 154 mg Cr(VI) per g adsorbent</p> <p>2. The adsorbent could be regenerated with 0,1 M NaOH over 10 bed cycles.</p>	There was no report of this adsorbent's selectivity to the removal of Cr(VI).	Nomanbhay and Palanisamy ³²⁹
Chitosan coated onto alumina	Maximum uptake capacity of 153,85 mg/g which was higher than that of most low cost sorbents studied to date.	The uptake of Cr(VI) is inhibited in the presence of chloride and sulphate ions with the effect of sulphate ions being more pronounced.	Boddu et. al. ³³⁰
Hydrogel chitosan beads .	<p>1.Higher uptake capacity of 1g g⁻¹</p> <p>2. Crosslinking these beads with Cu(II) and Ag(I) was advantageous for low concentrations of Cr(VI).</p>	No data on possible chemical affinity competition from competing anions was presented.	Modrzcjewska et. al. ³³¹
Chemically modified cross-linked chitosan beads and flakes	Able to adsorb Cr(VI) at rates of 4 times and 7,4 times faster than unmodified chitosan respectively and report uptake capacities of 625 mg/g and 256 mg/g	The uptake of Cr(VI) is suppressed in the presence of high concentrations of chloride and sulphate ions and Cr(VI) could be desorbed using 0,01 N NaOH but the maximum percentage desorption of 85%.	Sankararamkrishnan et. al., ³³²

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Chitosan	<p>1.The Cr(VI) binding capacity of could be improved by pre-treatment with sulphuric acid.</p> <p>2. The uptake capacities were comparable with that of commercial ion-exchange.</p>	These workers still reported incomplete removal of Cr(VI) where concentrations were reduced from 25 ppm to ≤ 5 ppm and not 0 ppm.	Lasko et. al. ³³³
Calcium alginate beads	These beads together with humic acid could extract Cr(VI) from tannery effluent thereby reducing the toxicity of the effluent.	Only reported 54% removal of Cr(VI) which suggested that the removal was incomplete	Pandey et. al. ³³⁴
Calcium alginate encapsulated onto grape stalk waste	Uptake capacity of 86.42 mmol Cr(VI) per litre wet sorbent volume	. In another study the uptake capacity is quantified as 225 mg g ⁻¹	Fiol et. al. ^{335, 336}
Biopolymeric beads consisting of cross-linked sodium alginate and cross-linked gelatine	<p>1.Observed an adsorption coefficient of 22,0 which suggested that adsorption was favourable</p> <p>2. Increasing concentrations of sodium alginate, gelatine and gluteraldehyde also favoured the adsorption.</p>	The adsorption was suppressed in the presence of electrolytes (halides of potassium) and that this inhibitory effect became more pronounced when the radii of the halides increased.	Bajpai et. al. ³³⁷

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Crosslinked cationic starch maleate	<p>1. Favourable for Cr(VI) uptake because of its quaternary ammonium cationic centres</p> <p>2. The extent of adsorption was however highly dependent on the degree of substitution where low degrees of substitution (<0,2%) favour the uptake and increasing amounts of anionic maleate substituents decrease the uptake</p>	The authors also did not report on the likelihood of other anions competing with Cr(VI) for the cationic sites on this adsorbent.	Xing et. al. ³³⁸
Cationic starch enhanced ultrafiltration	Up to 98% Cr(VI) could be removed by if the cationic starch concentration is increased to 2,5 g/L	Did not report on the selectivity of this material for Cr(VI) removal.	Baek et. al. ³³⁹
The agricultural by-product of <i>Lentinus edodes</i> .	<p>1. Cr(VI) adsorption was highly pH dependent where most of the adsorption occurred at around pH 4.</p> <p>2. The biosorbent could reduce Cr(VI) to Cr(III) and thus could adsorb both oxidation states of chromium</p>	The maximum uptake capacity reported is only 21,5 mg/g which was lower than that of other low costs adsorbents and activated carbon.	Chen et.al. ³⁴⁰

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Hazelnut shell	The uptake of Cr(III) was not affected by the presence of Cd(II) and Zn(II) in a mixture and that Cr(VI) is removed by reduction to Cr(III).	The effect of competing anions on the uptake of Cr(VI) was not studied though.	Cimino et. al. ³⁴¹ .

The studies conducted on the uptake of Hg by biosorbents are summarised in **Table 2-17**.

Table 2-17: Studies on the uptake of Hg by biosorbents

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Non-living protonated biomass of algae <i>Ulva Lactuca</i>	1. A maximum uptake capacity of 149,25 mg/g was observed. 2. Reported easy desorption and regeneration of the biomass using 0,3 N H ₂ SO ₄	Did not extend these studies to industrial effluents and other complex chemical matrices which contain competing cations.	Zeroual et. al. ³⁴²
<i>Phanerochaete chyrosporium</i> basidiospores immobilised onto carboxymethylcellulose	1. Lower uptake capacity of 102,15 mg/g for the uptake of Hg(II) was observed 2. 95% of the adsorbed mercury (II) could be desorbed. 3. Good regeneration	Did not report on its selectivity for Hg(II) removal in the presence of other cations.	Saglam et. al. ³⁴³

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Aminated chitosan beads	<p>1. Almost complete removal of Hg(II) within 100 minutes</p> <p>2. High selectivity of this biopolymer for Hg(II) removal in the presence of other ions and organic matter,</p> <p>3. 95% desorption in EDTA and regenerability of this adsorbent over 5 cycles.</p> <p>4. uptake capacity of 1127,1 mg g⁻¹</p>	None	Jeon and Park ³⁴⁴ , Shafaei et. al. ³⁴⁵
Dithizone anchored microbeads	Chemical affinity competition occurred where competing metal cations such as Pb(II) and Cr(III) were adsorbed to a greater extent than Hg(II).	The adsorption capacities were also reduced in artificial wastewater which suggested that competition from other ions could occur as well	Salih et. al. ³⁴⁶
Polymer based gel beads modified with polyethyleneimine	Could remove up to 90% Hg(II) from aqueous solution and report the highest uptake capacity for Hg (from an artificial wastewater) when compared to that of other metal ions.		Denizli et. al. ³⁴⁷

BIOSORBENT	OBSERVATIONS	COMMENTS	REFERENCE
Magnetically modified yeast cells from <i>Sacchromyces cerevisiae</i>	<ol style="list-style-type: none"> 1. Fairly high uptake capacity of 114,6 mg/g. 2. 95% of the adsorbed Hg(II) can be desorbed in 0,1 M HNO₃ 3. This biosorbent could also removed Hg(II) together with other divalent cations such as Cu(II) and Ni(II) from an artificial waste stream. 	The uptake capacity for Hg(II) was somewhat lower in this waste stream (76,2 mg/g versus 114,6 mg/g). This suggested that the uptake of Hg(II) was suppressed in the presence of other divalent metal cations.	Yavuz et. al. ³⁴⁸
Immobilised <i>Microcytis aeruginosa</i>	Observed high removal percentages (80% for Pb(II) and 90% for Cd(II) and Hg(II)).	In both binary and ternary systems this organism selectively adsorbed Pb(II) over Hg(II) and Cd(II) .	Chen et. al. ³⁴⁹

2.6.4 The Limitations of the Studies Conducted on Low Costs Adsorbents

There have thus been numerous reports on the uptake of Cr(VI) and Hg (mainly Hg(II)) by low costs adsorbents and biosorbents. However, even though some of these have demonstrated good potential to remediate these metals, some low cost materials have their inherent limitations.

Firstly, some of the uptake capacities observed have been inferior to that of activated carbon. Attempts to find low cost adsorbents has resulted in limited studies on removal efficiencies. This is evident in the cost and benefit study undertaken by Demir and Arisoy³⁵⁰ which showed that although biological methods of Cr(VI) removal are cheaper than chemical methods the removal

percentages are still lower (59,3% for biological versus 99,68% for chemical). Only chitosan showed a reasonably high or comparable uptake capacity to that of activated carbon. However, even this biosorbent shows a lack of selectivity for metal ions.

As reported in **Tables 2-12 to 2-17** there have been numerous reports on the poor selectivity of low cost adsorbents for the uptake of Cr(VI) and Hg in the presence of competing cations and anions, particularly in saline environments. Some studies have reported excellent removal efficiencies for Cr(VI) and Hg but have not considered chemical affinity competition from other ions. From a wastewater treatment point of view, this is not ideal as ions can co-exist in wastewater and the selective removal of hazardous metals such as chromium and mercury is important. There are studies which have even reported incomplete removal of these ions. Since the toxic effects of both chromium and Hg can be lethal, reducing the concentrations to zero in wastewater treatment is required.

Some of the studies detailed above have also reported poor regeneration of the sorbents and poor recovery of the sorbed metal ions. Although desorption and regeneration are not critical if the sorbent material is low cost, the environmental implications of disposing metal loaded sorbents must be critically evaluated. In the case of using living organisms as adsorbents, the toxic effects of the metals on the organism must be considered. Some reports have in fact shown that the bioaccumulation of Cr(VI) in living organisms can have lethal effects on these organisms.

There are again very few reports on the uptake of ppb levels of Cr(VI) and Hg. Wang and Chen ³⁵¹ presented a review article in which they indicated that although the concentrations studied ranges from 1-100 mg/L, biosorbents in general have an ability to reduce both ppt levels and ppb levels. To date many researchers have not exploited this advantage offered by biosorbents.

Some authors also pointed out that biosorption has only proven to be successful on a laboratory scale and can present difficulties in practical use. Improvements in immobilisation, regeneration and reuse are required before this can be practically implemented. This has been reiterated by Kurniawan et. al.³⁵² in a review article where it was stated that the cost effectiveness of adsorbents such as hazelnut shell can be increased if these are regenerated for multiple use.

Furthermore, Igwe and Abia³⁵³ have also pointed out in their review article that the mechanism of biosorption is still not completely understood and that this information is crucial in terms of scaling up a process for practical use. There have been reports in the literature of bioreduction occurring in reactions occurring between the biosorbent and the pollutant. However, there are other postulates that the metal ions merely bind to specific adsorption sites or functional groups on the adsorbent. The mechanism seems to depend largely on the type of biosorbent and is a reaction.

In an editorial correspondence Park et. al.³⁵⁴ pointed out that many workers in the field of study of Cr adsorption have simply measured total chromium concentrations and have reported this as a decrease in Cr(VI) concentration. This has been attributed to the adsorption of this anion onto the sorbent. The possibility of the reduction of Cr(VI) to Cr(III) (which is highly likely to occur in acidic media) and uptake of Cr(III) by the biosorbent was ignored. These workers also point out in another editorial correspondence³⁵⁵ that the removal mechanism depends on factors such as solution pH, temperature, species of biomass and concentrations of biomass and Cr(VI). Concerns similar to those expressed by these workers are also reiterated in an editorial letter by Aoyama.³⁵⁶ and Yun³⁵⁷.

Furthermore Kurniawan et. al.³⁵² indicated that even though these adsorbents are low in cost the industrial use of these materials may involve other costs such as regeneration costs and operating costs such as chemicals, electricity, labour, transportation and maintenance. These authors also indicated that before these

adsorbents become available for commercialisation, more research on the mass production of the most efficient adsorbents and the most appropriate chemicals for their regeneration is needed.

Table 2-18 summarises some of the major advantages and disadvantages of the uses of some selected low cost adsorbents. It is these disadvantages and the shortcomings discussed above which have led to the need for the development of new adsorbents that are more selective to Cr(VI) and Hg uptake, have better regeneration capacities superior adsorption efficiencies to that of activated carbon and the ability to reduce the concentrations of contaminants to sub-ppb levels.

Nanosorbents have been identified as potential new adsorbents.^{358,359,360} Studies initiated on these types of materials include the use of nanoparticles and carbon sorbents. For example, Lalvani et. al.³⁶¹ have shown that a carbon material prepared by an arc discharge method (carbon soot) was able to selectively adsorb Cr(VI) from a mixture of cations such as Pb(II) and reported that this material had a superior adsorption capacity to that of commercial activated carbon. Cao et. al.³⁶² also showed that ceria hollow nanospheres could achieve an uptake capacity of 22,4 mg g⁻¹ for As(V) and 15,4 mg g⁻¹ for Cr(VI). However, the type of nanosorbents that have gained the most recognition for environmental remediation are carbon nanotubes.

Table 2-18: Some important advantages and disadvantages of ion exchange, adsorption by activated carbon and some low cost adsorbents⁶⁵

Process	Advantages	Disadvantages
Ion Exchange	<ul style="list-style-type: none"> ➤ Wide range of porosity and physiochemical characterisation ➤ Favourable surface area ➤ High efficiency ➤ Good regeneration capacity 	<ul style="list-style-type: none"> ➤ Expensive ➤ Made up of petroleum-based raw materials ➤ Sensitive to particle size ➤ Poor contact with aqueous pollutants ➤ Requires modifications to enhance the water wettability
Adsorption by activated carbon	<ul style="list-style-type: none"> ➤ Highly efficient adsorbent ➤ High degree of porosity ➤ Very high surface area ➤ Can adsorb a wide range of pollutants ➤ Results in high quality industrial effluents ➤ Fast kinetics of adsorption 	<ul style="list-style-type: none"> ➤ Expensive –cost is proportional to quality ➤ Performance depends on the type of carbon used ➤ Requires complexing agents to improve its adsorption capacity <ul style="list-style-type: none"> ➤ Poor selectivity ➤ Problems with hydrophilic substances ➤ High reactivation costs ➤ Reactivation results in a loss of carbon
Adsorption by chitosan-based materials	<ul style="list-style-type: none"> ➤ Cost effective and environmentally friendly ➤ Good metal-binding capacity ➤ High selectivity for both high and low concentrations ➤ Exceptional diffusion properties ➤ Results in a high quality treated effluents ➤ Versatile and easily regeneratable 	<ul style="list-style-type: none"> ➤ Porosity is poor ➤ Adsorption capacity depends on its origin ➤ Bead characteristics vary
Adsorption by starch-based materials	<ul style="list-style-type: none"> ➤ Readily available and economical ➤ Requires inexpensive reagents for preparation ➤ High swelling capacity in water ➤ Good removal capacity for a wide range of pollutants ➤ High selectivity for different concentration ranges 	<ul style="list-style-type: none"> ➤ Low surface area ➤ Variable bead characteristics ➤ Use in sorption columns is limited due to hydrodynamic limitations and column fouling

2.7 Carbon Nanotubes

Carbon nanotubes (CNTs) are allotropes of carbon which have a characteristic cylindrical or tubular structure.³⁶³ Different types of carbon nanotubes can be distinguished depending on their structure or form. **Figure 2-5** shows the two major types of carbon nanotubes which are known.

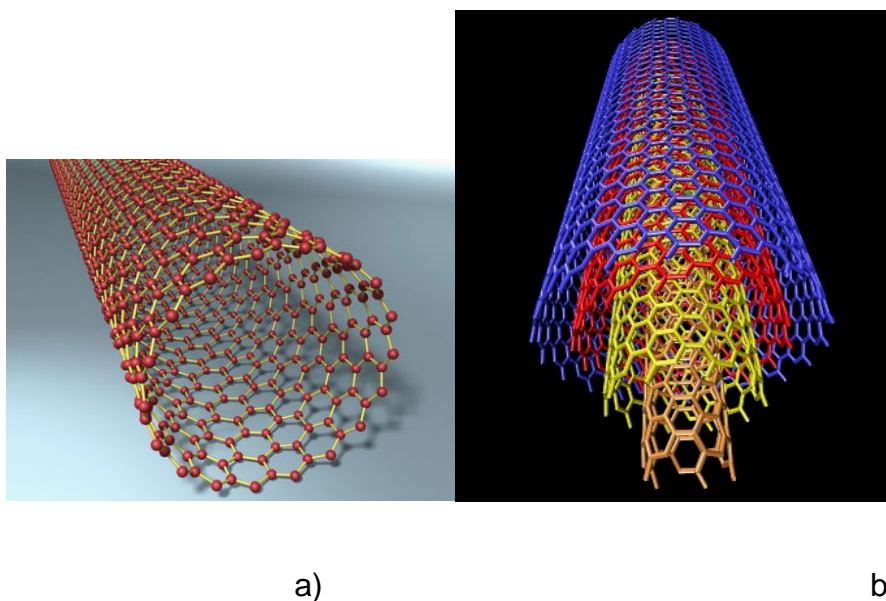


Figure 2-5: The two main types of carbon nanotubes a) Single –walled carbon nanotubes (from: <http://www.cnano-rhone-alpes.org/spip.php?article57&lang=en>³⁶⁴ b) Multi-walled carbon nanotubes (from: <http://www.cnano-rhone-alpes.org/spip.php?article57&lang=en>)³⁶⁵

The primary difference between single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) is the number of graphene sheets which each structure is made up of. As the names imply, SWCNTs are comprised of a single graphite layer and MWCNTs are made up of multiple graphite layers.

2.7.1 Origin and Synthesis of Carbon Nanotubes

Carbon nanotubes were first discovered by Radushkevich and Lukyanovich in 1952.³⁶⁶ However, these materials have only gained scientific recognition since the report submitted by Iijima on these materials in 1991.³⁶⁷

Much emphasis has been placed on synthesising these materials in macroscale quantities for commercial applications.^{368,369,370,371} Currently the common conventional methods that have been used for their synthesis include arc discharge, laser ablation, chemical vapour deposition (including hot-wire CVD) and nebulized spray pyrolysis.^{371, 372,373,374} Recently, microwave radiation has also become a popular method for synthesizing carbon nanotubes.³⁷⁵

In general, MWCNTs are more readily synthesised in good purity and yield and are also cheaper than SWCNTs.³⁷⁶ For these reasons MWCNTs have been mostly studied in this thesis as an ion adsorbent although some studies on carbon spheres are reported in **Chapter 7**.

2.7.2 Functionalization of Carbon Nanotubes

In order to utilize carbon nanotubes in various applications, their structures are often manipulated to suit the specific application. For example, the surface of the nanotubes may be chemically modified for the adsorption of specific molecules or ions where functionalities or defect sites on the nanotube surface may play a role in the adsorption of specific molecules or ions.^{360,383} Covalent functionalisation has been identified as one of these methods.³⁸² This entails adding known functional groups to the walls of the nanotubes. The functional groups which have been added to carbon nanotubes include hydroxyl and carboxylic acid groups. These and other groups can be formed on the CNT surface by oxidation and acid treatment eg. treatment with nitric acid³⁷⁷, hydrogenation by Birch reaction, fluorination, ozonization and the addition of radicals.³⁸³ Other methods of functionalisation include oxidation with potassium permanganate using a phase transfer catalyst followed by treatment with chemicals such as 3-methylacryloxypropyltrimethoxysilane.³⁷⁸

Studies on the thiolation of MWCNTs have also been reported.^{379,380,381,382}

2.7.3 Applications of Carbon Nanotubes

A number of applications of carbon nanotubes have been reported. This has been mainly due to their exceptional mechanical properties, unique electrical properties, high chemical and thermal stability and their large specific surface areas.³⁸³ Some of these applications include their use in nanodevices³⁸⁴, in field emissions³⁸⁵, plasma apheresis³⁸⁶, as catalyst supports³⁸⁷, biosensors³⁸⁸ and chemosensors.^{389,390} In 2004 the US Environmental Protection Agency (EPA) expressed a need for the environmental applications of carbon nanotubes to be explored and remediation or treatment was identified as one of the key areas that needed to be investigated.³⁶⁰ Since then carbon nanotubes have gained increasing recognition for their adsorption capabilities. It has also been stated that their well-defined porosity and functionality renders them superior adsorbents to other adsorbents like activated carbon.³⁹³

Both SWCNTs and MWCNTs have been studied for the uptake of a number of organic and inorganic pollutants, and numerous reports have appeared indicating their use. These studies are outlined in **Table 2-19**.

The carbon nanotubes have typically shown uptake capacities which are superior to that of activated carbon and other low cost adsorbents. Oxidised CNTs in particular have shown a great potential for cation uptake. Rao et. al.³⁸³ reported in a review article that surface oxidised CNTs are promising adsorbents for water treatment applications not only because they show superior adsorption capabilities to that of activated carbon but also because their adsorption capabilities are superior to those of other low cost adsorbents. It is also stated in this article that oxidised SWCNTs perform better at adsorption of Ni²⁺ and Zn²⁺ than MWCNTs because their zeta-potentials are more negative and the electrostatic interaction between the SWCNTs and cations is greater. However, this has not been shown for other divalent cations such as Hg(II), Zn(II), Pb(II), Cu(II) and Cd(II).

Table 2-19: Some Important Environmental Studies on Carbon Nanotubes

TYPE OF NANOTUBE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
Unmodified form a microwave modified CNTs	Bisphenol A	Slightly higher uptake capacity for the modified form at 7°C (69,93 mg/g as opposed to 60,98 mg/g for the unmodified CNTs).	Selectivity studies were not attempted.	Kuo ³⁹¹ .
SWCNTs	17- α -ethinyl estradiol and Bisphenol A.	Can adsorb rapidly and retain these strongly.	None	Pan et. al. ³⁹²
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) 	<ol style="list-style-type: none"> 1. The concentration range studied was 10-80 mg L⁻¹. 2. Did not conduct any competitive adsorption studies with competing cations that may co-exist with Zn(II) in wastewater. 3. No report on removal mechanism. 	Lu and Chiu ³⁹³

TYPE OF NANOTUBE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
MWCNTs containing γ - Fe_3O_2 nanoparticles	Organic dyes methylene blue (MB) and neutral red. (NR)	<ol style="list-style-type: none"> Superior uptake capacities (42,3 mg/g for MB and 77,5 mg/g for NR). Equilibrium was attained within 60 min. 	Did not study the competitive adsorption of these dyes in a binary system and also do not report on the reuse and regenerability of these MWCNTs.	Qu et. al. ³⁹⁴
Oxidised MWCNTs	Ni(II)	<ol style="list-style-type: none"> Up to 93% Ni(II) could be desorbed from the oxidised MWCNTs at pH< 2 using distilled water as the desorbing agent. Lack of dependence on ionic strength. Equilibrium is attained within 40 min of contact time 	Despite proving that these materials can be regenerated by desorption, the authors still argued that costs limit the practical utility of these MWCNTs and did not study the selectivity of these materials.	Chen and Wang ³⁹⁵

TYPE OF NANOTUBE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
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 of this material was also superior to that of peanut shell 	These workers also neglected to study the effect of competing cations and did not conduct any desorption experiments.	Kandeh and Meunier ³⁹⁶
NaOCl oxidised SWCNTs and MWCNTs	Ni(II)	<ol style="list-style-type: none"> 1. More efficient at adsorbing and desorbing over 10 cycles than granular activated carbon. 2. Conducted a statistical analysis which proved that these materials can possibly act as cost effective replacements for granular activated carbon. 	None	Lu et al. ³⁹⁷

TYPE OF NANOTUBE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
Oxidised MWCNTs	Cd(II)	<p>1. MWCNTs oxidised with KMnO_4 gave the best results.</p> <p>2. Oxidation also lowered the pH_{pzc} of these materials and increased the quantity of surface functional groups.</p>	Did not examine the effects of competing anions or determine the regenerability of these materials.	Li et. al. ³⁹⁸
SWCNTs.	Benzene, Toluene and Chlorobenzene	The uptake of was hindered by the presence of oxygen containing functional groups	These authors accounted for this in terms of steric hindrance presented by the functional groups.	Chin et. al. ³⁹⁹
SWCNTs.	Naphthylamine, 1-Naphtol and 1-Phenol	The uptake was suppressed by the presence of oxygen-containing functional groups.	Authors attributed this to the weakening of π - π interactions and increased electrostatic repulsions by carboxylic groups.	Sheng et. al. ⁴⁰⁰

TYPE OF NANOTUBE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
Acid-treated MWCNTs	Pb(II).	<p>1. The adsorption capacity reported was 85 mg g⁻¹ which is higher than that reported for unmodified MWCNTs and activated carbon.</p> <p>2. The equilibrium adsorption time was shortened to 20 minutes.</p> <p>3. Provided experimental evidence that chemical interactions between Pb(II) and oxygen containing functional groups accounts for 75,3% of the Pb(II) adsorption while the formation of PbO, PbCO₃ and Pb(OH)₂ account for only 3,4% of the adsorption</p>	The adsorbed Pb(II) aggregates occur mainly on the ends and defect sites of the MWCNTs.	Wang et. al. ⁴⁰¹ ; ⁴⁰² .

TYPE OF NANOTUBE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
Oxidised MWCNTs	Ni(II)	<p>1. The presence of polyacrylic acid (PAA) enhanced the uptake of by at low pH.</p> <p>2. That the adsorption was independent of the addition sequence of PAA and Ni(II).</p> <p>3. The presence of foreign ions had no effect at low pH.</p>	The strength of the complexes of Ni(II) with PAA adsorbed onto the MWCNTs was higher than the strength between Ni(II) and oxygen containing functional groups.	Yang et. al. ⁴⁰³
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. ⁴⁰⁴
SWCNTs doped with iron	Benzonitrile	More effective at removal than the undoped materials.	No reports of the ability of Fe-doped CNTs to remove inorganic metal ions.	Aguiar et. al. ⁴⁰⁵
High crystalline MWCNTs (HC-MWCNTs)	Volatile organic carbons (VOCs)	Highly selective uptake	No report on regeneration capacities	Sone et. al. ⁴⁰⁶

TYPE OF NANOTUBE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
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 ⁴⁰⁷
Pristine MWCNTs	2,3-dichlorophenol and pentachlorophenol	<ol style="list-style-type: none"> 1. 94% removal 2. The adsorption was dependent on factors such as pH, temperature, mass of adsorbent and analyte concentration. 3. Rapid extraction from solution 	Both studies also did not report on the regenerability and selectivity of the adsorbent.	Salam et. al. ⁴⁰⁸ ; Salam and Burk ⁴⁰⁹

One potential disadvantage of using CNTs as adsorbents is the cost involved in synthesising these materials. Although cheaper methods of CNT synthesis are

under investigation desorption and regeneration could also solve this problem. Few reports on this topic have been presented. However, recently Wang et. al.⁴¹⁰ were able to show that microwave irradiation under nitrogen is an effective means of regenerating CNTs used to adsorb the dye, Reactive Red 3BS. These workers reported a 92,8% regeneration efficiency after four cycles of regeneration.

Chemical affinity competition studies using CNTs are also lacking. Li et. al.⁴¹¹ are the only workers thus far to report on the competitive adsorption capabilities of CNTs. These workers showed that MWCNTs selectively adsorb Pb(II) over Cd(II) and Cu(II) in multi-component systems and they even showed that the highest uptake capacity was observed for Pb(II) even in single component systems. This indicated that selectivity for a specific metal ion can be achieved. The authors also indicated that adsorption capabilities are much better without competition. The adsorption capacity in competitive systems therefore needs improvement.

Tan et. al.⁴¹² noted that the presence of surfactants influenced that uptake of nickel by MWCNTs by providing a counterion system for the binding of Ni to surface functional groups. These workers concluded that MWCNTs can be used for the simultaneous removal of surfactants and metal ions from polluted water but also stated that the cost and the ability to synthesise MWCNTs in large quantities will determine the feasibility of this process.

Recent studies on the use of CNTs as adsorbents have also focussed on using doped CNTs. Besides the study on iron doped CNTs by Aguiar et. al.⁴⁰⁵, Perez-Aguilar et. al.⁴¹³. showed that oxidised nitrogen-doped multi-walled carbon nanotubes (CN_x) have a better uptake capacity for Pb(II) and Cd(II) than undoped oxidised MWCNTs (adsorption capacity two times higher) and that the uptake capacity of these materials was 1,4 times higher than that oxidised activated carbon. These workers also reported good regeneration capacities for these materials (90%) and showed that these materials are more selective to the uptake of Pb(II) in a binary system containing both Pb(II) and Cd(II). However, the uptake capacities of these materials were 1,3 times lower than that of oxidised SWCNTs. The authors attributed this to a higher oxygen content on the SWCNTs

which implied more surface functional groups. They did not consider the possibility of using microwave radiation to increase the surface functionalisation of the MWCNTs which may have resulted in a higher oxygen content than that of the SWCNTs. Furthermore, these authors indicated that nitrogen-doping aids the uptake of cations by creating more reactive sites for the attachment of functional groups. However, the possibility that the nitrogen-doping itself may influence the cation uptake was not considered and control experiments involving the unoxidised nitrogen-doped materials to verify this were not conducted. Recent observations have shown that nitrogen doped CNTs show enhanced uptake for gaseous O₂ when compared to undoped materials.⁴¹⁴

Studies involving the use of composites of CNTs with activated carbon and low cost sorbents have also been initiated. These are outlined in **Table 2-20**.

2.7.4 Removal of Cr(VI)

Work on the uptake of Cr(VI) by carbon nanotubes has only been initiated fairly recently. Di et. al.⁴¹⁵ used ceria nanoparticles supported on aligned carbon nanotubes for the uptake of Cr(VI) and reported an uptake capacity of 30,2 mg g⁻¹. These workers also noted that the best uptake of Cr(VI) occurred over a wide pH range of 3,0-7,4. and that the adsorption capacities of these materials were 1,5 times higher than that of activated carbon, 2,0 times higher than that of Al₂O₃ and 1,8 times higher than that of ball-milled CNTs. Qui⁴¹⁶ and Di⁴¹⁷ also made similar observations for the uptake of Cr(VI) by MWCNTs but indicated that these materials are too expensive for practical use.

Table 2-20: Studies on the Use of Nanocomposites as Sorbents

TYPE OF NANOCOMPOSITE	POLLUTANT	MAIN OBSERVATIONS	COMMENTS	REFERENCE
Activated carbon nanotube-orange peel composite	Synthetic cationic dyes	<p>1. Much higher extent of adsorption with this material (78%) when compared to suspended orange peel powder (46%) and an orange peel strip (67%)</p> <p>2. This material could be regenerated and reused over six adsorption-desorption cycles</p>	Another advantage presented by this material was the reduced biodegradation of orange peel strips thereby increasing the lifespan of these strips.	Jain et. al. ⁴¹⁸
Nanocarbo-conjugated polymer nanocomposite	Zn(II), Cd(II) , Cu(II), Hg(II), Ni(II) and Cr(VI)	Over 99% of metal ions such as could be removed by this material.	The lifespan of this material ranged from 1s-1000 min and was highly dependent on the ratio of polymeric molecules and carbon nanoparticle concentrations.	Khaydarov et. al. ⁴¹⁹

Hu et. al.⁴²⁰ studied the uptake of Cr(VI) by oxidised MWCNTs and proposed a mechanism that involved surface complex formation rather than ion-exchange. These workers also observed that the adsorption process was highly dependent on pH but independent of ionic strength. Experimental evidence that Cr(VI) is reduced to Cr(III) and that a combination Cr(VI) and Cr(III) was retained on the surface of the MWCNTs was presented in this paper. The authors indicated that the release of Cr(III) into an aqueous solution is negligible. These workers made these observations for ppm concentrations of Cr(VI) and not ppb levels. The selectivity of the oxidised MWCNTs in the presence of competing ions was not studied. These workers also indicated that the unit cost of the MWCNTs must be reduced for further applications but they did not study the possibility of regenerating and reusing this adsorbent. Furthermore in all Cr(VI) remediation studies conducted to date, workers have only investigated the uptake of ppm levels of Cr(VI) and not ppb levels.

2.7.5 Removal of Hg

The studies of interactions between mercury and carbon nanotubes have focused mostly on electrochemical issues where electrowetting to improve conductance and the transport of liquid mercury was investigated.^{421,422} Recently Tawabini et. al.⁴²³ have reported on the uptake of Hg(II) by MWCNTs that contained carboxyl, carbonyl and hydroxyl functional groups. These workers showed that a high adsorption efficiency could be achieved even when the concentration of Hg(II) was as low as 0,1 mg L⁻¹. The optimal conditions were pH 8 and a 10 mg dose of MWCNTs which resulted in 100% removal of Hg(II). However, these workers did not report on the selectivity of this material for Hg(II) in the presence of other competing cations. The possibility of improving the selectivity for Hg(II) by doping the MWCNTs with sulphur was not considered. Comparisons to other carbon sorbents such as activated carbon were not made and these workers also did not report on the extent of reuse and regenerability of the MWCNTs. Furthermore these workers also did not examine the uptake of organic forms of mercury which are far more toxic than the inorganic forms.

2.7.6 Use of CNTs in Trace Analysis

The adsorption capabilities of MWCNTs have even been exploited for the development of new analytical methods for some contaminants. These are summarised in **Table 2-21**.

Table 2-21: Studies on the Applications of CNTs in Trace Analysis

TYPE OF NANOTUBE	APPLICATION	MAIN RESULTS	COMMENTS	REFERENCE
MWCNTs.	Developed a new analytical method for the selective determination of the silver ion	The silver ion could be quantitatively and selectively determined in the pH range of 7-9 with a detection limit of 0,60 ng mL ⁻¹ and a relative standard deviation of 3,8% at 10 ng mL ⁻¹ Ag	These workers also successfully applied this method for the determination of silver in geological and water samples.	Ding et. al. ⁴²⁴
SWCNTs and MWCNTs	Solid phase adsorbents for highly polar analytes (cephalosporins antibiotics, sulfonamides and phenolic compounds).	1. With the exception of 3,5-dihydroxy benzene, most of the polar analytes were adsorbed to a greater extent on the CNTs than on graphitized carbon (C ₁₈). 2. were able to develop an analytical method	None	Niu et. al. ⁴²⁵

TYPE OF NANOTUBE	APPLICATION	MAIN RESULTS	COMMENTS	REFERENCE
		<p>using sulphonamide as the model analyte and found that this substance could be determined at a detection limit of 27-38 ng L⁻¹</p> <p>3.. Optimum recovery of 80-100% was also achieved by using ammonium acetate as the eluting agent</p>		
Hemicelle capped Cetylmodified MWCNTs (CMMWCNTs)	Arsenic could be quantitatively determined by adsorption onto these materials followed by elution with 2 M HNO ₃ in the presence of cetyltrimethylammonium chloride.	These workers also observed recoveries of 94-100% and noted that the presence of other metals such as Mn did not deter the determination of arsenic.	These workers did not examine the effect of competing anions such as chromates and selenates on the determination of arsenic.	Li et. al. ⁴²⁶

TYPE OF NANOTUBE	APPLICATION	MAIN RESULTS	COMMENTS	REFERENCE
SWCNTs	Speciation selective analysis of chromium in water and other matrices.	<p>1. Cr(III) could be quantitatively adsorbed in the pH range 2,0-4,0 leaving Cr(VI) behind in solution</p> <p>2. Reported the successful elution of the retained Cr(III) using nitric acid, a detection limit of 0,01 ng mL⁻¹ and recoveries of >92,5 % for spiked samples.</p>	Cr(III) concentration was subsequently determined by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).	Chen et. al. ⁴²⁷
A carbon nanotube paste electrode	The speciation of Sb(III) and Sb(V) by using in a potentiometric stripping analytical method	Good recoveries observed.	None	Santos et. al. ⁴²⁸ .
SWCNTs	New sensor for the determination of Hg(II) by Cold Vapour Atomic Absorption Spectroscopy (CVAAS)	1. Reported a limit of detection of 0,64 µg mL ⁻¹ and a relative standard deviation of 2,7% for eight replicate analyses of 15 µg mL ⁻¹ Hg(II).	Simplicity, freedom from interferences, high selectivity and low consumption of reagents and samples when compared to conventional CVAAS.	Safavi et. al. ⁴²⁹ .

TYPE OF NANOTUBE	APPLICATION	MAIN RESULTS	COMMENTS	REFERENCE
A thiol-functionalised chitosan-MWCNT nanocomposite	Thin film electrode for the determination of Hg(II) by square wave voltammetry.	Reported linear responses in the range of 10 to 140nM with a limit of detection of 3nM under optimised conditions	This method could be applied to determination of Hg(II) in water samples with satisfactory recoveries.	Deng et.al. ⁴³⁰
ABTS-Multi-walled carbon nanotubes nanocomposite / Bi film electrode	The determination of Cd(II) and Pb(II) by differential pulse stripping voltammetry	Reported detection limits of 0,1 $\mu\text{g L}^{-1}$ and 0,2 $\mu\text{g L}^{-1}$ for Cd(II) and Pb(II) respectively	The simultaneous determination of both metal ions in water samples could be achieved with good recoveries.	Deng et. al. ⁴³¹ .
Bismuth-modified carbon nanotube electrode	Determination of Pb(II) , Cd(II) and Zn(II) by square wave stripping voltammetry	Good detection limits	None	Hwang et. al. ⁴³²
Screen imprinted carbon nanotubes	Determination divalent metal ions by sequential injection analysis-anodic stripping voltammetry	Good detection limits	None	Injang et. al. ⁴³³

In addition to the those reported in **Table 2-21**, other analytical applications of carbon nanotubes include the following: the determination of chromium and iron in food and plant herbal samples by solid phase extraction onto SWCNTs and

atomic adsorption spectroscopy (AAS)⁴³⁴, the use of functionalised MWCNTs as a stationary phase for the gas chromatographic separation of alkane and aromatic compounds⁴³⁵, the use of *Pseudomonas aeruginosa* immobilised onto MWCNTs for the solid phase extraction and determination of selected metal ions from environmental samples,⁴³⁶ the determination of chromium speciation in natural water samples using MWCNTs as solid phase extractants,⁴³⁷ the determination of polycyclic aromatic carbons by GC-MS using MWCNTs as solid phase extractants,⁴³⁸ determination of As(III) by anodic stripping voltammetry using gold nanoparticle modified carbon nanotubes,⁴³⁹ the voltammetric determination of trace Hg(II) by gold nanoparticle CNTs synthesised by microwave radiation⁴⁴⁰, the determination of lead on MWCNT-Nafion glassy carbon electrodes⁴⁴¹, the detection of Eu(III) by a glassy carbon electrode modified with CNTs⁴⁴² the use of ethylenediamine-modified CNTs for the selective extraction and preconcentration of metal ions⁴⁴³ and the use of a carbon nanotube DNA hybrid fluorescent sensor for the selective and sensitive determination of Hg(II).⁴⁴⁴

2.7.7 The Adsorption Properties of CNTs

Studies on the adsorption properties of CNTs have been initiated. For example, Chen et al,⁴⁴⁵ showed that the surface area and pore volume decreased with increasing diameter of MWCNTs. These workers also showed that thermal annealing of MWCNTs helps to remove amorphous carbon thus leading to purification of the MWCNTs. Microwave digestion also helps to remove metal impurities and to open the ends of the tubes thereby increasing the surface area of CNTs. However, the study focussed on improving the CNT surface area for adsorption as this is a key property that influences the uptake of gases.

Zilli et. al.⁴⁴⁶ showed that vertical alignment (increased interstitial channels between the individual nanotubes) rather than the diameter of the nanotubes increased the nitrogen adsorption capacity of MWCNTs. In another study, Otvos et.al.⁴⁴⁷ showed that oxygen-containing surface functional groups strongly influenced the dynamic adsorption properties for the uptake of hydrogen and nitrogen by CNTs.

CNTs are thus a group of nanosorbents that have demonstrated excellent potential for applications in environmental remediation and in the trace analysis of environmental pollutants. One of the most interesting attributes of these materials is their superior adsorption capability relative to that of conventional carbon sorbents like activated carbon. However, a number of other aspects of utilising these materials as adsorbents need to be investigated before CNTs are used in industrial scale remediation.

2.8 Conclusion

Chromium and mercury are key elements used in the industrial sector due to their unique properties and numerous industrial applications. However, the toxicities of these elements warrants the removal of these elements from industrial wastes prior to disposal. Some existing technologies including adsorption by activated carbon, other low cost adsorbents and biosorbents demonstrated good uptake capacities for these pollutants. But they have also presented disadvantages such as poor selectivity, poor adsorption capacities and poor regeneration capacities. The practical utility of biosorbents has not been implemented yet due to a lack of understanding of the mechanism of biosorption and reports that other cost ineffective factors such as the costs of chemicals required for regeneration etc. could arise.

The recent revolution in nanotechnology has provided a means to synthesise and characterise nanomaterials. This provides an opportunity to investigate these materials for metal ion adsorption. Carbon nanotubes are promising adsorbents as these materials have a superior adsorption capacity to that of activated carbon. They have been used for the uptake of a number of pollutants including Cr(VI) and Hg(II). However, the uptake of trace concentrations (ppb levels) of Cr(VI) and mercury have to date not been studied. Since the toxicity of these elements has led to the need for a nil concentration of these metals in the environment, it is important to examine the uptake of these contaminants of at ppb levels.

The uptake of mercury by carbon nanotubes has been little studied. For example, mercury's affinity for sulphur has not been exploited in the studies on the uptake of Hg(II) by MWCNTs. This is an important aspect in mercury remediation as this could improve the selectivity of the MWCNTs for Hg(II). The uptake of organic forms of mercury which are more toxic than the inorganic forms also needs to be studied.

Furthermore, studies on the adsorption performance of carbon nanotubes in a complex chemical matrix such as an industrial effluent (where chemical affinity competition can prevail) are limited. The high cost of carbon nanotubes has also restricted their practical use and cheaper methods of making these materials on an industrial scale need to be explored. The possibility of desorption and regeneration and reuse of metal ions on CNTs has been examined in very few studies to date.

The studies conducted on metal ion remediation to date have indicated that oxidised CNTs are the best adsorbents for the removal of metal ions simply because these provide reactive binding sites for the metal ions and also because these lower the point of zero charge of the CNTs thereby making the adsorption of cations possible. Although mechanisms involving reduction of Cr(VI) to Cr(III) on the surface of oxidised MWCNTs have been proposed it is still unclear as to what makes these materials favourable for anion uptake. Oxidised nitrogen doped CNTs have shown the ability to effectively extract divalent cations but the issue of whether nitrogen doping itself can play a role in cation and anion uptake is still unclear.

There has also been an emphasis on the uptake of metal ions on CNTs using oxygen-containing functional groups. These are introduced either via acid treatment or with a suitable oxidising agent such as KMnO_4 . The effect of other functional groups such as sulphur and nitrogen containing functional groups have not been examined. The effect of base treatment together with the functional groups introduced via this treatment have also not been studied. Other factors

such as microwave induced acid and base treatment, heat treatment and the effect of impurities on the MWCNTs have not been considered.

Although MWCNTs are gaining recognition in environmental analysis due to their adsorption capabilities, their ability to selectively extract oxyanions and oxycations from ternary and multi-components systems for analytical method development has also not been explored.

The current study therefore presents results from experiments that have been devised to address the above issues in the chapters that follow.

CHAPTER 3

MULTI-WALLED CARBON NANOTUBES AS ADSORBENTS FOR THE REMOVAL OF PARTS PER BILLION LEVELS OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTION¹

3.1 Introduction

In this chapter the ability of MWCNTs to adsorb ppb levels of Cr(VI) is examined. The adsorption capacities of both functionalised and unfunctionalised MWCNTs as well as activated carbon are compared and discussed. The influence of critical parameters such as contact time and solution pH are studied. The ability of Cr(VI) to desorb from the surfaces of MWCNTs is also evaluated and mechanism of Cr(VI) adsorption was proposed. Finally, adsorption isotherm models are used to describe the equilibrium adsorption process.

3.2 Materials and Method

3.2.1 Adsorbents

3.2.1.1 Functionalised MWCNTs

The functionalised MWCNTS were purchased from SUNNANOTM. These MWCNTs had a purity of > 90% and a diameter of 10 – 30 nm. An IR spectrum of these nanotubes was run to verify the presence of the electron rich functional groups such as hydroxyl and carboxyl groups (See **Figure A1** in **Appendix 1**).

¹ This chapter has been published in Journal of Hazardous Materials Vol. 126 (2009) 1067-1075

3.2.1.2 Unfunctionalised MWCNTs

Unfunctionalised MWCNTs were synthesised at the University of the Witwatersrand by the chemical vapour deposition method over a Fe/CaCO₃ catalyst.⁴⁴⁸

3.2.1.3 Activated Carbon

The powdered activated carbon was commercially obtained from Merck. This was already purchased in the activated form but was further activated with KOH. This type of activation is usually conducted at 800 -1000⁰C in order to develop a basic surface oxide layer and to raise the solution pH.⁶⁵ This method of activation also increases the activated carbon surface area and pore volume.

3.2.2 Chemicals

A 1000 ppm stock Cr(VI) solution was prepared by dissolving 2.874 g K₂Cr₂O₇ (analytical grade) in 1 L distilled water. This solution was diluted to 1000 ppb which was in turn diluted to a 100 ppb Cr(VI) solution. Solutions of 0.1 M HCl and 0.1 M NaOH were used for pH adjustment.

3.2.3 Batch Adsorption Experiments

For the batch adsorption experiments, 0.1 g of each adsorbent was weighed out and placed in contact with 10 mL of the 100 ppb Cr(VI) solution in sample vials. The adsorbents were placed in contact with the Cr(VI) solution for contact times of 1, 2, 3, 4, 6, 8, 12 and 24 hours, respectively.

Contact between the adsorbents and the Cr(VI) solution was facilitated by agitation on a shaker. After each specified contact time, the Cr(VI)–adsorbent suspension was filtered through a 0.45 µm EconoClear filter, commercially obtained from Microsep. The filtrates were retained for analysis of their Cr(VI) content by Adsorptive Stripping Voltammetry.

To investigate the influence of pH, the adsorbents were placed in contact with the Cr(VI) solution and the pH was adjusted using either 0.1 M HNO₃ or 0.1 M NaOH. All samples were agitated on a shaker for a contact time of 12 hours. The pH was varied across the entire pH scale.

The influence of the initial Cr(VI) concentrations was investigated by preparing standard solutions of Cr(VI) ranging from 100 – 3000 ppb. These solutions were left in contact with 0.1 g of the adsorbent for 12 hours with agitation on a shaker.

The effect of competing anions was examined by spiking the Cr(VI)–adsorbent suspensions with 0.1 M sodium sulphate where the sulphate ions which are chemically similar to the dichromate ions would act as competing anions. In a separate experiment, the Cr(VI) - adsorbent suspensions were also spiked with a 0.1 M sodium chloride solution where the chloride ions could also act as potential competing ions. These suspensions were agitated on a shaker for contact times of 1, 2, 3, 4, 6, 8, 12 and 24 hours, respectively.

3.2.4 Desorption Experiments

Desorption and regeneration was explored on these materials. To investigate the possibility of regeneration, desorption experiments were conducted where 0.1 g of each type of MWCNT was kept in contact with 10 mL of 100 ppb K₂Cr₂O₇ solution for 24 hours in order to ensure that maximum adsorption was achieved. The pH in this case was maintained at 7. After this equilibration time, the suspension was centrifuged and filtered. The remaining MWCNT residue onto which Cr(VI) had been adsorbed was subsequently washed with 100 mL distilled water once after 1, 2, 3, 4, 6, 8, 10, 12 and 24 hours respectively. These desorption experiments were repeated using 0.1 M NaOH as a washing agent. Samples were collected after each wash and analysed on the MetroOhm Polarograph in order to determine how much Cr(VI) had desorbed.

3.2.5 Analysis

All filtrates collected from the adsorption and desorption experiments were analysed for their Cr(VI) content using a MetroOhm polarograph in the Adsorptive Stripping Voltammetry mode. This method was selected since it is not only speciation specific to Cr(VI) but is also highly sensitive to parts per billion levels of Cr(VI) where the lower limit of detection is said to be $0.5 \mu\text{g L}^{-1}$ ⁴⁴⁹. The background electrolyte used for this study was prepared by dissolving 21.2 g NaNO_3 , 1.968 g diethylenetriamine pentaacetate (DTPA) and 0.16 g CH_3COONa in distilled water in a 100 mL volumetric flask. The voltammetric parameters were set as follows:

Purge time: 300 s, Conditioning time: 600 s, Conditioning potential: 0 V,
Deposition potential: -1.0 V, Deposition time: 60 s, Equilibration time: 10 s
Initial Potential: -1.0 V, Final Potential: -1.5 V

Each sample was analysed by adding 2.5 mL of the sample, 1.5 mL of background electrolyte and 1 mL of deionised water to the voltammetric cell. NaOH (40%) was also added to adjust the pH to ± 6.2 . The pH was monitored using a MetroOhm pH meter. The samples were also analysed by the standard addition method where each sample was spiked with 1 μL increments of 1 ppm Cr(VI). Standard coefficients of 0.99 indicated good precision of the analytical results.

3.2.6 Quality Assurance

A number of quality control steps were taken to ensure the reliability of the analytical data. Thus, all batch experiments were conducted in duplicate to check the reproducibility of the analytical data and average results are reported here. The analytical data was found to be reproducible with a relative error of $\pm 2\%$.

To verify that the decrease in Cr(VI) concentration was indeed due to adsorption by the various adsorbents, a blank experiment without the MWCNTs was run. The results of this experiment indicated that there was no change in Cr(VI) concentration with time.

The relative standard deviation of the analytical data was also determined to evaluate the accuracy of the data. This was found to be 5% thereby indicating good accuracy of the data.

3.2.7 Zeta Potential Measurements

Zeta potential measurements on each type of adsorbent were conducted on a Malvern Zetasizer. Basically the zeta potential was measured as a function of pH so that the point of zero charge (pH_{PZC}) of each adsorbent could be determined.

3.2.8 Brunauer-Emmett-Teller Method (BET)

About 0,2 g of both the functionalised and unfunctionalised MWCNTs were degassed in nitrogen at 120°C for 4 hours before undergoing analysis on a Micromeritics Flow Prep 060 sample degassing system. The surface areas and pore size distributions were measured at 120°C. The pore size distributions with specific surface areas of both types of MWCNTs were measured by N₂ adsorption/desorption according to the BET method on a Micromeritics Tristar, surface area and porosity analyser.

3.3 Results and Discussion

3.3.1 Contact Time

Figure 3-1 shows the influence of contact time on the adsorption capacity of the MWCNTs (both functionalised and unfunctionalised) and activated carbon. Less

than 1% adsorption by activated carbon was observed. According to the literature reports activated carbon is expected to have a poor adsorption capacity for ppb levels of contaminants^{206,396} This loss in adsorption effectiveness is thought to be due to the filling of pores by water.⁶⁵ Basically, Cr(VI) is a highly mobile form of chromium which can easily migrate into the moisture that is trapped in the pores and is therefore not very easily retained on the solid activated carbon surface. This argument is supported by the review article by Mohan and Pittman⁶⁵ where it is indicated that one of the disadvantages of using activated carbon is that it presents problems with the adsorption of hydrophilic substances.

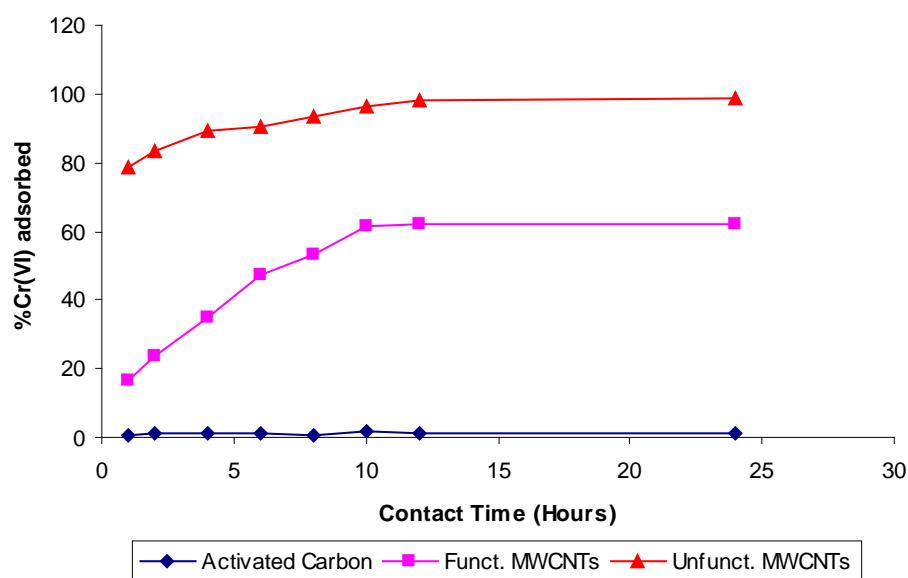


Figure 3-1: The effect of contact time on the amount of Cr(VI) adsorbed by each adsorbent

Both types of MWCNTs, by contrast, show a good ability to remove Cr(VI) from aqueous solution and attain equilibrium within 12 hours of contact time. The unfunctionalised MWCNTs however, show a greater ability (98% adsorption) to adsorb Cr(VI). Repeat experiments confirmed these results. From the IR spectrum of the functionalised MWCNTs (see **Figure A1** in **Appendix 1**) it is noted that there are hydroxyl groups (3436 cm^{-1} ; O-H stretching mode) present.

To verify that the functional groups were indeed affecting the adsorption of Cr(VI), the functional groups were removed by heating the MWCNTs under argon in a tube furnace at 900°C for 9 hours. An IR spectrum (not shown) verified that all the functional groups were indeed removed. **Figure 3-2** shows that the adsorption capability (96% adsorption in 12 hours) of these MWCNTs improved significantly after the functional groups were removed and are similar to the adsorption capacity of the original unfunctionalised MWCNTs. This observation is in agreement with the literature reports for the uptake of Cr(VI) by activated carbon which have been functionalised or oxidised.¹⁰⁹ Park and Jang¹¹³ also showed that the adsorption of Cr(VI) onto a carbon surface decreased in the presence of oxygen surface complexes. There is a possibility that some reoxidation of the MWCNTs could have resulted after the heating process. However, the IR data showed no evidence for the presence of acid.

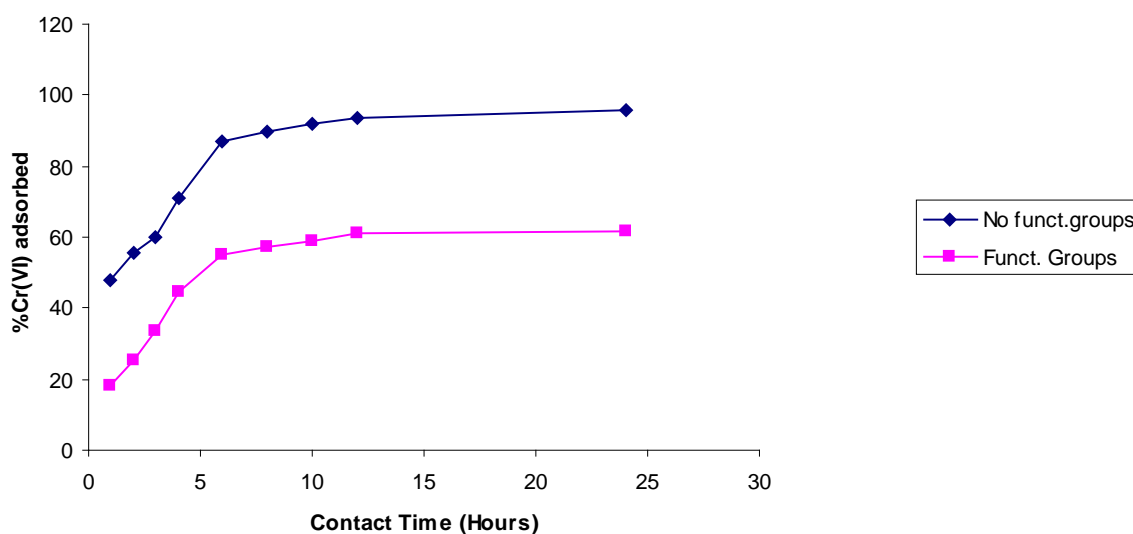


Figure 3-2: The adsorption capability of the functionalized MWCNTs after the functional groups had been removed

3.3.2 Initial Solution pH

Figure 3-3 shows the influence of initial solution pH on the adsorption capacity of all three adsorbents. It must be borne in mind that at low pH (<3) Cr(III) is the thermodynamically stable form of chromium, not Cr(VI).^{6,126,417,450,451} This is verified by the Eh-pH diagram of Cr(VI) which shows that the predominant form of Cr(VI) at low pH is Cr^{3+} (see **Figure 2-1** in Chapter 2). Beukes et.al.⁴⁵² also showed that the reduction of Cr(VI) to Cr(III) was very rapid at low pH and reported a pK_a value of 2.4. Thus, at lower pH it is actually Cr(III) in the form of polymerised Cr oxides^{6,113} that is being adsorbed. A possible explanation for the adsorption that is taking place could be competition between Cr(III) ions and H^+ ions for active sites on the MWCNT surface. Other workers have reported similar phenomena for the uptake of Cr(VI) by activated charcoal.¹²⁶ The results therefore suggest that all the chromium regardless of whether it is present as Cr(III) or Cr(VI) can be removed. The Eh-pH diagram (**Figure 2-1**) also shows that some Cr(VI) can also exist as HCrO_4^- at low pH. Thus some of these species are also adsorbed at low pH. So, in a typical industrial waste the MWCNTs can remove both forms of chromium by the adsorption process.

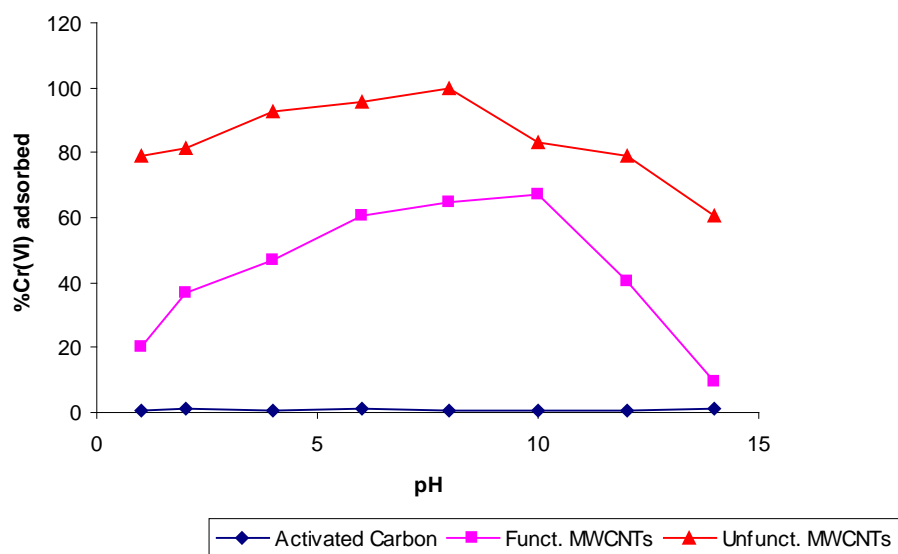
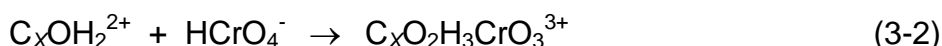


Figure 3-3: The effect of pH on the uptake of Cr(VI) by the three adsorbents

However, this can be explained further in terms of equilibrium solution pH. The equilibrium pH was not determined but according to Mor et. al.⁶ the equilibrium solution pH should increase when there are oxo groups present on the surface of the adsorbent. Any oxo group on a carbonaceous surface reacts with water as follows:-



When Cr(VI) ions are introduced into the system, the following reaction occurs:-



Combining equations (1) and (2) we get:



Thus the net effect is that every mol of Cr(VI) ion adsorbed gives two moles OH⁻ and hence an increase in solution pH.

In the context of the results presented here, this will apply to the functionalised MWCNTs containing the oxo functional groups and activated carbon and thus explains why the adsorption capacities of these two adsorbents are lower than that of the unfunctionalised MWCNTs. Basically the excess OH⁻ ions that are generated out-compete the dichromate ions for active surface sites on the adsorbent surfaces leading to saturation of the active sites.

Thus, activated carbon still shows no significant affinity for Cr(VI). Both types of MWCNTs show a high adsorption capacity at low initial pH, and a diminishing adsorption capacity at higher initial pH with the maximum adsorption being attained at ca. pH 6. Clearly, this can be explained in terms of surface charge; a positive surface charge facilitates the adsorption of dichromate ions as suggested in the literature.^{6,100, 124, 229 , 305,453}

The redox mechanisms must also be carefully considered. Cr(III) forms at lower pH as a result of the reduction of Cr(VI) to Cr(III). Such a reduction is coupled to the oxidation of carbon surfaces resulting in carboxyl surface moieties.⁴⁵⁰ Thus, it can be argued that there are carboxyl functionalities on the oxidised carbon nanotube surface which are binding and adsorbing Cr(III) at low pH.

3.3.3 Point of Zero Charge (pH_{PZC})

As indicated in Section 3.2.7 the zeta potentials of each type of adsorbent was measured as a function of pH in order to determine the point of zero charge (pH_{PZC}) of each adsorbent. **Figure 3-4** shows the zeta potential curves for each type of adsorbent. From these curves it can be seen that the pH_{PZC} is around 3.8, 7 and 8.5 for activated carbon, the functionalised and unfunctionalised MWCNTs respectively. The fact that activated carbon has the lowest pH_{PZC} suggests that its surface charge is the most negative. This further explains why its adsorption capacity is so poor. The negative surface charge facilitates electrostatic repulsion of the dichromate ions. On the other hand, the unfunctionalised MWCNTs have the highest pH_{PZC} implying that it has a more positive surface charge compared to the other two adsorbents. This favours the adsorption of the negatively charged dichromate ions. The difference in pH_{PZC} between the functionalised and unfunctionalised MWCNTs also accounts for the difference in their adsorption capacities. The pH_{PZC} of the functionalised MWCNTs is lower which implies that it has a more negative surface charge which hinders the adsorption of the negatively charged dichromate ions.

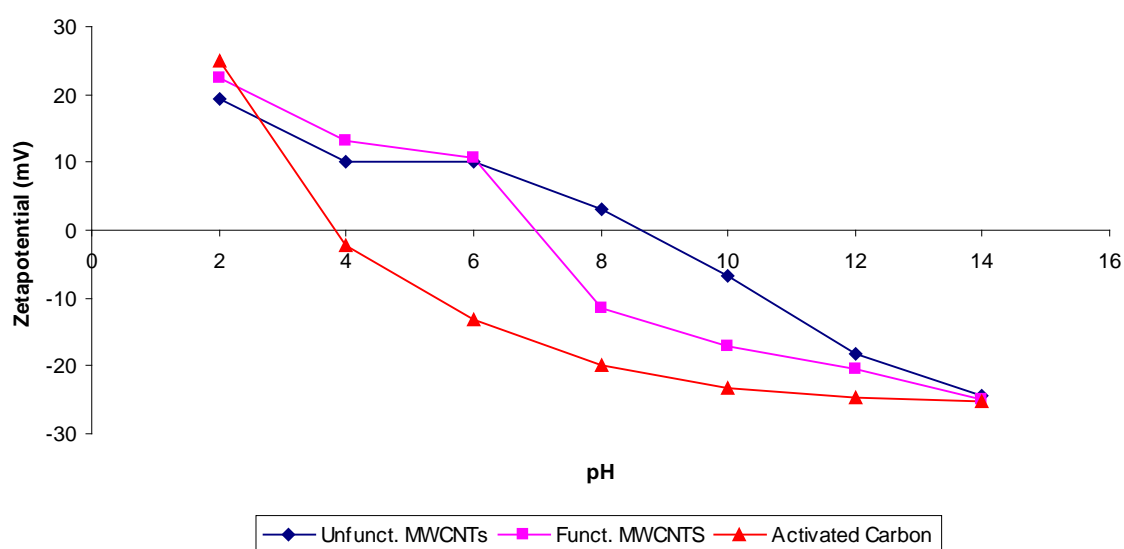


Figure 3-4: The zeta potential curves for each type of adsorbent as a function of pH

3.3.4 BET Surface Area and Porosity Measurements

As indicated in Section 3.2.8 surface area and pore size measurements were recorded on the functionalised and unfunctionalised MWCNTs. The BET surface area data revealed that the functionalised MWCNTs had a higher surface area ($130 \text{ m}^2\text{g}^{-1}$) than the unfunctionalised MWCNTs ($30 \text{ m}^2\text{g}^{-1}$). The porosity data as expected revealed that both types of MWCNTs showed little microporosity. The diffusion issues, expected with activated carbons that have a high microporosity are therefore not expected for the MWCNTs.

3.3.5 Initial Cr(VI) Concentration

Figure 3-5 shows the effect of the initial Cr(VI) concentrations on the adsorption capacities of the adsorbents. The percentage Cr(VI) adsorbed decreases as the initial Cr(VI) concentration increases where the %Cr(VI) adsorbed decreases steadily to about 15% as the initial concentrations increase to 3000 and 4000 ppb respectively. Since the quantity of nanomaterials used was fixed at 0.1 g the number of active adsorption sites remained constant. These sites eventually become saturated with dichromate ions and therefore are unable to accommodate any more ions at higher concentrations. It is of interest to note that the unfunctionalised MWCNTs still adsorb to a greatest extent at lower concentrations. However, at higher concentrations when saturation starts to set in the adsorption capacities of both the functionalised and unfunctionalised MWCNTs are almost the same. As expected, activated carbon again showed no significant uptake of Cr(VI).

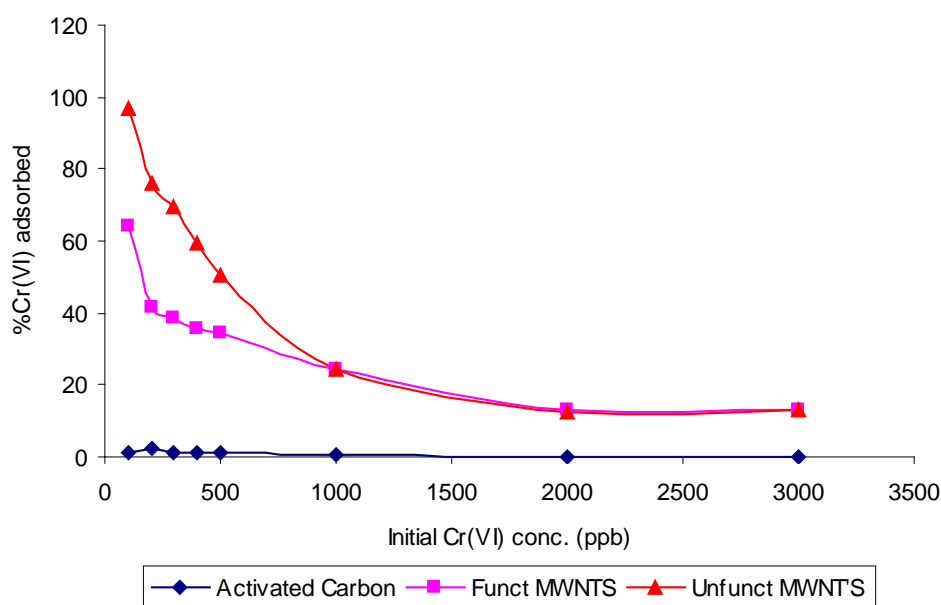


Figure 3-5: The effect of initial Cr(VI) concentrations on the uptake of Cr(VI) by the various adsorbents

3.3.6 Competing Anions

Competing anions are known to influence Cr(VI) uptake^{126,229,252,298}. The chloride ion was selected as a possible competing anion as this ion is often added to industrial effluents for water treatment and has already displayed a potential to hinder the adsorption of Cr(VI) on adsorbents like activated carbon¹²⁶. The other ion that was selected was the sulphate ion. This ion is chemically similar to dichromate ion with respect to charge. **Figure 3-6** shows the influence of these interfering ions (0.1 M) on the uptake of Cr(VI). The adsorption of the dichromate ions is clearly hindered by the presence of potentially competitive anions. The negatively charged dichromate ions are easily repelled by the negatively charged chloride and sulphate ions.

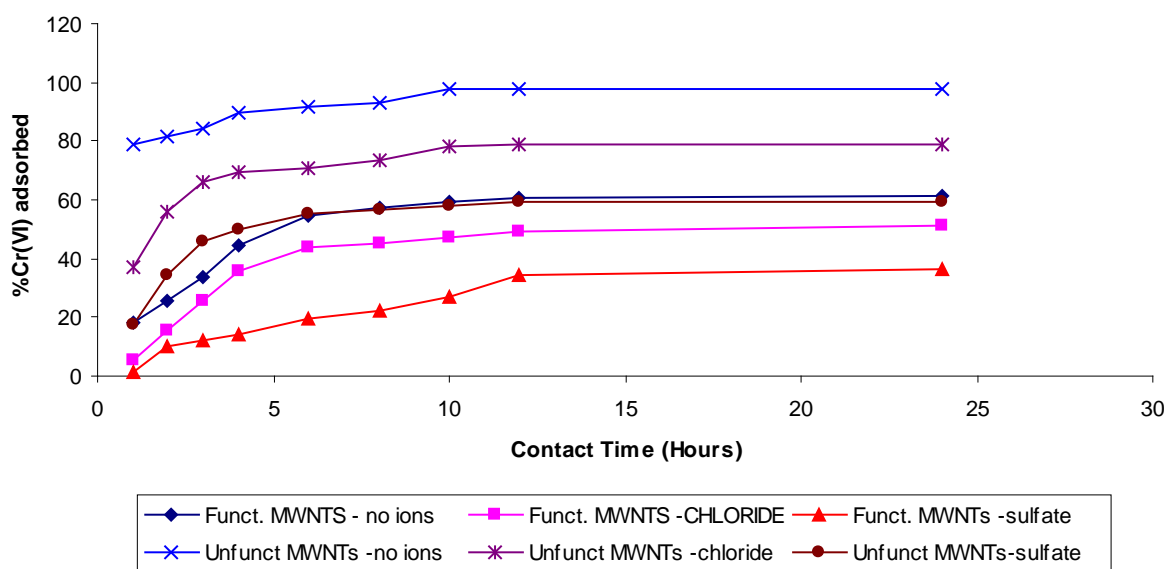


Figure 3-6: The effect of competing anions on the uptake of Cr(VI) from aqueous solution

The sulphate ion inhibits the adsorption process to a much greater extent than the chloride ions. This is possibly due to the chemical similarity between the dichromate and sulphate ions and the extra negative charge on the sulphate ion.

It is possible that the nanotube surface has a greater affinity for the chloride and sulphate ions than for the dichromate ions. Thus, a possible ion-exchange mechanism could account for the adsorption that has occurred. This is confirmed by the results shown in **Figure 3-7** which clearly shows that the uptake of Cr(VI) by both types of MWCNTs is hindered by the presence of both sulphate and chloride ions and these ions thus work synergistically in hindering the adsorption process. In other words, the decrease in adsorption is additive when both types of competing anions are present.

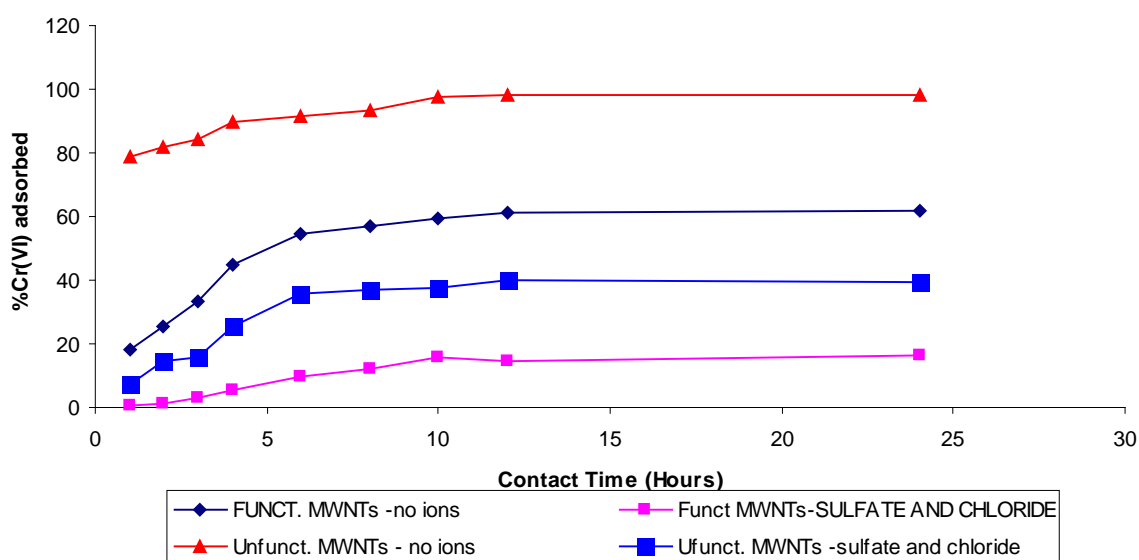


Figure 3-7: The combined effect of sulfate and chloride ions on the uptake of Cr(VI)

3.3.7 Adsorption Isotherms

The Langmuir and Freundlich isotherms are the two most common isotherms that describe the distribution of a metal ion between a solid and a liquid phase and have been extensively used in the literature to model the uptake of various adsorbents.^{6,98,100,126,453} The adsorption data obtained for both the functionalised and unfunctionalised MWCNTs as a function of initial Cr(VI) concentrations was used to fit the linear forms of the Freundlich and Langmuir adsorption isotherms. The linear form of the Freundlich equation is given as:-

$$\log(X/m) = \log K + \frac{1}{n} \log C_e \quad (3-4)$$

where X is the amount of Cr(VI) adsorbed (μg), m is the mass of adsorbent onto which Cr(VI) is adsorbed, and C_e is the equilibrium concentration of Cr(VI) in solution, K is a fitting parameter which is a constant and $\frac{1}{n}$ is a measure of

adsorption intensity.⁴⁵³ Basically this isotherm indicates that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of solute in solution varies as a function of solution concentration. **Figure 3-8** shows the plot of $\log (X/m)$ against $\log C_e$ for both the functionalised and unfunctionalised MWCNTs.

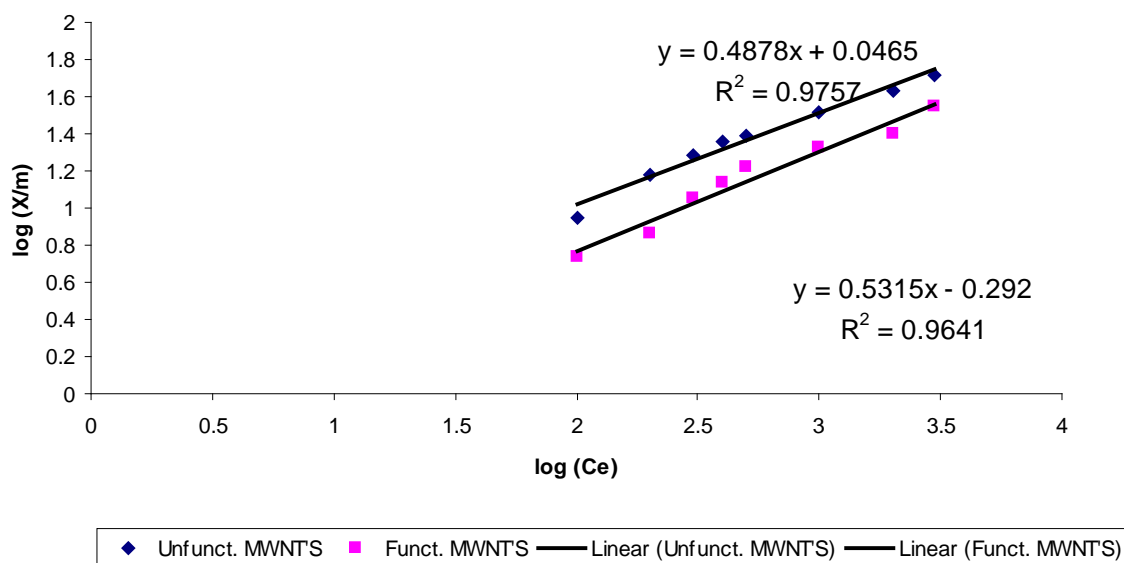


Figure 3-8: The Freundlich adsorption isotherm for both functionalised and unfunctionalised MWCNTs

It can be seen from **Figure 3-8** that the plots obtained for both types of adsorbents are linear with R^2 values of 0.98 and 0.96 respectively. This suggests that the Freundlich Isotherm applies to both adsorbent – adsorbate systems. The $\frac{1}{n}$ values for the unfunctionalised and functionalised MWCNTs are calculated as 0.49 and 0.53 respectively from the data. Thus, not much difference in the adsorption intensities of both adsorbents is observed and since these values are less than 1, favourable adsorption occurs.^{6,98} The linear nature of both the adsorption isotherms suggest the adsorption process is a surface phenomenon.²²⁹ The data was plotted using the linear form of the Langmuir equation:

$$C_e/[X / m] = 1/bQ + C_e/Q \quad (3-5)$$

where C_e is the equilibrium concentration of Cr(VI) in solution, Q is the number of moles of Cr(VI) adsorbed per unit mass of adsorbent (adsorption capacity) upon forming the monolayer on the adsorbent surface, and b is the Langmuir constant which is related to binding energy.⁴⁵³ This isotherm applies only to monolayer adsorption on a surface which contains a finite number of binding sites.⁴⁵³ This is also based on the assumption that the energies of adsorption are uniform and no transmigration of adsorbate occurs in the plane of the adsorbing surface. **Figure 3-9** shows the plot of $C_e/(X/m)$ against C_e for both the unfunctionalised and functionalised MWCNTs. **Figure 3-9** shows clearly that both the functionalised and unfunctionalised MWCNTs obey the Langmuir Isotherm.

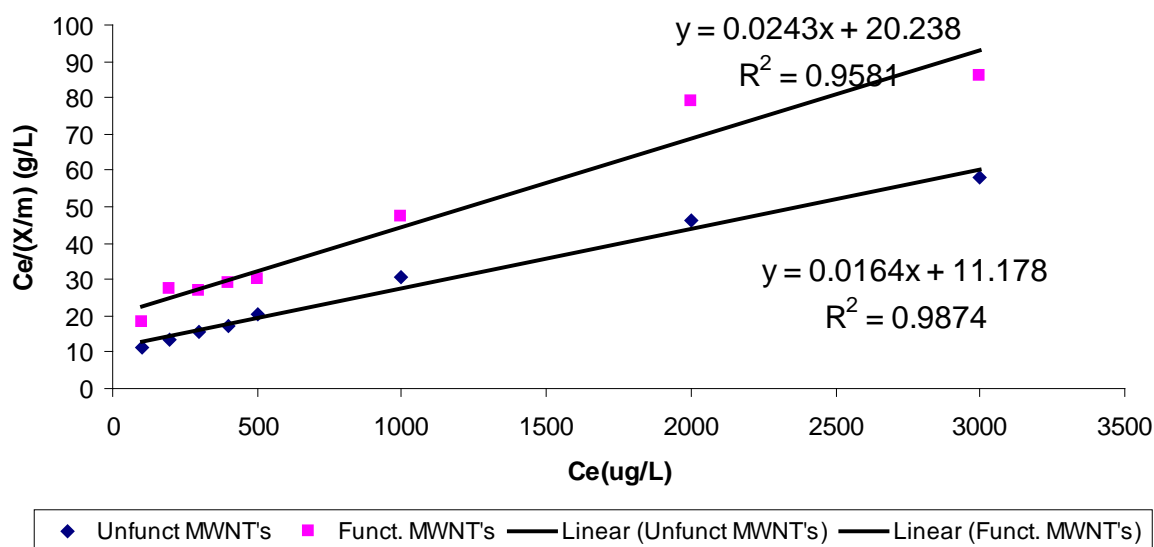


Figure 3-9: The Langmuir adsorption isotherm for both functionalised and unfunctionalised MWCNTs

3.3.8 Desorption

Figure 3-10 shows the plot of the % Cr(VI) desorbed against *washing time*. From **Figure 3-10** it is seen that almost all the Cr(VI) adsorbed onto the surfaces of the functionalised and unfunctionalised MWCNTs is desorbed after washing the adsorbed Cr(VI) off at hourly intervals ranging up to 24 hours with 100 mL distilled

water per washing. Both types of MWCNTs can therefore be regenerated and reused after desorption has occurred provided that the structural integrity of these materials is not significantly altered by the desorption process.

Further, it was found that at a higher pH (pH 14) desorption occurs to a faster extent for both types of MWCNTs. This suggests that the excess hydroxyl ions present at high pH aid in the desorption of Cr(VI) by repelling the negatively charged dichromate ions or rather by out competing these ions for active surface sites. Mungasavalli et. al.³⁰⁵ also made a similar observation for the uptake of Cr(VI) by the biological organism, *Aspergillus Niger*.

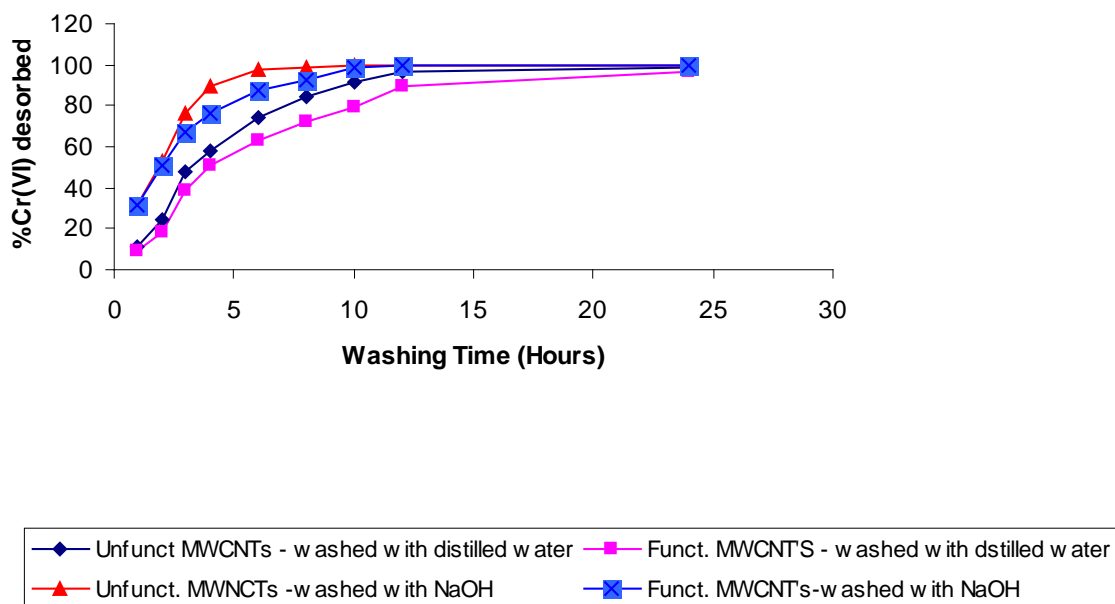


Figure 3-10: The % Cr(VI) desorbed from the surface of functionalised and unfunctionalised MWCNTs

3.3.9 Mechanism of Cr(VI) removal

Four primary mechanisms can account for the uptake of Cr(VI) by the MWCNTs. These are an ion-exchange mechanism, electrostatic interactions, a redox mechanism and intraparticle diffusion. The redox mechanism is supported by the

higher degree of adsorption that is observed at lower pH where Cr(VI) is known to be reduced to Cr(III). This can be coupled to the oxidation of the nanotube surface which will consequently contain carboxyl moieties. The Cr(III) ions generated are then adsorbed by forming bonds with the oxygen atoms on the carbonyl group (chemisorption). However, the fact that the adsorbed chromium readily desorbs rules out the possibility of this mechanism.

Adsorption is also reduced at higher pH where Cr(VI) predominates as $\text{Cr}_2\text{O}_7^{2-}$. This strongly suggests that there is competition between the excess hydroxyl ions present at higher pH and the negatively charged dichromate ions for active adsorption sites on the nanotube surfaces. This ion-exchange or chemical affinity competition is also supported by the fact that the competing anions such as chloride and sulphate ions reduce the uptake of Cr(VI). These ions are clearly out competing the dichromate ions for active adsorption sites.

An ion-exchange mechanism can be explained in terms of anion sizes. Even though the pH_{PZC} of the three adsorbents suggest that electrostatic repulsion also plays a key role, the dichromate ions are larger than the hydroxyl, chloride and sulphate ions and can thus be easily displaced from the adsorption sites. The competing anions were also present in larger concentrations than the dichromate ions (0,1M in each case as opposed to 100 ppb dichromate) and this can also play a role in the competition process.

The n values of the adsorption isotherms also indicate that intraparticle diffusion slows down the rate of adsorption. This accounts for the equilibrium being only attained after 12 hours of contact time.

Electrostatic interactions between the anions and the electron rich functional groups on the surfaces could also hinder the adsorption process to a minor extent.

3.4 Conclusion

The data presented in this chapter has shown conclusively that both functionalised and unfunctionalised MWCNTs can adsorb ppb levels of Cr(VI) from aqueous solution. Both adsorbents have a superior adsorption capability to that of activated carbon. The unfunctionalised MWCNTs have demonstrated a superior adsorption capability to that of the functionalised MWCNTs. This has been attributed to the fact that the functionalised MWCNTs contain electron rich atoms in their functional groups which repel the negatively charged dichromate ions and inhibit the adsorption process. This is verified by the fact that the adsorption capability of the MWCNTs improves by 30% once all the functional groups have been removed. This is further supported by the fact that the unfunctionalised MWCNTs have a higher pH_{PZC} than the functionalised MWCNTs.

The key factors which favour the adsorption process are increasing contact time, low pH and low initial concentrations of Cr(VI). The adsorption process is significantly inhibited by the presence of competing anions such as chloride and sulphate.

Both adsorbents obey the Langmuir and Freundlich Isotherms. The Langmuir Isotherm is consistent with monolayer adsorption on the MWCNTs. Both isotherms indicate that favourable adsorption occurs and that intraparticle diffusion could be a rate-limiting step resulting in the slow attainment of equilibrium.

Besides intraparticle diffusion, an ion-exchange mechanism has been identified as the key mechanism governing the adsorption process. This is supported by the fact that the adsorption process is enhanced at low pH and hindered by the presence of competing anions.

The dichromate ions are easily desorbed from the surfaces of both types of MWCNTs. The desorption is also enhanced at high pH due to the fact that the dichromate ions are deprotonated at high pH and are easily repelled and out competed by the excess hydroxyl ions. Thus both adsorbents can be regenerated

and reused to reduce cost factors. However, the desorption must be carefully conducted where the adsorbed chromium must be retained on the solid surface at low pH until this can be released back into aqueous solution for recycle and reuse.

Unfunctionalised MWCNTs have proven to be excellent adsorbents for the effective removal of parts per billion levels of Cr(VI) from aqueous solution. It is now of interest to see whether these MWCNTs can be used on actual industrial effluents containing ppb levels of Cr(VI). Chapter 4 therefore presents a study in which the adsorption performance of MWCNTs on an actual industrial effluent is evaluated and where recommendations for a good industrial practice are made.

CHAPTER 4

EVALUATION OF MULTI-WALLED CARBON NANOTUBES FOR THE EXTRACTION OF Cr(VI) FROM A COMPLEX CHEMICAL MATRIX

4.1 Introduction

It was established in Chapter 2 that studies of competitive adsorption on the ability CNTs to selectively extract a specific pollutant from a complex matrix are lacking. This chapter therefore focuses on evaluating the ability of both unfunctionalised and functionalised MWCNTs to selectively extract Cr(VI) from a complex chemical matrix such as an industrial effluent. A typical South African metal-plating effluent was used in this study. Much emphasis is placed on the chemical composition of the effluent which was manipulated to optimize the uptake of Cr(VI). The results from continuous flow studies are also reported. Recommendations for an industrial practice to treat industrial effluents that contain Cr(VI) (using MWCNTs) are also made.

4.2 Materials and Method

4.2.1 Adsorbents

4.2.1.1 Synthesis and Characterisation of Unfunctionalised MWCNTs

MWCNTs were synthesised by the nebulised spray pyrolysis of a solution containing 2.00 g of ferrocene, ethanol and enough toluene to make up 50.0 mL of solution.³⁷³ The “mist” was produced in a Dr. Hielscher UM20-1,6 MHz nebuliser and frequency controller and then carried into a furnace (Elite TSH 12/500-2216) which was set at 900°C using argon as the carrier gas. The flow rate was maintained at 500 sccm using a mass flow controller (Seven Star 07). The quartz tube used was 70 cm in length and 40 mm in diameter. The synthesis progressed for 45 minutes and the MWCNTs were collected from the tube furnace

after being cooled down to room temperature under argon. The MWCNTs were characterised by Transmission Electron Microscopy (TEM) using a JEOL 1000 transmission electron microscope, High Resolution Transmission Electron Microscopy (HRTEM) using a Philips CM200 equipped with a LaB6 emitter and Scanning Electron Microscopy (SEM) using a JEOL 5600 scanning electron microscope. The MWCNTs were found to possess a well-aligned tubular structure.

4.2.1.2 Functionalised MWCNTs

The same functionalised MWCNTs which were used in the study reported in Chapter 3 were also used in this study.

4.2.1.3 Silicon Carbide

The silicon carbide was commercially obtained from Sigma Aldrich (see **Table A1** in **Appendix 1** for physicochemical properties of the silicon carbide which includes the particle size). This material was obtained in the nanopowder form so that it would have similar characteristics to the MWCNTs.

4.2.2 Mixing of the MWCNTs into the Silicon Carbide Matrix

The synthesised MWCNTs (1,00 g) were physically mixed into the silicon carbide matrix (5,00 g) prior to packing in a column (60 mm long and 10 mm wide). For the control experiments, 6,00 g of the silicon carbide nanopowder was used but only 1.00 g of the MWCNTs was used in the control experiment when pure MWCNTs were used as the sole adsorbent.

4.2.3 Sampling of a Local Industrial Effluent

The industrial effluent was collected from a local chrome metal plating plant. The original effluent was treated with sodium sulfite (Na_2SO_3) to reduce Cr(VI) to Cr(III) and the Cr(III) was precipitated as $\text{Cr}(\text{OH})_3$. The final effluent released into the environment is therefore assumed to be “chromium free”.

Two samples were collected, one at the point of discharge into the environment and the other at a point where the effluent had combined with the local water supply. The purpose of collecting a sample after the leachate had combined with the drinking water was to examine the effect of dilution on the Cr(VI) content of the disposed effluent. The samples were collected in polypropylene bottles which were thoroughly washed with acid followed by deionised water prior to sampling. The samples were kept refrigerated when not in use and were also analysed for their initial Cr(VI) content using Adsorptive Stripping Voltammetry. In addition to this the complete chemical composition of the effluent was determined by Atomic Adsorption Spectroscopy (AAS), Inductively Coupled Mass Spectrometry (ICP-MS) and other analytical methods in order to establish the full range of components in the sample. The data are shown in **Table 4-1**.

4.2.4 Laboratory Scale Studies

For the laboratory scale batch adsorption experiments, 0.1 g of both the functionalised and unfunctionalised MWCNTs respectively was weighed out and placed in contact with 10 mL of the sample of the industrial effluent in sample vials. The MWCNTs were placed in contact with both samples of industrial effluents for contact times of 1, 2, 3, 4, 6, 8, 12 and 24 hours, respectively. Contact between the MWCNTs and the industrial effluents were facilitated by agitation on a shaker. After each specified contact time, the waste–nanotube suspension was filtered through a 0.45 µm EconoClear filter, commercially obtained from Microsep. The filtrates were retained for analysis of their Cr(VI) content by Adsorptive Stripping Voltammetry. The basic experimental protocol for these experiments is summarised in **Figure 4-1**.

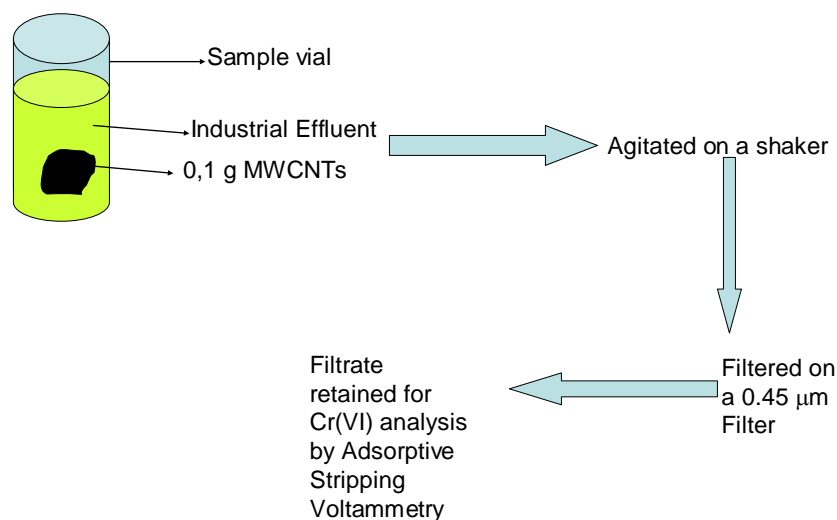


Figure 4-1: The experimental protocol followed for the laboratory scale batch adsorption studies

The influence of the chemical composition of the local industrial effluent was examined by identifying potential interfering species in the matrix and then removing these prior to contact with the MWCNTs. The industrial effluent was also spiked with higher concentrations of each species so that the effects of these species could be more carefully examined.

The effect of dilution was examined by collecting a sample of the effluent which had already combined with the drinking water and this was compared with the extent of adsorption of the original effluent.

4.2.5 Continuous Flow Experiments

A continuous flow experiment was set up as shown in **Figure 4-2**. Basically the industrial effluent was placed into a 200 mL glass vessel and pumped at a flow

rate of 10 mL per minute via a peristaltic pump into a column (60 mm long and 10 mm wide) containing the solid adsorbent i.e. the MWCNTs that were embedded into silicon carbide. As control experiments the silicon carbide (SiC) was also packed into the column without the MWCNTs. Another control experiment in which the MWCNTs were used as the only adsorbent was also conducted.

In each study, the column was eluted at contact times ranging from 1-24 hours. The eluants were analysed for their residual Cr(VI) content by Adsorptive Stripping Voltammetry.

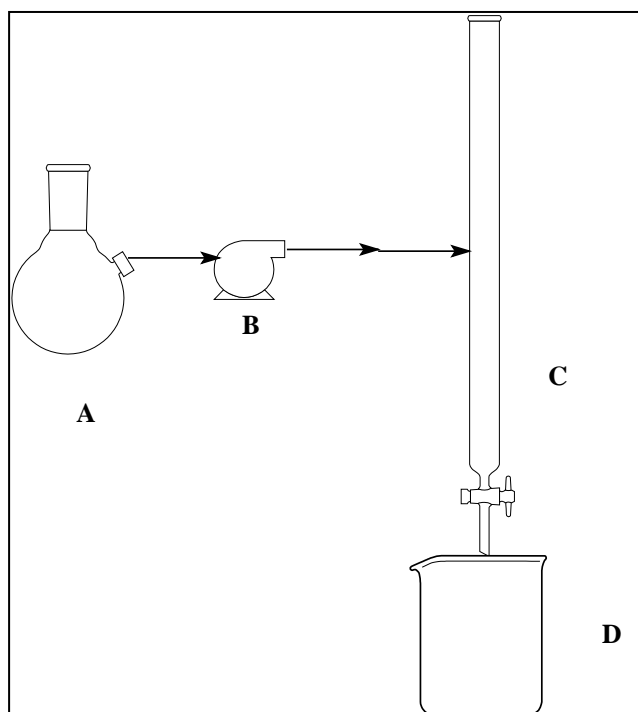


Figure 4-2: A schematic diagram showing the experimental set-up for the continuous flow studies A - glass vessel, B- peristaltic pump, C- ion-exchange column, D- collecting beaker

4.2.6 Desorption and Recycling Experiments

The desorption and recycling studies were conducted by setting up the mini-plant as described in Section 4.2.5 and by keeping the effluents in contact with the various solid adsorbents for 24 hours in the column described above. After the 24 hours of contact time had passed, the solutions were eluted by washing with a 1.00 M NaOH solution. The column was thoroughly washed at a flow rate of 10 mL per minute with NaOH over a 24 hour period to ensure that all the adsorbed Cr(VI) had been desorbed. The experimental protocol for the desorption experiments is outlined in **Figure 4-3**

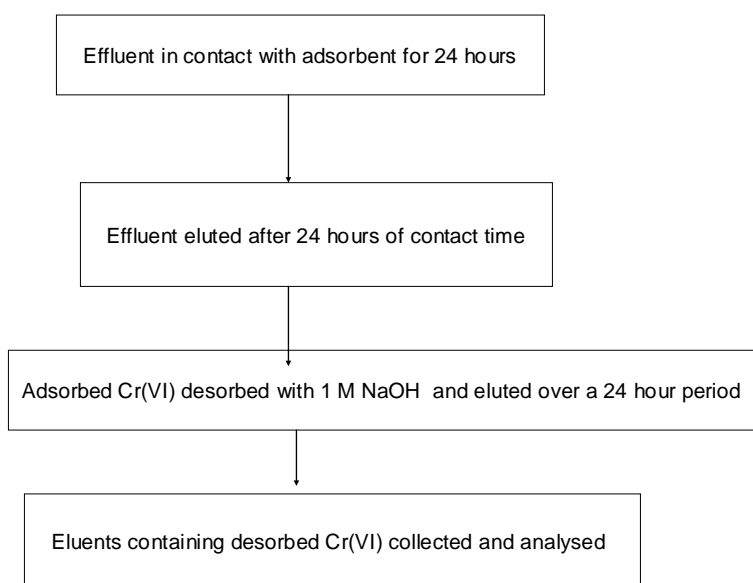


Figure 4-3: An outline of the experimental protocol for the desorption experiments

After desorption the column was reloaded with industrial effluent. The desorption and recycling experiments were repeated for 6 cycles in order to establish the regenerability of the adsorbents.

4.2.7 Analysis

All filtrates collected from the adsorption and desorption experiments were analysed for their Cr(VI) content using a MetroOhm polarograph in the Adsorptive Stripping Voltammetry mode. The same analytical protocol which was reported in Chapter 3 was followed.

4.2.8 Quality Assurance and Validation of the Analytical Data

All the batch experiments were conducted in duplicate and the average of two Cr(VI) concentrations is reported here. An allowance of 5% relative error was made. If the relative error exceeded 5% the analytical data was discarded and the experiment was repeated until the coefficient of variation was within 5%. The analytical data was found to be quite reproducible with a relative error of $\pm 2\%$. All data was analysed using a Statcalc package (Statistica 3.0).

An initial ICP-MS analysis was conducted to determine the total chromium content of the industrial effluent. These analytical results were very similar to those obtained for Cr(VI) analysis by Adsorptive Stripping Voltammetry thereby indicating that the only form of chromium present in the industrial effluent was Cr(VI). Therefore, all filtrates were also analysed by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) to validate the results obtained from Adsorptive Stripping Voltammetry. The results from both analytical methods were found to be reproducible and comparable within $\pm 5\%$.

4.3 Results and Discussion

4.3.1 Chemical Composition of the Industrial Effluent

Table 3-1 shows the complete chemical composition of the industrial effluent that had been treated with Na_2SO_3 to reduce all the Cr(VI) species to Cr(III). From this table it is evident that in addition to Cr, the industrial effluent also contains other heavy metals namely, Pb, Cu, Ni, Fe and Zn. It is possible that ions of these metals could affect the uptake of Cr(VI).

Table 4-1: The Chemical Composition of the Industrial Effluent

Chemical Species	Analytical Method	Concentration (ppb)	Concentration (ppm)
Total Cr	ICP-MS	351.	
CrO_4^{2-}	Adsorptive Stripping Voltammetry	350	
SO_3^{2-}	UV Visible Spectroscopy using Ellman's Reagent		0.05
OH-	Ion-exchange chromatography		Not detected
Total Pb	AAS		0.27
Total Fe	AAS		1.82
Total Cu	AAS		3.59
Total Ni	AAS		4.41
Total Zn	AAS		1.22

The presence of sulphite (SO_3^{2-}) ions in the industrial effluent is to be noted. The source of these ions was Na_2SO_3 which was added to the effluent to reduce Cr(VI) to Cr(III). Since these ions are chemically similar to the chromate ions they could also potentially hinder the uptake of the chromate ions. In previous studies we have noted that the adsorption of Cr(VI) by MWCNTs is inhibited by the presence of competing anions such as sulphate (SO_4^{2-}) and chloride (Cl^-) via an ion-exchange mechanism (Chapter 3). Thus the possibility of inhibition by the sulphite ions cannot be discounted.

Finally, it is important to note that the concentrations of total chromium and chromate are almost identical. This suggests that the chromium is present predominately in the form of Cr(VI) in the industrial effluent. This is not surprising as all the Cr(III) which results from the reduction of Cr(VI) is removed by the precipitation as $\text{Cr}(\text{OH})_3$ prior to disposal of the industrial effluent. The fact that trace concentrations of Cr(VI) still prevail in the effluent after reduction and precipitation indicates that the reduction process does not completely eliminate chromium from the industrial effluent.

4.3.2 Laboratory Scale Studies

Figure 4-4 shows that both types of MWCNTs used in the experiment adsorb Cr(VI) from the industrial effluents. As expected from previous observations (Chapter 3) the adsorption capability of the unfunctionalised MWCNTs is higher than that of the MWCNTs which contain functional groups (Chapter 3). The high pH_{pzc} (8.9) of these materials renders them more favourable for anion uptake (see Chapter 3). It is to be noted that the maximum percentage of Cr(VI) adsorbed is only about 50%; (100% adsorption is expected (see Chapter 3)). The reason for this effect is discussed below.

The failure to attain the maximum removal percentage of 100% observed for pure aqueous Cr(VI) solutions (Chapter 3) could therefore be due to dilution effects. It was indicated in Section 4.2.3 that a sample of the industrial effluent was taken after it had combined with the local water supplies. This was done in order to examine the effect of dilution. This sample of the industrial effluent was analysed by Adsorptive Stripping Voltammetry for chromate and was found to have a Cr (VI) concentration of 154 ppb. This gave a dilution factor of nearly 50%.

Figure 4-5 compares the uptake of Cr(VI) from the dilute and concentrated effluent by the unfunctionalised MWCNTs after the removal of sulphite ions. The maximum uptake is indeed achieved in the dilute effluent. This has been attributed to the saturation of active adsorption sites such that the excess

chromate ions at higher concentrations cannot be accommodated (Chapter 3). The maximum uptake capacities were calculated from the following equation:

$$q_e = (C_i - C_e) \frac{V}{m} \quad (4-1)$$

Where q_e is the uptake capacity in mg per g, C_i and C_e are the initial and equilibrium concentrations of Cr(VI) respectively, V is the volume of the solution in litres and m is the mass of the adsorbent.

It was found that the maximum uptake capacities were 1,03 mg per g and 1,87 mg per g for the concentrated and dilute effluents respectively thereby indicating that the capacity of the MWCNTs is higher when dilution occurs.

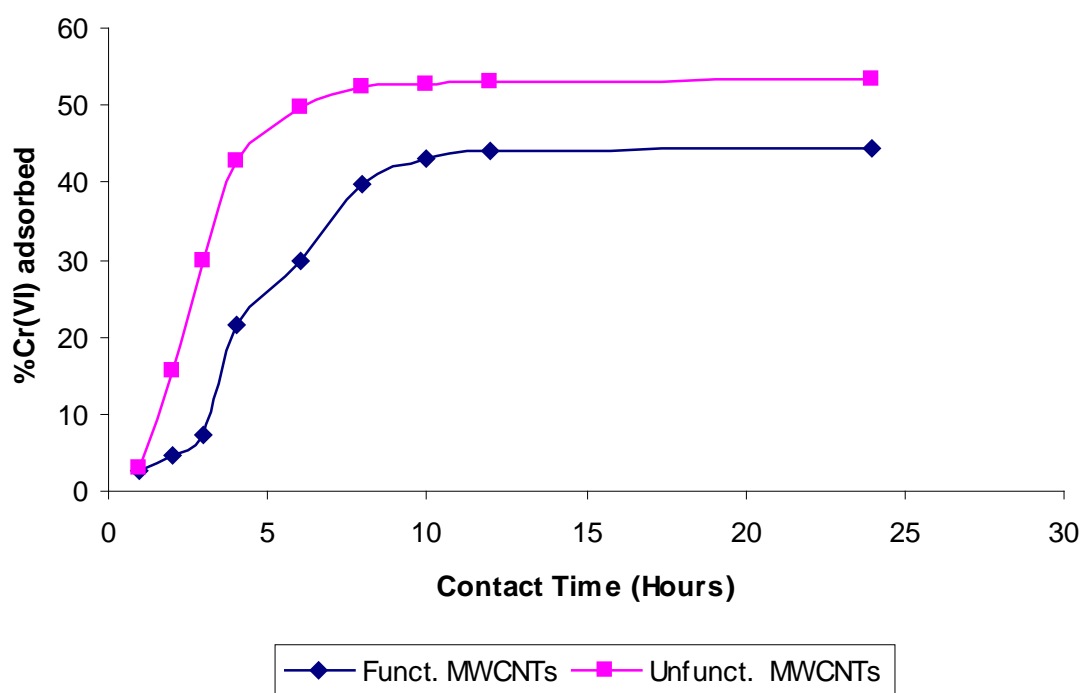


Figure 4-4: The uptake of Cr(VI) from the industrial effluent as a function of contact time

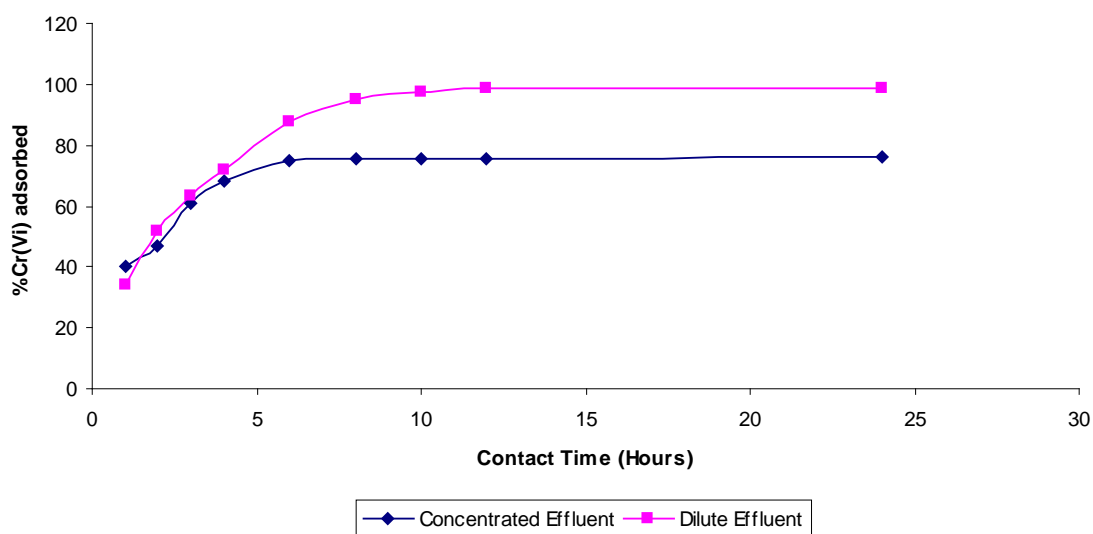


Figure 4-5: The effect of dilution on the uptake of Cr(VI) by unfunctionalised MWCNTs

4.3.3 Matrix Effects

4.3.3.1 Effect of the Presence of Sulphite Ions

Since sulphite ions were identified as chemical components that could hinder the adsorption process, the effect of the removal of sulphite ions on the uptake of Cr(VI) was examined. The sulphite ions were completely precipitated as calcium sulphite by adding 200 mL of 0.1 M calcium acetate to the industrial effluent. Analysis for sulphites by UV-visible spectroscopy showed that sulphite ions were not detected in the treated sample. The precipitate was removed by filtration and the filtrate was kept in contact with both the functionalised and unfunctionalised MWCNTs for contact times ranging from 1-24 hours. Since no Cr(III) was detected in the effluent and Cr(VI) is known to be highly mobile, the presence of both forms of chromium in the precipitate was not determined. **Figure 4-6** shows the results from these experiments.

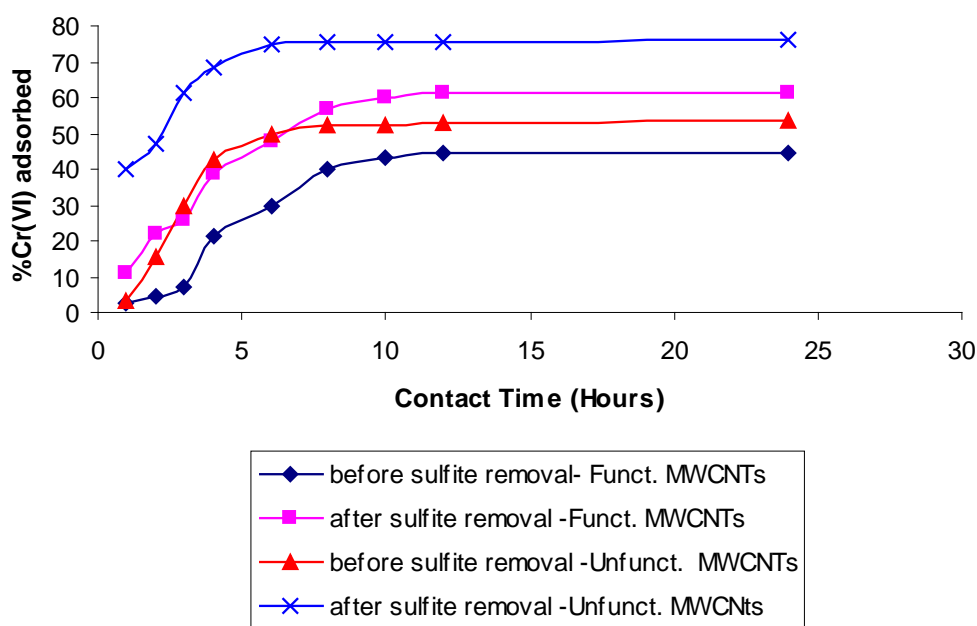


Figure 4-6: The effect of the presence of sulphite ions on the uptake of Cr(VI)

The adsorption by both types of MWCNTs increases by almost 20-30% once the sulphite ions were removed. To further validate these results the industrial effluent was spiked with Na_2SO_3 . The concentrations of Na_2SO_3 used were 0.1 M, 0.5 M and 1.0 M respectively. Since the unfunctionalised MWCNTs showed the highest adsorption capacities thus far, the experiments described herein were conducted on only these types of MWCNTs. The results are shown in **Figure 4-7** where it is noted that the adsorption capacity of the unfunctionalised MWCNTs decreased with increasing Na_2SO_3 concentrations. This verifies that the sulphite ions hinder the uptake of Cr(VI). This could occur by an ion-exchange mechanism where these ions out-compete the chromate ions for active adsorption sites on the MWCNT surface. The results in Chapter 3 have presented experimental evidence for the uptake of Cr(VI) on MWCNTs by an ion-exchange mechanism.

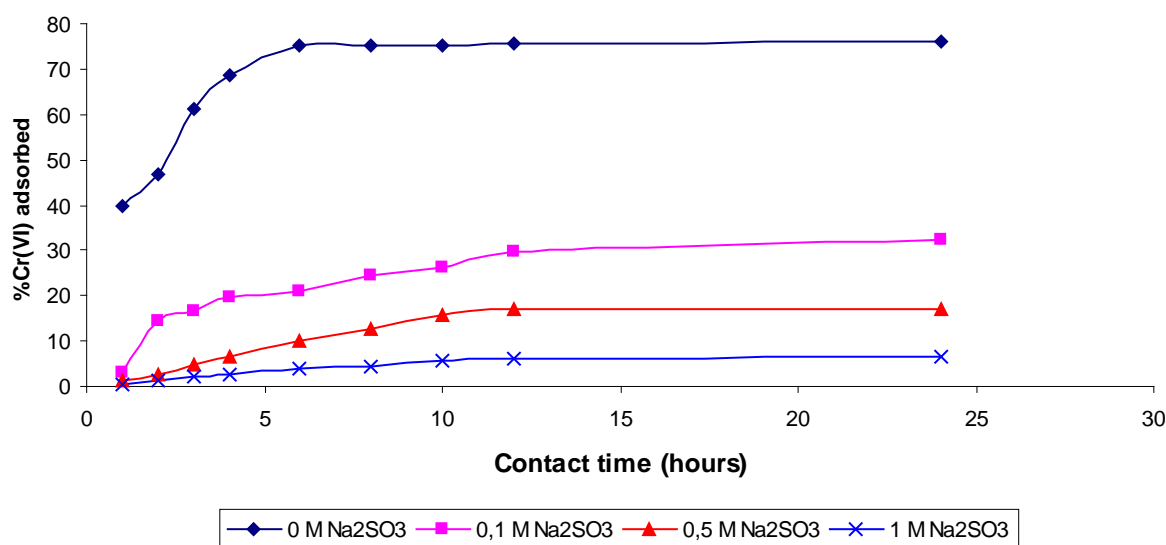


Figure 4-7: The influence of increasing Na₂SO₃ concentrations on the uptake of Cr(VI) by unfunctionalised MWCNTs

4.3.3.2 Effect of the Introduction of Acetate Ions

Acetate ions were also introduced into the matrix of the industrial effluents by adding calcium acetate to precipitate the sulfite ions. Experiments in which the industrial effluent was spiked with 0.1 M, 0.5 M and 1.0 M calcium acetate respectively (after sulphite removal) were conducted. Results showed that the uptake of Cr(VI) remained constant regardless of the concentration of acetate ions added (**Figure 4-8**). This indicates that the acetate ions do not hinder the adsorption process.

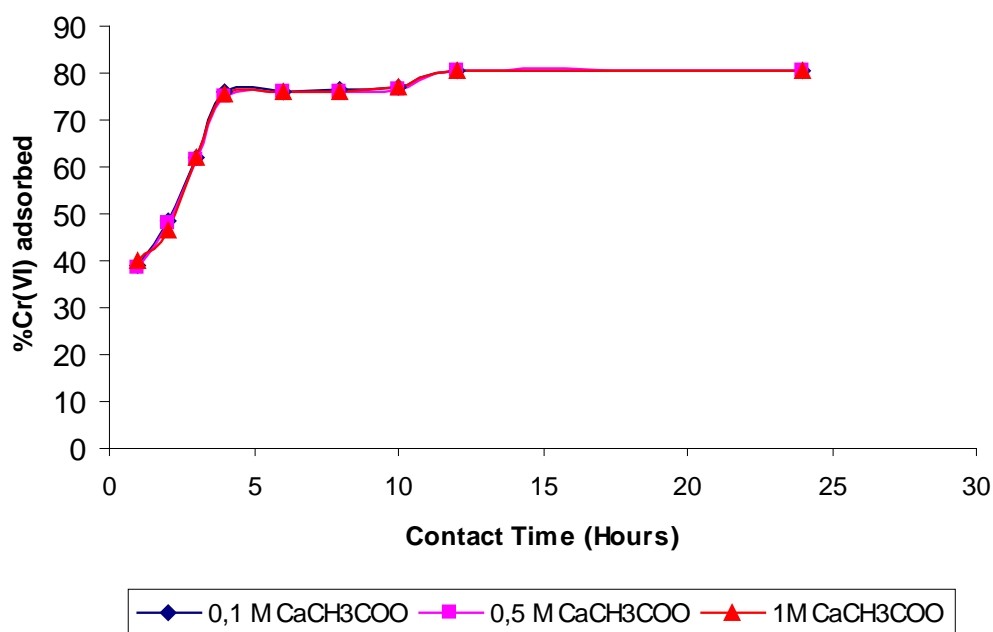


Figure 4-8: The effect of increasing concentrations of acetate ions on the uptake of Cr(VI) after the precipitation and removal of sulphite ions

4.3.3.3 Effect of the Presence of Other Heavy Metal Ions

Although **Figures 4-6 to 4-8** indicate that the uptake of Cr(VI) is enhanced after the complete removal of sulphite ions, the maximum adsorption observed is still only about 80% of the theoretical maximum. Clearly there is some chemical interference from other chemical species e.g. from other heavy metals which are present. To verify this 200 mL of 0.1 M sodium sulphide (after sulphite removal) was added to the effluent to remove the heavy metals by precipitation since all of the heavy metals are known to form insoluble sulphides with K_{sp} values ranging from $1,0 \times 10^{-35}$ to 1×10^{-17} at room temperature⁴⁵⁴. A complete chemical analysis was again conducted using AAS, ICP-MS and UV-visible Spectroscopy to verify that all the heavy metals were removed and that no sulfide ions which could interfere with the adsorption process remained. **Figure 4-9** compares the adsorption capacities of the MWCNTs before and after the removal of the heavy metals.

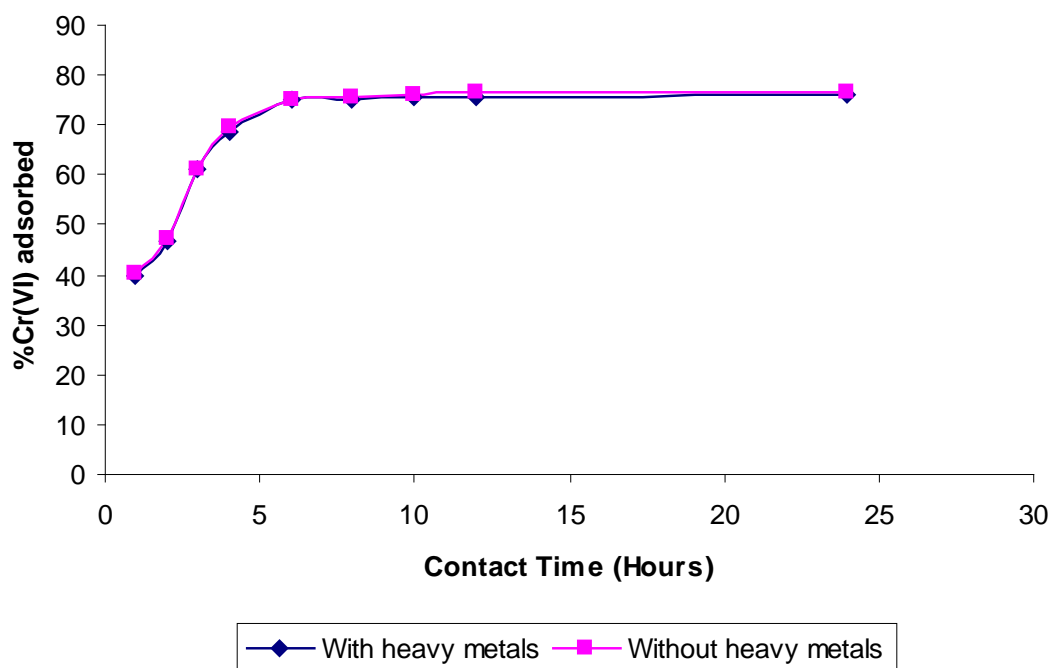


Figure 4-9: The effect of removing other heavy metals on the uptake of Cr(VI) by unfunctionalised MWCNTs

The removal of the heavy metals had no significant effect on the adsorption process. Thus, the presence of other heavy metal ions at these concentrations does not hinder the adsorption of Cr(VI). Other workers⁴⁵⁵ have reported interference by Zn(II) for the uptake of Cr(VI) (0,05 g/L of each metal solution in 0,5 M HCl) by cyanex 923. However, in this case it seems that the synthesised MWCNTs are highly selective to the uptake of Cr(VI).

4.3.4 Continuous Flow Studies

The continuous flow experiments were set up as described in Section 4.2.5 and in **Figure 4-2**. In these experiments the column was loaded with i) MWCNTs, ii) MWCNTs mixed into silicon carbide and iii) silicon carbide only. Before conducting the continuous flow studies the sulphite ions which presented chemical interference were removed by precipitation with calcium acetate. The industrial effluent was also diluted by a factor of 50% (150 ppb) to ensure that all the chromium could be removed. The effect of pure MWCNTs was first determined to

provide a standard for the process. The results from the continuous flow studies are shown in **Figure 4-10**.

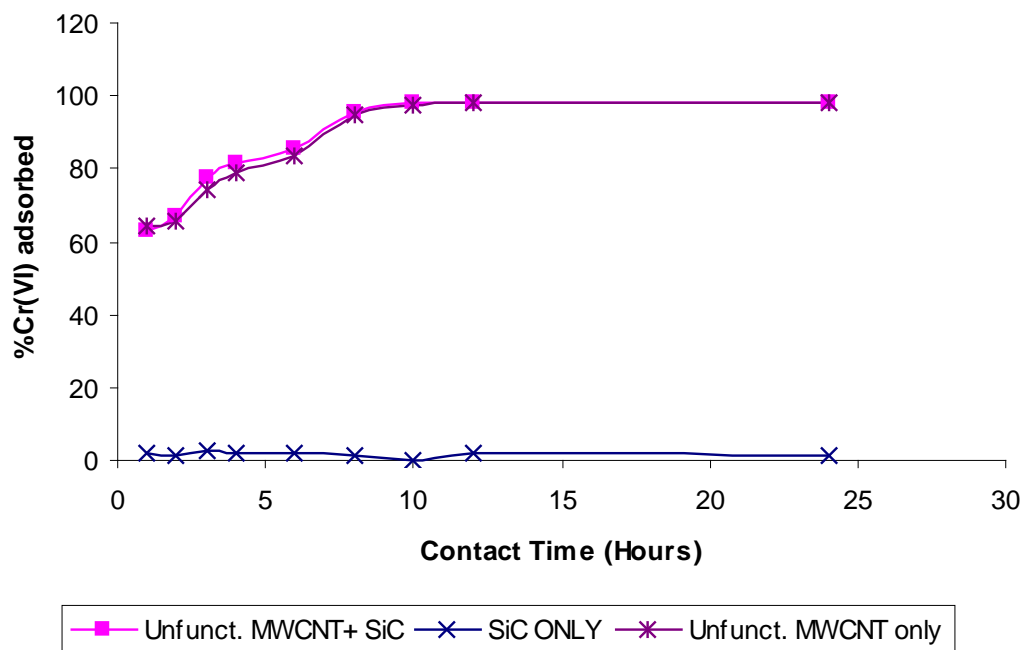


Figure 4-10: Continuous Flow Studies on the uptake of Cr(VI) from the industrial effluent using various adsorbents

The results show that the amount of Cr(VI) adsorbed increased with an increase in contact time but that the maximum removal of chromate ions is attained within 12 hours of contact time. This observation is consistent with other studies on similar laboratory scale experiments (Section 4.3.2). The attainment of the maximum removal of chromate ions after 12 hours of contact time has been attributed to intraparticle diffusion and was supported by the relevant adsorption isotherm models (Chapter 3).

No chromium adsorption occurs when silicon carbide is used as the only adsorbing matrix. Silicon carbide is known to be inert and non-porous and therefore is not expected to adsorb any Cr(VI).⁴⁵⁶ Its strength also renders it

suitable as a composite material for MWCNTs when used on an industrial scale. Thus, the adsorption that occurs when the MWCNTs are mixed into silicon carbide is due only to the action of the MWCNTs (17% by mass). Even when diluted in SiC the MWCNTs are still as effective at adsorbing the chromate ions (98% adsorption attained) as with no SiC present. The maximum adsorption capacity (breakthrough) with and without the silicon carbide support was 3,97 mg Cr(VI) per gram MWCNTs. This was calculated from the following equation:

$$q_e = (C_i - C_e) \frac{V}{m} \quad (4-1)$$

where q_e is the uptake capacity in mg per g, C_i and C_e are the initial and equilibrium concentrations of Cr(VI) respectively, V is the volume of the solution in litres and m is the mass of the adsorbent.

4.3.5 Desorption and Recycling Experiments

As described in Section 4.2.3 and **Figure 4-3.**, the desorption and recycling experiments were conducted by loading the column with effluent for 24 hours and thereafter washing the column with 0,1 M NaOH to desorb all the Cr(VI) that had been adsorbed.

Figure 4-11 shows the results obtained from the desorption and recycling experiments. This figure shows clearly that almost all the adsorbed Cr(VI) can be desorbed even after six cycles of adsorption and desorption. The MWCNTs mixed into SiC only lost 2% of their mass after six cycles of adsorption and desorption. A 1% mass loss (of the original 1.00 g used) was noted when the synthesised MWCNTs were used as the only adsorbents. However, this did not affect the adsorption and desorption efficiencies.

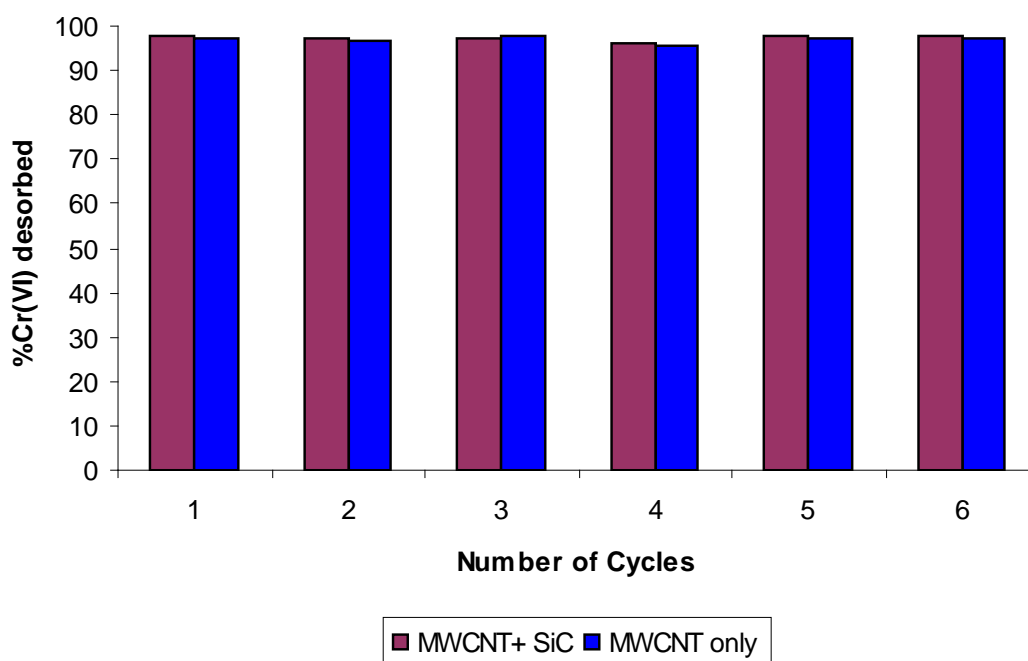


Figure 4-11: The extent of desorption of Cr(VI) from the surfaces of MWCNTs (both in the presence and absence of SiC) after six adsorption-desorption cycles

4.4 Conclusion

Unfunctionalised MWCNTs which were synthesised have demonstrated a superior ability to adsorb Cr(VI) than functionalised MWCNTs. In Chapter 3 it was noted that functionalised MWCNTs have a lower a pH_{PZC} than unfunctionalised MWCNTs which renders them unfavourable for anion uptake. The same applies in this study (pH_{PZC} of 8,9 for unfunctionalised MWCNTs versus 7,0 for functionalised MWCNTs). However, studies on industrial effluents have indicated a 50% reduced capacity for the uptake of Cr(VI) relative to Cr(VI) contained in pure aqueous solutions (See Chapter 3). This was due to the presence of sulphite ions. The introduction of acetate ions by the addition of calcium acetate did not hinder the adsorption process. Other heavy metals e.g. Pb were also detected in the sample matrix of the industrial effluent but these did not hinder the uptake of chromate ions.

Diluting the industrial effluent by 50% resulted in complete removal of Cr(VI). This was explained in terms of saturation of active adsorption sites by excess chromate ions.

Since the total chromium and Cr(VI) concentrations in the effluent were very similar it was concluded that all the chromium in the industrial effluent was present as Cr(VI). This provided evidence that the reduction of Cr(VI) to Cr(III) does not completely remove Cr(VI).

Attempts were made to add the MWCNTs into an inert matrix. The data revealed that higher adsorption capacities (maximum of 3,79 mg per g) are achieved when the unfunctionalised MWCNTs are used as the sole adsorbents. The MWCNTs and the MWCNTs-SiC columns gave similar results. The adsorbents described above could be regenerated and reused after six adsorption-desorption cycles.

The results have therefore revealed that MWCNTs with no functional groups are the best adsorbents for the uptake of Cr(VI) from industrial effluents due to a high pH_{pzc} which favours anion uptake. The selectivity of this material for Cr(VI) removal is poor (reduced removal percentage in the presence of sulphite ions). Thus, these MWCNTs-SiC mixtures may be used as solid phase adsorbents in the remediation of industrial wastes containing Cr(VI). A good industrial practice would be to mix the MWCNTs into an inert matrix like silicon carbide. Such a technology may complement existing technologies by removing the trace levels of Cr(VI) which prevail after reduction of Cr(VI) to Cr(III) and precipitation of Cr(III) as $\text{Cr}(\text{OH})_3$. However, the removal of competing ions needs to be established.

CHAPTER 5

PARTS PER BILLION (ppb) UPTAKE OF MERCURY BY SULPHUR-CONTAINING CARBON NANOTUBES²

5.1 Introduction

It was noted in Chapter 2 that mercury is an extremely toxic element. At the same time, mercury has important industrial applications which results in its presence in industrial wastes. Although the removal of mercury by other adsorbents like activated carbon has been successful, the need to explore carbon nanotubes as potential adsorbents has arisen. Only one study on this subject ⁴²³ has been conducted to date. Such a study reported a good uptake capacity for Hg(II) by MWCNTs functionalised with carbonyl, carboxyl and hydroxyl groups (100% removal of a 0,1 mg/L Hg(II) solution). However, there have thus far been no reports on the selectivity of MWCNTs for Hg(II) in the presence of competing cations. The possibility of making the CNTs more selective for mercury uptake by doping these with sulphur (since mercury does have a high affinity for sulphur) has not been considered. The uptake of ppb levels of mercury by CNTs also needs to be studied.

Hence, in this study the ability of MWCNTs to selectively extract ppb levels of Hg(II) and organic forms of mercury was investigated by exploiting mercury's affinity for sulphur and focussed on the adsorption performance of MWCNTs that were functionalised with sulphur-containing groups (S-MWCNTs). The adsorption capacity of S-MWCNTs was also compared with that of sulphur-containing activated carbon (S-AC) and unmodified MWCNTs and activated carbon. The influence of some key parameters such as sulphur content, contact time and solution pH are also discussed. Emphasis was placed on the relative selectivities

² A manuscript based on this chapter is currently in preparation for submission

of S-MWCNTs and S-AC especially in the presence of pollutants like sulphur dioxide (SO₂). The ability of mercury to desorb from all the adsorbents studied was also examined. Adsorption isotherm models were used to evaluate the maximum adsorption capacities of S-MWCNTs and S-AC. Finally, a mechanism for the uptake of mercury by S-MWCNTs is proposed.

5.2 Materials and Method

WARNING: Since mercury-containing compounds, especially the organic forms, are extremely toxic⁴¹ the necessary precautions were taken when working with these chemicals. These included wearing a dust mask so that these chemicals cannot be inhaled and the use of safety goggles, safety gloves and the necessary protective clothing so that these chemicals do not come into contact with the skin and eyes.

Powdered activated carbon was obtained from Merck. This was a base (KOH)-activated carbon. The MWCNTs were synthesised by the method described in Chapter 4.

Unless otherwise stated all chemicals used were purchased from Sigma Aldrich and are of analytical grade. The sources of Hg(II), monomethyl and dimethyl mercury were mercuric nitrate, monomethyl mercury chloride and a synthetic chloride derivative of dimethyl mercury (3,6-didodecyloxy-4,5-dimethyl-*o*-phenylene-bis(mercury chloride)) (See **Figure A2** in **Appendix 1** for structure) respectively. Basically a stock solution of 1000 ppm of each solution was prepared and then diluted to give a 100 ppb solution of each form of mercury.

The synthesised MWCNTs were heated in a tube furnace under argon at 900°C prior to use. An IR spectrum (not shown) verified the removal of functional groups from these MWCNTs.

5.2.1 Synthesis of Sulfur-containing Multi-walled Carbon Nanotubes (S-MWCNTs) and Sulfur-containing Activated Carbon (S-AC)

Sulfhydryl groups were added to the unfunctionalised MWCNTs by a method employed by Cech et. al.³⁷⁹ The method entailed treating 5.00 g of unmodified MWCNTs in a mixture of 98% H₂SO₄ (70 mL) and 55 % HNO₃ (30 mL) for 24 hours to introduce carboxyl and hydroxyl moieties. Extensive washing in 100 mL distilled water was then conducted to remove the acid. This was followed by refluxing the MWCNTs at 300⁰C in a suspension of 5,00 g phosphorus pentasulfide in 100 mL anhydrous toluene for 7 days. However, this method of adding sulphur to the MWCNTs only resulted in a sulphur content of 0.73% in the MWCNTs.

A suspension of 5.00 g MWCNTs, 50.00 g phosphorus pentasulfide and 100 mL anhydrous toluene were heated in a microwave oven (1000 Watt) for 2 hours to give a material with a sulphur content of 0.92%. The sulphur content of the MWCNTs was gradually increased by increasing the quantity of phosphorus pentasulfide used (**Table 5-1**) and repeating the reaction under microwave irradiation. All excess phosphorus pentasulfide was then removed by a 24 hour soxhlet extraction in 1 M NaOH. The presence of phosphorus pentasulfide was monitored by measuring the sulphur content before and after a 24 hour and 48 hour soxhlet extraction process respectively. The results have revealed that the excess sulphur content decreased substantially from 30.7% before soxhlet extraction to 4.00% after the 24 hour soxhlet extraction and stayed more or less constant (4.00%) after the 48 hour extraction. This verified that all excess sulphur (the phosphorus pentasulfide) had been successfully removed.

A similar method was employed to introduce sulphur containing groups onto 5.00 g `activated carbon by heating in a microwave oven for 2 hours of (**Table 5-1**).

The original reaction employed by Cech et.al.³⁷⁹ was also repeated using 500 g phosphorus pentasulfide and the sulphur content of the adsorbents (S-MWCNTs and S-AC) was compared to that obtained under microwave irradiation. Lastly, the amount of sulphur loaded onto the MWCNTs and activated carbon were tested as a function of time under microwave irradiation.

5.2.2 Batch Adsorption Studies

Batch adsorption studies were performed by placing 0.1 g of adsorbent into a sample vial and then 20 mL of each mercury solution was added to the vial. The MWCNT-mercury solution mixture was then agitated on a shaker (OrbiShake-Labotec) for a specified contact time (see **Figure 5-5**) to facilitate contact between the MWCNTs and the mercury solutions. The resulting suspensions were then filtered through a 0.45 μm filter which was purchased from Microsep. Typically contact times of 10, 20, 30, 40, 60, 80, 100 and 120 min were used.⁴⁵⁷ Similar control studies using S-AC, unmodified MWCNTs and unmodified activated carbon as adsorbents were also conducted. The filtrates were analysed by Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS). Further details of the analysis are described in Sections 5.2.5 and 5.2.6 and **Appendix 2**.

To investigate the influence of the pH of each MWCNT-mercury solution, the mixture was adjusted either with 0.1 M NaOH or 0.1 M HCl until the desired pH value was obtained. The pH of each solution was carefully monitored during the reaction using a MetroOhm pH meter and the pH of the solutions was varied across the pH scale (1,2,4,6,8,10,12 and 14).

The adsorption capacities of the S-MWCNTs and S-AC were also tested as a function of temperature. In these studies each form of mercury was kept in contact with the adsorbents for various contact times and in water baths maintained at 50°C and 100° C respectively.

5.2.3 Selectivity Studies

The selectivity of S-MWCNTs and S-AC for the uptake of mercury in a chemical matrix where the chemical species are likely to interfere with the adsorption of mercury was evaluated by conducting a series of studies discussed below:

5.2.3.1 The Effect of Competing Cations

The effect of Pb ($\text{Pb}(\text{NO}_3)_2$), Cd ($\text{Cd}(\text{NO}_3)_2$) and Cu ($\text{Cu}(\text{NO}_3)_2$) cations was investigated by spiking the mercury-adsorbent suspension with 10-2000 ppb of the metal cation solutions.

5.2.3.2 The Effect of SO_2 .

The effect of SO_2 was studied by bubbling excess SO_2 through the mercury adsorbent suspensions for contact times ranging from 10 to 240 min and examining the effect on the maximum adsorption capacity of Hg as a function of contact time. The effect of excess SO_2 was also tested as a function of pH by bubbling this through Hg(II) solutions (100 ppb) in which the pH had been adjusted to values ranging from 1-14 using either 0.1 M NaOH or 0.1 M HCl.

5.2.3.3 The Effect of Increasing Chloride Ion Concentrations

Since chloride ions can hinder the uptake of Hg(II)⁴⁵⁸, the uptake of Hg(II) by S-MWCNTs and S-AC was studied in the presence of varying chloride ion concentrations. This was achieved by spiking the Hg(II) adsorbent suspensions with different concentrations of a NaCl solution (10-2000 ppb). In an additional study, the effect of chloride ions on the uptake capacity using 2000 ppm sodium chloride was examined.

5.2.4 Desorption Experiments

The desorption capacity of each type of adsorbent was studied by maintaining the mercury solutions in contact with each type of adsorbent for a contact time of 120 min. The Hg-adsorbent suspensions were then filtered and washed with 0.1 M HCl. The washings were collected and then analysed for mercury by ICP-MS. In

an additional desorption experiment, the S-MWCNTs and S-AC were also washed with 0.5% thiourea in 0.05 M HCl.⁴⁵⁹ The purpose of this additional study was to examine the capacity of a sulphur-containing desorbent to release mercury from a mercury-sulphur complex and to evaluate the extent of regenerability of both adsorbents. The volumes of the thiourea solution (0.5% thiourea in 0.05 M HCl) used varied between 1-10 mL.

5.2.5 Analysis

All filtrates and washings collected from the adsorption and desorption experiments were analysed for their mercury content using an ICP-MS (Spectromass 2000). The software package used for the data analysis was Smart Analyzer supplied by Spectro. The optimized instrumental parameters are given in **Appendix 2**. The instrument was calibrated using standards with concentrations of 5, 10, 20, 50 and 100 ppb, respectively. The standards were prepared in 1% HNO₃ from a 100 ppb stock solution. The analysis was conducted in accordance with a known and developed method.⁴⁶⁰

The point of zero charge of each type of adsorbent used in this study was determined by measuring the zeta-potential of each adsorbent as a function of pH on a Malvern Zetasizer (type: Zetasizer Nano). These results are shown in **Table 5-3**.

5.2.6 Quality Assurance and Validation of Analytical Data

All the adsorption and desorption experiments were conducted in duplicate and the average of two mercury concentrations is reported. An allowance of 5% relative error was made. If the relative error exceeded 5%, the analytical data was discarded and the experiment was repeated until the relative error was within 5%. The analytical data was found to be quite reproducible with a relative error of $\pm 2\%$. All data was validated using Statistica 3.0.

Additionally, the analytical measurements were conducted in triplicate. Precautionary measures such as cleaning the torch and nebuliser and rinsing the

spray chamber with de-ionised water were taken to avoid sample contamination. The plastic sample tubing was also replaced with silico steel tubing (Restek) in order to minimise mercury adsorption in the walls of the sample tubing. Finally, the instrumental parameters were optimized to ensure the best resolution and analyte-background intensity ratio.⁴⁶⁰

5.2.7 Characterisation of S-MWCNTs and S-AC

The S-MWCNTs and S-AC were characterised using a Jobin Yvon T6400 Raman spectrometer to verify the presence of carbon-sulphur bonds. The spectrophotometer was linked to an Olympus microscope onto which a glass slide containing the S-MWCNTs and S-AC samples was mounted. The magnification of the microscope was set at twenty times (20 X) the objective lens magnification to focus the argon ion (Ar^+) laser to an excitation wavelength of 514,5 nm. The laser power of the sample was maintained at 1,2 mW to prevent local heating. The Raman spectrometer was backscattering configured and equipped with a liquid nitrogen cooled charge coupled detector (CCD). The Raman spectra were recorded on over the range of 200 to 3000 cm^{-1} but only the major peaks identified in the region of 300-700 cm^{-1} are reported here. The spectra of S-MWCNTs and S-AC are shown in **Figures 5-2** and **5-3** respectively.

5.2.8 Determination of the Sulphur Content of S-MWCNTs and S-AC

The sulphur content of both adsorbents were measured on a Perkin-Elmer C, H, S analyser (CHS-500). The mercury uptake capacity of each adsorbent was studied as a function of sulphur content using a 100 ppb Hg(II) solution and a pH of 12.15. The data is reported in **Figure 5-1** and **Table 5-1**.

5.3 Results and Discussion

5.3.1 Effect of Sulphur Content

The sulphur content of a series of activated carbons and MWCNTs was varied by reaction of the carbons and MWCNTs with phosphorus pentasulfide. The mercury uptake thus could also be used to determine the sulphur content. **Table 5-1** and

Figures 5-1 show a linear increase in mercury uptake (100 ppb solution) with increasing sulphur content for both the S-MWCNTs and S-AC.

Table 5-1: The Extent of Sulphur-loading and Mercury Uptake Capacities for S-MWCNTs and S-activated carbon

Amount of Phosphorus Pentasulfide added (g)	S-MWCNTs		S-AC	
	%S (± 0.01)	%Hg(II) Adsorbed (± 0.02)	%S (± 0.01)	%Hg(II) Adsorbed (± 0.02)
50	0.73	25.6	0.55	14.4
100	0.92	30.4	0.71	20.2
150	1.27	44.5	0.97	29.5
200	1.99	55.9	1.29	35.4
250	2.27	66.7	1.65	42.3
300	2.35	77.2	1.87	54.4
350	2.85	88.4	1.95	67.5
400	3.16	90.1	2.58	72.3
450	3.42	98.2	2.73	81.0
500	3.97	99.9	2.87	82.4
550	3.98	99.9	2.85	82.4
600	3.99	99.9	2.89	82.4

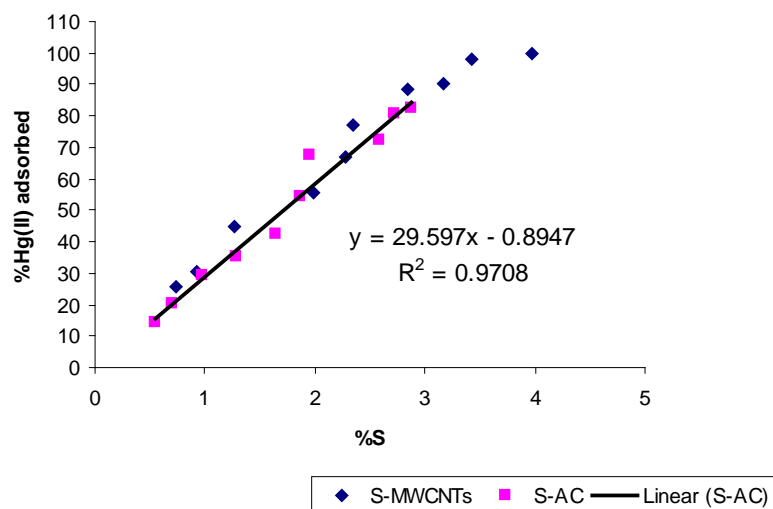


Figure 5-1: The effect of sulphur content on the uptake of Hg(II) by S-MWCNTs and S-AC

It has been stated in the literature that microwave-induced reactions are advantageous over conventional chemical syntheses in the sense that this improves the selectivity of the functionalisation and reduces reaction times³⁷⁵. The advantage of conducting the addition of sulphur to the MWCNTs under microwave irradiation is also highlighted in these results. In the original synthesis conducted by Cech et. al.³⁷⁹ only 0.73% sulphur functionalisation of the surface of the MWCNTs was achieved. Even when 500 g phosphorus pentasulfide was used this method only results in a sulphur content of 1.12% for S-MWCNTs and 0.95% for S-AC. Microwave radiation of 50 g phosphorus pentasulfide and 5.00 g MWCNTs and activated carbon respectively (2 hours) also gave similar results (**Table 5-1**). As the quantity of phosphorus pentasulfide was increased more sulphur was incorporated into the MWCNTs and activated carbon respectively (**Figure 5-1**, **Table 5-1**). The maximum amount of sulphur that could be incorporated onto the MWCNTs and activated carbon was 3.97% and 2.98% respectively. This was achieved by adding 500 g phosphorus pentasulfide. Increasing the phosphorus pentasulfide content beyond 500 g did not significantly increase the sulphur content of the MWCNTs and activated carbon presumably

due to surface saturation. The quantity of P_2S_5 needed to achieve the optimal sulphur content is however, very high. According to a review article by Ozturk et. al.⁴⁶¹ the mechanism of thionation by P_2S_5 proceeds firstly via the dissociation of P_4S_{10} followed by the replacement of oxygen atoms on oxo groups with sulphur atoms and the extent of thionation is controlled by the quantity of P_2S_5 released. For instance, less P_2S_5 results in monothionation but excess P_2S_5 results in complete thionation. Thus, it is proposed that the enormous amount of P_2S_5 used results in complete thionation and the dissociation of P_4S_{10} is the rate-limiting step which controls the extent of thionation and hence the sulphur content.

Figure 5-2 shows that increasing the reaction time (for the reaction under microwave) did not result in any significant changes in the sulphur content of S-MWCNTs and S-AC. The amount of sulphur which can be incorporated into MWCNTs (as compared to single-walled carbon nanotubes, SWCNTs) is thus limited due to lower binding energies and poor exposure of the CNT walls to the reaction medium.³⁸⁰

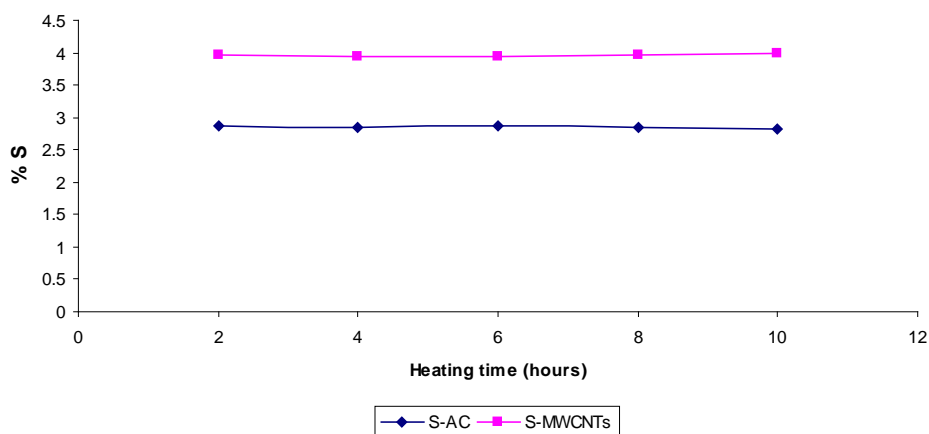


Figure 5-2: The effect of increasing heating time on the amount of sulphur incorporated into S-AC and S-MWCNTs

The S-MWCNTs and S-AC with the highest sulphur content were used as adsorbents i.e. 3.97% and 2.87%, respectively for the studies described below.

5.3.2 Synthesis and Characterisation of the S-MWCNTs and S-AC

Figure 5-3 shows the Raman spectra of the S-MWCNTs obtained before and after treatment with the suspension of phosphorus pentasulfide in anhydrous toluene for the MWCNTs. The spectra were recorded after removal of excess phosphorus pentasulfide by soxhlet extraction. From this figure, a strong peak at 500 cm^{-1} is noted due to the presence of thiol groups. According to Cech et.al.³⁷⁹ this peak is due to a combination of three vibrational modes at 475 cm^{-1} , 495 cm^{-1} , 503 cm^{-1} which correspond to three different S=C-S stretching modes. These are associated with thiol and thioester groups attached to the MWCNTs via sidewall thiolation³⁷⁹. The peak at 640 cm^{-1} is attributed to O-H vibrational modes which results from the initial acid treatment.³⁷⁹ Thus, there are two potential binding sites on the modified MWCNTs for mercury attachment - the thiol and OH groups. Similar Raman spectra were found for S-AC (see **Figure 5-4**)

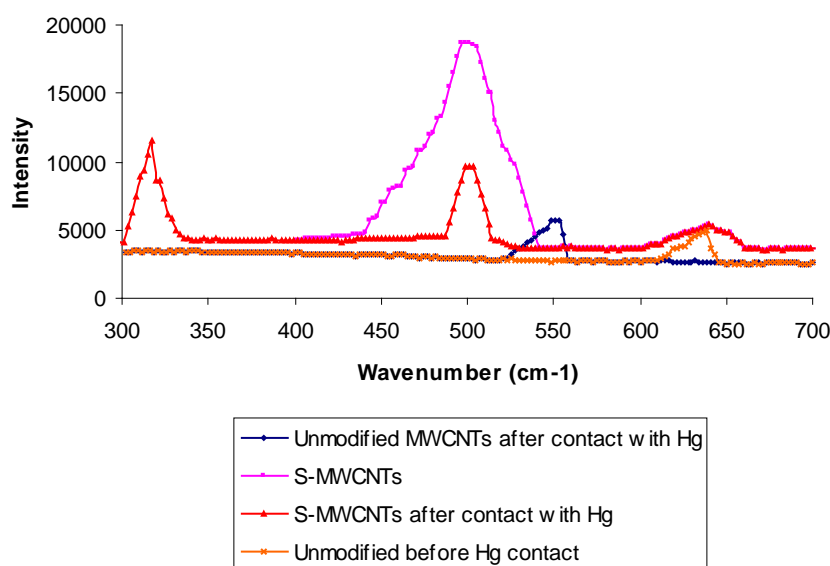


Figure 5-3: The Raman spectrum of the unmodified and S-MWCNTs (before and after contact with the mercury solutions)

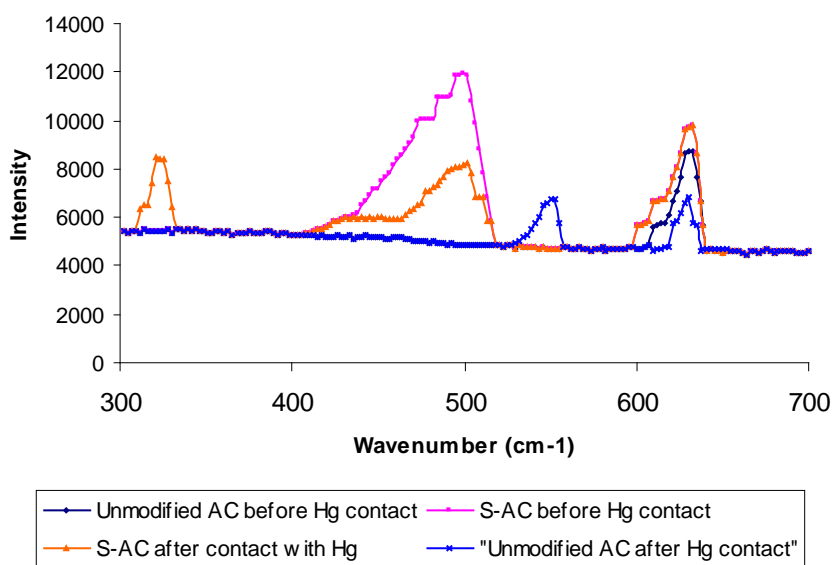


Figure 5-4: The Raman spectrum of S-AC and unmodified AC (before and after contact with mercury)

5.3.3 Effect of Contact Time

Figure 5-5 shows that the uptake of Hg(II) increases with increasing contact time and that the adsorption process is saturated after 120 minutes contact time. The contact times at which the adsorption reaches equilibrium differs as revealed by saturation studies reported other workers for the uptake of Hg(II)^{37,39,40,54,77,163,283} and can be related to the number of sulphur binding sites.⁴⁵⁷

The S-AC and S-MWCNTs enhanced the adsorption capacities for the uptake of mercury relative to the non-sulphur containing activated carbon and MWCNTs. This is not a surprising observation as mercury is known to have a high affinity for sulphur.³⁰ This chemical interaction between mercury and sulphur often leads to the formation of HgS, a less harmful form of mercury due to its insolubility and low volatility.³⁰ **Figures 5-3** and **5-4** present further evidence that it is the sulphur containing groups which interact with the mercury ions. In the Raman spectra it is noted that the bands corresponding to the thiol groups are significantly diminished after contact with mercury ions. Furthermore a new band which can be assigned to S-Hg-S vibrations⁴⁶² is noted at approximately 321 cm⁻¹. The primary mercury

species which could account for this chemical interaction have been identified as $\text{Hg}(\text{SH})_2$ and $\text{Hg}_2(\text{SH})_2$ ³⁶. In this case it is hypothesised that the adsorbed mercury is bonded to sulphur centres on the sidewalls of the MWCNTs. Cech et.al. have presented evidence of sidewall thiolation.^{379,380} No change in the O-H peak at 640 cm^{-1} after contact with the mercury solutions is noted. This suggests that the mercury ions selectively bind to the thiol groups on the MWCNTs.

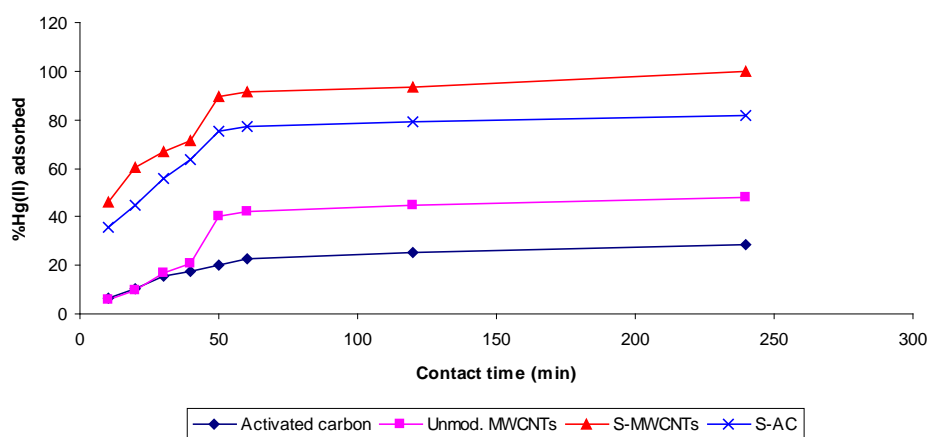


Figure 5-5: The effect of contact time on the uptake of Hg(II) from aqueous solution

The Raman spectra of both the *unmodified* MWCNTs and *unmodified* activated carbon (see **Figures 5-3** and **5-4**) reveal that the OH functional groups (620 cm^{-1}) interact with the mercury ions via a weak chemisorption process. Evidence of this interaction is shown by reduction in the peak at 620 cm^{-1} and the formation of a new peak at 550 cm^{-1} which has been assigned to Hg-O bonds.⁴⁶³ This suggests that there is some chemisorption of mercury occurring when mercury binds to the oxygen on the hydroxyl groups. This is however a weak interaction and the Hg-O bond is easily cleaved at low pH as seen by desorption data (see Section 5.3.9) and the possibility of mercury clusters forming via a physisorption onto the MWCNT surface must not be discounted.

Surface modified MWCNTs are known to have a more negative surface charge than unmodified MWCNTs (depending on the type of functional groups and heteroatoms introduced) and this helps to improve their cation exchange capacity.^{393, 396, 398} This is supported by the pH_{PZC} data shown in **Table 5-2**. Here it is noted that the S-MWCNTs have a lower pH_{PZC} than the unmodified MWCNTs thereby indicating that these have a more negative surface charge which is suitable for cation uptake.

Table 5-2: The Point of Zero Charge Data for each Adsorbent

Adsorbent	Point of Zero Charge (pH_{PZC})
S-MWCNTs ³	2.06
S-AC ⁴	3.14
Unfunctionalised MWCNTs	8.08
Activated Carbon ⁵	10.1

³ Maximum loading of sulphur 3.97%

⁴ Maximum loading of sulphur 2.98%

⁵ Base-activated

5.3.4 Initial Solution pH

It is evident from **Figure 5-6** that the uptake of mercury is pH dependent. This is consistent with the literature reports and is explained in terms of (i) the surface charge and (ii) the forms of mercury which are present in each pH range.^{37,39,40,54,464} At low pH the predominant form of mercury is HgCl_2 .³⁷ Excess H^+ ions also compete with the positively charged mercury ions for the surface of the adsorbents thereby hindering the extent of adsorption.

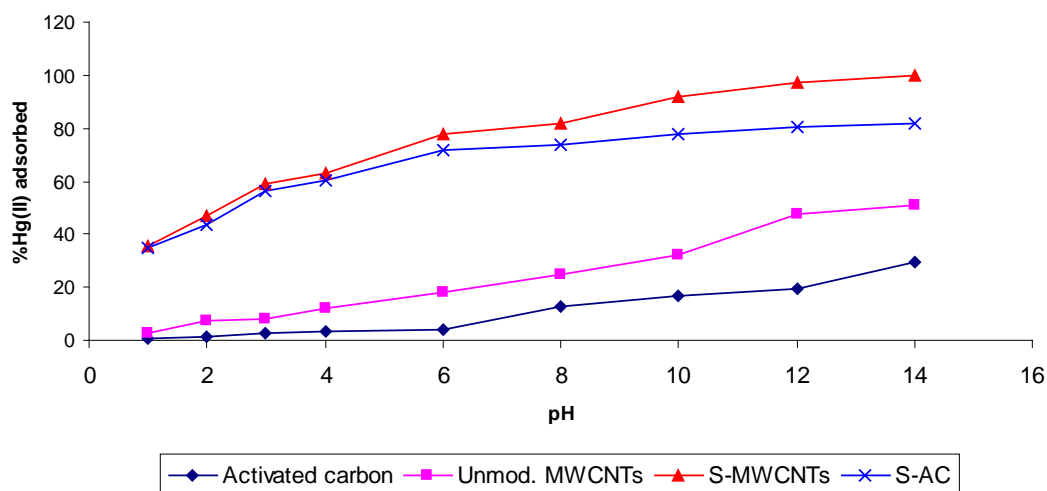


Figure 5-6: The effect of initial pH on the uptake of Hg(II)

Adsorption on the S-MWCNTs and S-AC appears to be less adversely affected at low pH. There is still some adsorption at low pH which is possibly due to some degree of protonation of the thiol groups which compete with the positively charged mercury ions.

The uptake of mercury is more pronounced at high pH. This can be explained in terms of the high electrostatic forces of attraction between the mercury ions and the excess hydroxyl ions at high pH. In fact, the predominant forms of mercury at high pH are $\text{Hg}(\text{OH})_3^+$,³⁷ $\text{Hg}(\text{OH})_2$ and HgOH^+ ³⁸ as seen on the Eh-pH diagram of mercury (see **Figure 2-4** in Chapter 2) and as reported in the literature.^{37,39,40} It is actually these forms of mercury that undergo adsorption.

5.3.5 The Influence of Temperature

Figure 5-7 shows that the time taken to reach the equilibrium adsorption capacity (breakthrough) is shortened when the reaction temperature is increased. Typically the breakthrough is reached within 50 and 20 minutes contact time for temperatures of 50°C and 100°C, respectively. This confirms that chemisorption is occurring and this process is endothermic.

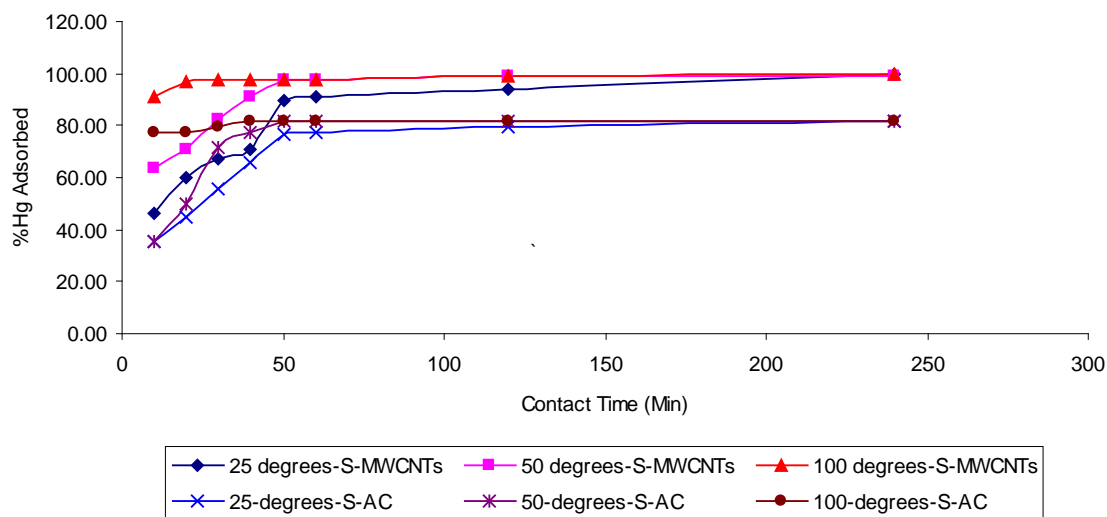


Figure 5-7: The effect of temperature on the uptake of Hg(II) by S-MWCNTs and S-AC (Maximum sulphur contents of 3.97 % and 2.87% respectively which gave maximum mercury uptake capacities of 99.87% and 82.37% respectively)

5.3.6 Selectivity studies`

5.3.6.1 The Effect of Competing Cations

Figure 5-8 shows that the uptake capacity of S-MWCNTs and S-AC are unaffected by increasing concentrations of competing cations (viz. Pb^{2+} , Cd^{2+} and Cu^{2+}). These ions were selected since they are also known to have an affinity for sulphur and can therefore compete with the mercury ions for sulphur binding sites.

The results therefore imply that both adsorbents are highly selective for the uptake of Hg(II). This applies even when the uptake capacity of S-MWCNTs is only 50%.

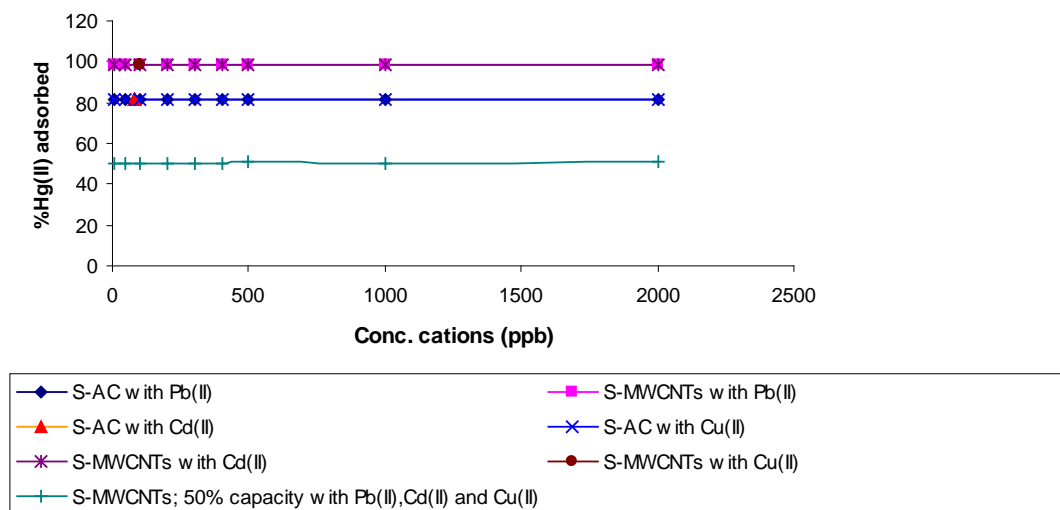


Figure 5-8: The effect of competing cations on the uptake of Hg(II)

5.3.6.2 The Effect of SO₂

It is known from the literature that the uptake of mercury by activated carbon is hindered in the presence of high concentrations of SO₂ and SO₃.^{163,164} Thus, the relative selectivities of S-MWCNTs and S-AC to mercury adsorption in the presence of excess SO₂ were examined.

Figure 5-9 shows that while the uptake of Hg(II) by S-MWCNTs is unaffected by the presence of excess SO₂, the uptake by S-AC is significantly reduced. The difference in selectivities can be explained in terms of the porosity of S-AC. S-AC is highly microporous (surface area 952 m²/g; average pore volume 1.34 cm³/g) and can physisorb SO₂ into these micropores. Further, activated carbon is noted for its hygroscopic nature.⁴⁶⁵ Thus SO₂ can dissolve in the moisture found in these micropores resulting in the formation of sulfites, SO₃²⁻. It is also known from the literature that the sulfites can reduce divalent mercury (even under ambient conditions) to elemental mercury which is highly volatile and escapes easily into the atmosphere as mercury vapour.³¹

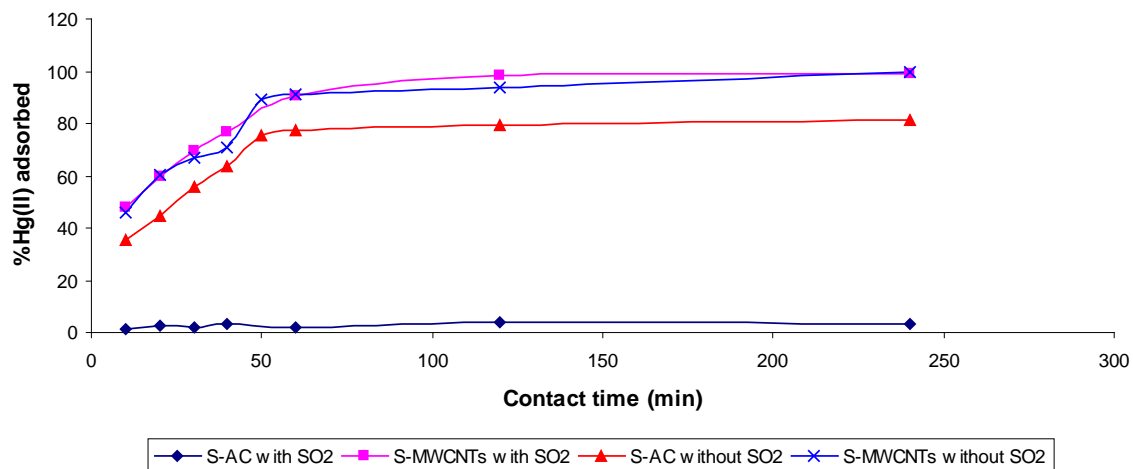


Figure 5-9: The effect of excess SO₂ on the uptake of Hg(II)

The uptake of Hg(II) by S-AC was hindered across the pH scale (Figure 5-10). At high pH, in particular, the uptake of mercury is very low since the sulfites predominate at high pH thereby facilitating the reduction.

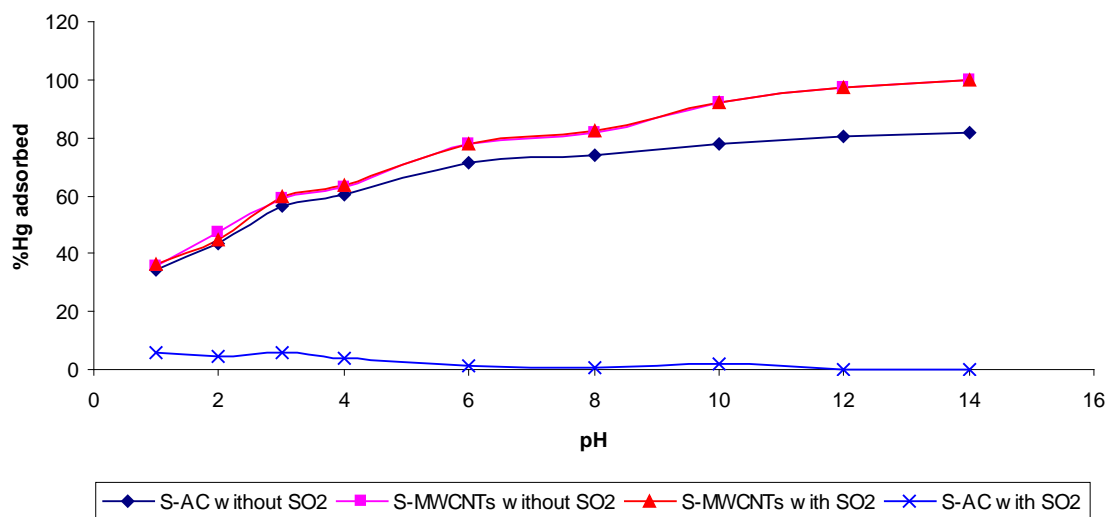


Figure 5-10: The effect of excess SO₂ on the uptake of Hg(II) as a function of pH

5.3.6.3 Effect of Other Mercury Species

The effect of S-MWCNTs on the uptake of methylated forms of mercury was also investigated. The adsorption of the organic forms of mercury was found to be somewhat lower when compared to the inorganic forms (See **Figures 5-11 and 5-12.**) Ramamoorthy and Miller⁴⁶⁶ made similar observations for the uptake of Hg(II) and methyl mercury by ground rubber and saw dust.

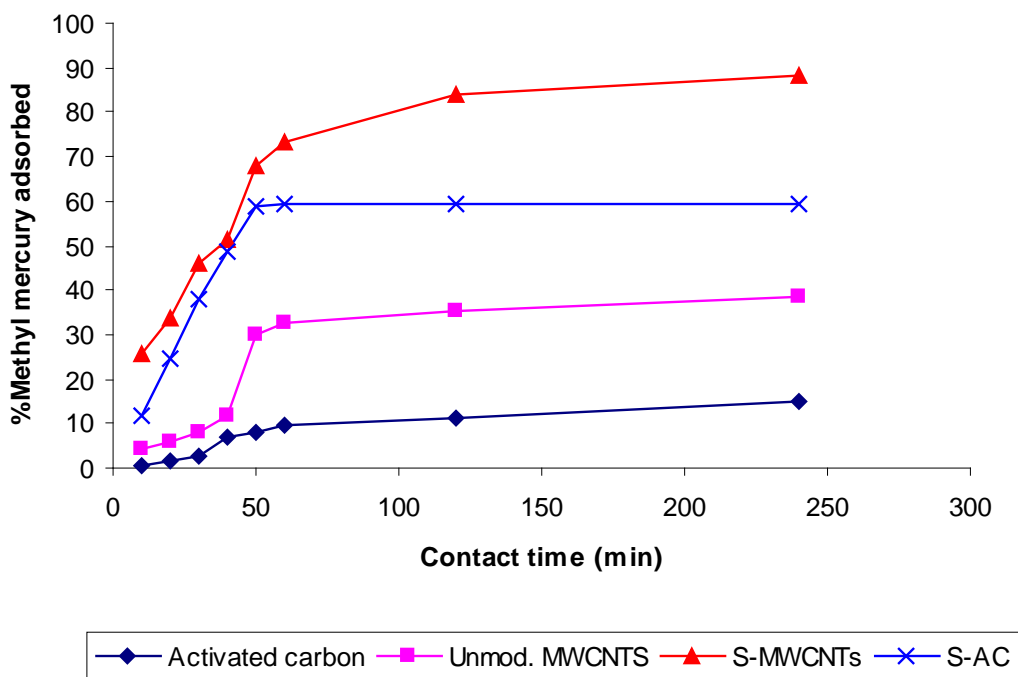


Figure 5-11: The effect of contact time on the uptake of CH_3Hg^+

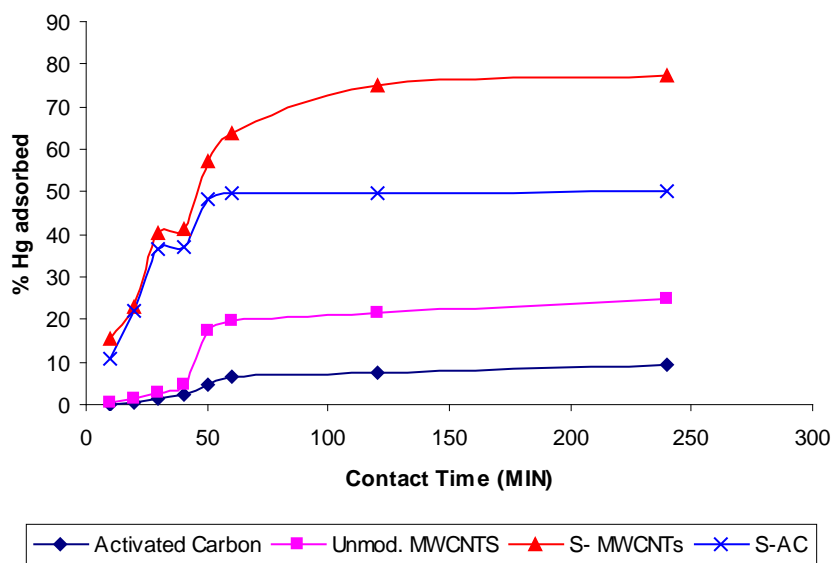


Figure 5-12: The effect of contact time on the uptake of $(\text{CH}_3)_2\text{Hg}^+$

Figures 5-13 and 5-14 also show that the trends observed for the effect of pH on the uptake of the organic forms of mercury was similar to that observed for the uptake of Hg(II) (Figure 5-6).

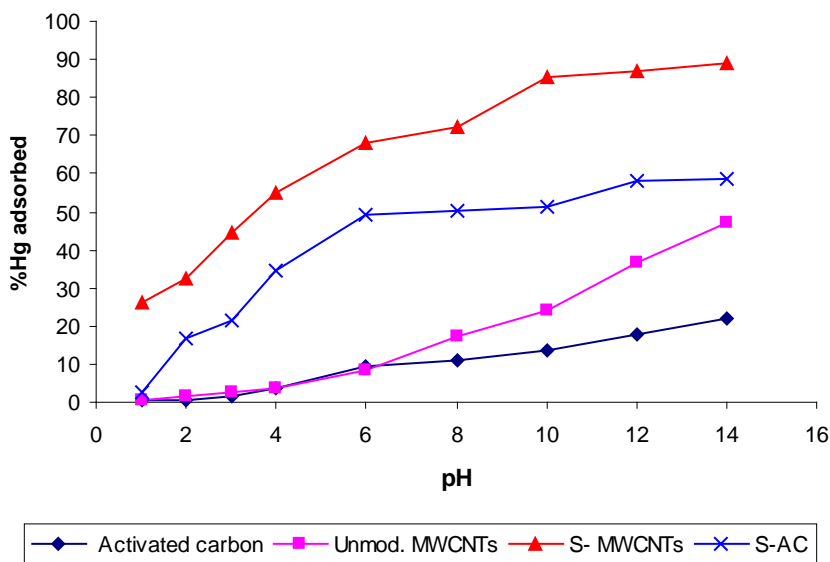


Figure 5-13: The effect of pH on the uptake of CH_3Hg^+

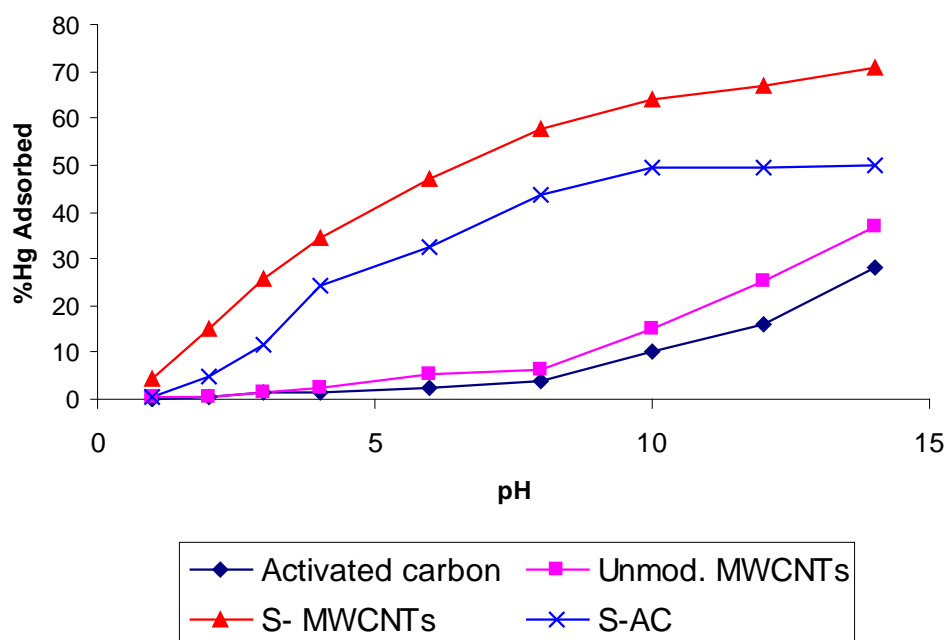


Figure 5-14: The effect of pH on the uptake of $(\text{CH}_3)_2\text{Hg}^+$

5.3.6.4 Effect of Increasing Chloride Concentrations.

Figure 5-15 shows that increasing concentrations of chloride ions do not affect the uptake of Hg(II) by S-MWCNTs and S-AC even though the chloride ions can bind to mercury. Thus these adsorbents are highly selective to mercury even in the presence of chloride ions. This is supported by the results in **Figure 5-16** which show that even when a 50% uptake of Hg(II) occurs and excess chloride ions (2000 ppm) are present, the uptake of Hg(II) is still unaffected by the chloride ions.

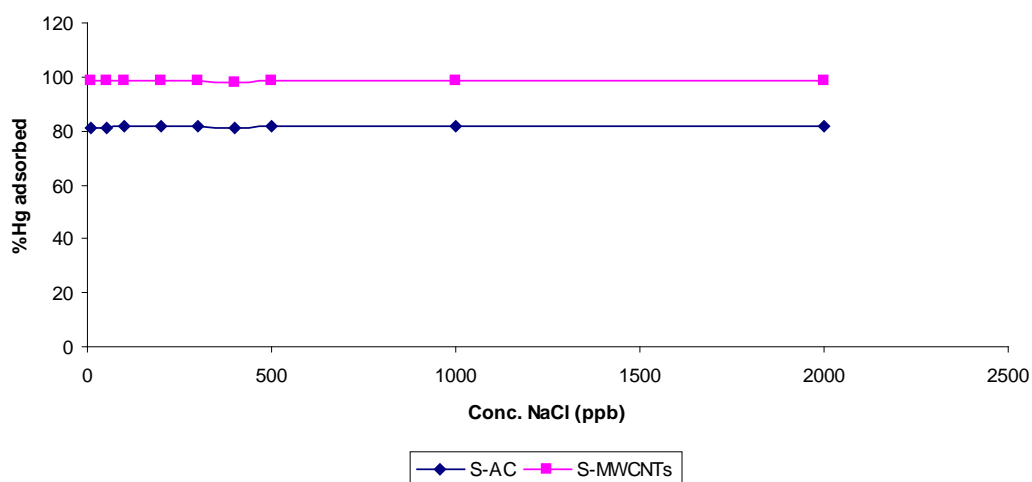


Figure 5-15: The effect of increasing chloride concentrations on the uptake of Hg(II)

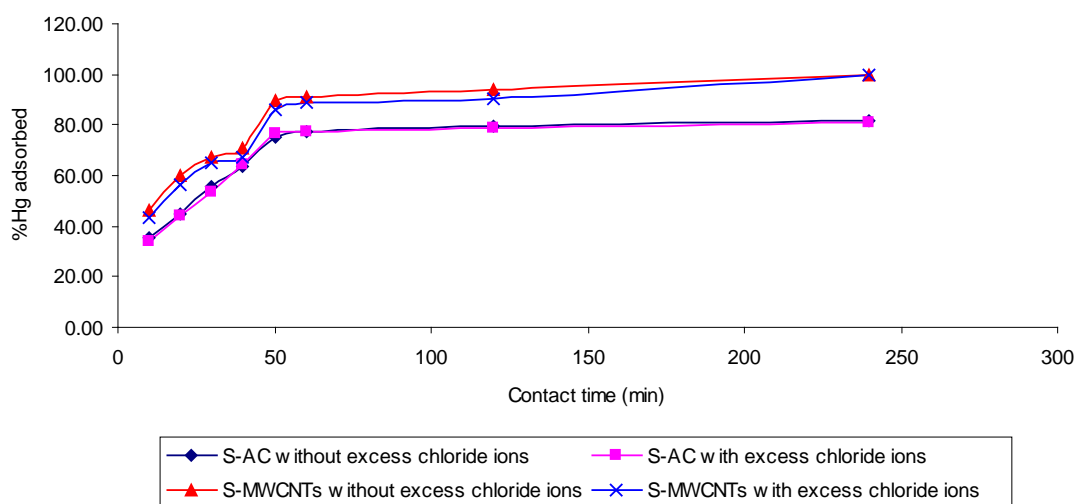


Figure 5-16: The effect of excess chloride ions on the uptake of Hg(II) by S-AC and S-MWCNTs

5.3.7 Desorption

The desorption of Hg(II) was conducted in two ways, firstly by using 0.1 M HCl and secondly, by using 0.5% thiourea in 0.5 M HCl as the desorbing media respectively. The reason for selecting HCl was that the acid would introduce H⁺ ions which can potentially compete with Hg²⁺ ions for active adsorption sites. The acid is also a source of chloride ions which can remove Hg²⁺ by forming Hg-Cl

bonds. Thiourea in HCl was selected as a desorbent since it has already been used to desorb mercury from sulphur-containing adsorbents.⁴⁵⁹

Figure 5-17 reveals that all the adsorbed mercury species desorb readily (> 98%) from the surfaces of unmodified activated carbon and the unmodified MWCNTs. However, in the case of the S-MWCNTs and S-AC no desorption is observed. In the case of unmodified activated carbon and the unmodified MWCNTs, evidence of interaction with the oxygen atoms on hydroxyl groups was presented in the Raman spectra of these adsorbents. However, HCl is able to cleave the Hg-O by creating acidic conditions and by supplying chloride ions which can bind to the Hg²⁺ ions. In fact, the Eh-pH diagram of mercury (**Figure 2-4** in Chapter 2) shows clearly that the predominant form of mercury at low pH is HgCl₂.

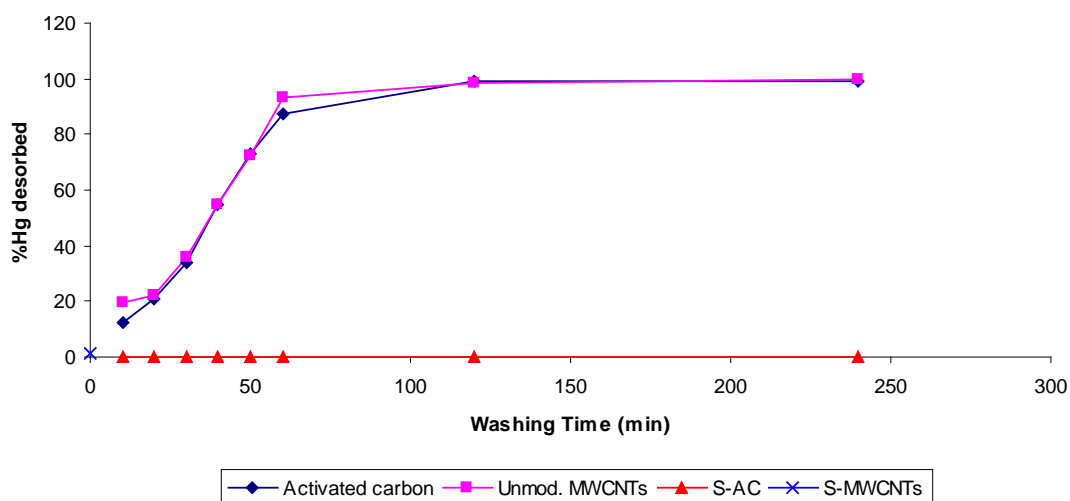


Figure 5-17: The extent of desorption of Hg(II)

In the case of the S-MWCNTs and S-AC the mercury ions are very strongly bound to the sulphur atoms of the sulphur functional groups and the acid is unable to release the mercury ions.

The desorption of Hg from ion-imprinted beads with thiourea has been found to be effective.⁴⁵⁹ **Figure 5-18** shows that mercury desorbs readily from both the S-MWCNTs and S-AC when washed with 0.5% thiourea in 0.05 M HCl. The thiourea has sulphur and nitrogen centres which can readily bond with mercury and

displace mercury from the carbon surface.⁴⁶⁷ Thus, the S-MWCNTs and S-AC carbon can be regenerated and reused provided that a suitable washing agent is used.

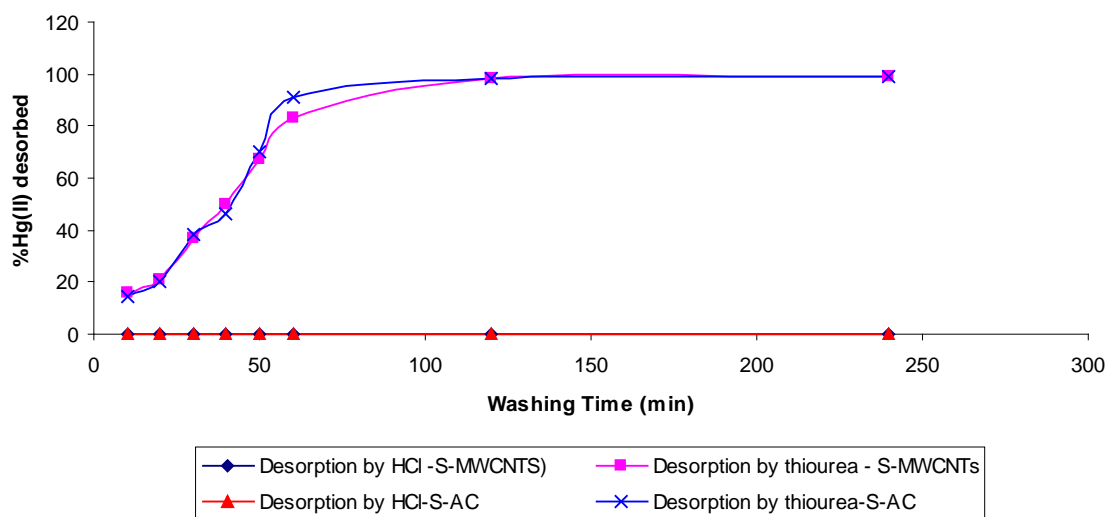


Figure 5-18: A comparison of the desorption extents from S-MWCNTs and S-AC when HCl and thiourea are used as the adsorbents respectively

5.3.8 Adsorption Isotherms

The Langmuir and Freundlich Isotherms are the most frequently used adsorption isotherms which describe the distribution of metal ions between the solid and liquid phases. The linear form of the Freundlich Isotherm is given by:

$$\log\left(\frac{X}{m}\right) = \log K + \frac{1}{n} \log C_e \quad (5-1)$$

where X is the amount of Hg adsorbed (μg), m is the mass of adsorbent, and C_e is the equilibrium concentration of Hg in solution, K is a fitting parameter which is a constant and $\frac{1}{n}$ is a measure of adsorption intensity.⁴⁵³ When $\log(x/m)$ is plotted against $\log C_e$ a straight line should result. The values of K and n can then be evaluated from the slope and intercept of the graph. **Figure 5-19** shows the plots of the Freundlich Isotherm for Hg(II) by S-MWCNTs and S-activated carbon. This Figure indicates clearly that the adsorption of mercury fits the Freundlich Isotherm well.

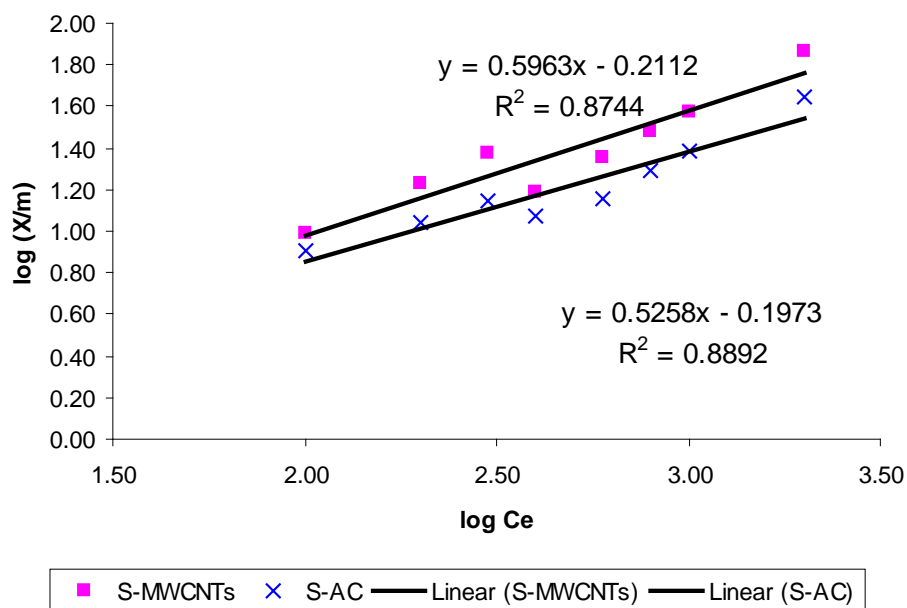


Figure 5-19: The Freundlich Isotherm for the uptake of Hg(II) by S-MWCNTs and S-activated carbon

The linear form of the Langmuir equation is given by:

$$C_e/[X/m] = 1/bQ + C_e/Q \quad (5-2)$$

where C_e is the equilibrium concentration of Hg in solution, Q is the number of moles of Hg adsorbed per unit mass of adsorbent (adsorption capacity) upon forming the monolayer on the adsorbent surface, and b is the Langmuir constant which is related to the binding energy. When fitting this isotherm to the data, the R^2 values ranged from 0.1 to 0.3 indicating a very poor fit.

5.3.9 Mechanism of Mercury Adsorption

The data reveals that chemisorption processes predominate for the uptake of sulphur by mercury. The first of these processes is a weak interaction between the oxygen atoms on hydroxyl groups and the mercury cations. This is characteristic of the adsorption onto unmodified activated carbon and the unmodified MWCNTs. The process is easily reversed by desorption with HCl. The adsorption on the S-

MWCNTs and S-AC on the other hand occurs by formation of a strong Hg-S bond. This Hg-S bond formation is supported by a change in the Raman spectra of the S-MWCNTs and S-AC where a distinct reduction in the C-S band and the formation of a new S-Hg-S band is noted.

The chemisorption mechanism is further supported by the fact that the mercury does not desorb readily from the surfaces of these adsorbents when HCl is used as the washing agent. Desorption only occurs when thiourea is present in the washing agent (**Figure 5-18**).

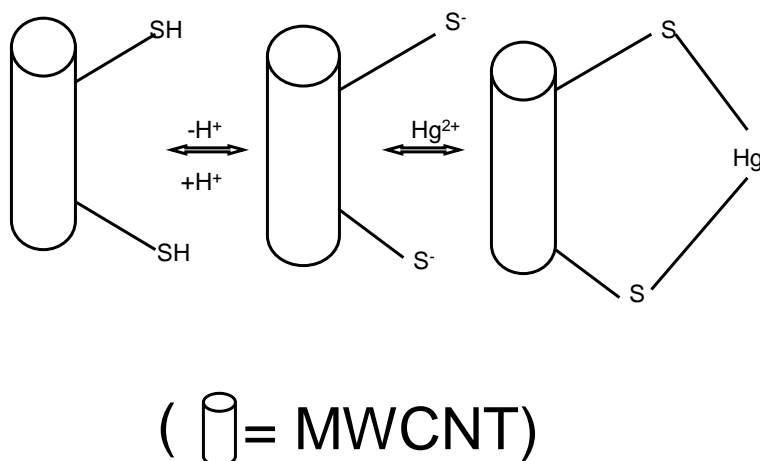


Figure 5-20: A proposed mechanism for the adsorption and desorption of Hg(II) (S-MWCNTs)

The ready desorption of Hg(II) from the acidified thiourea solution rules out the possibility of the precipitation of HgS in the solution (K_{sp} of 2×10^{-54}).⁴⁶⁸

Basically the cartoon shown in **Figure 5-20** shows the deprotonation of the thiol groups on the S-MWCNTs. This is favoured by basic conditions where the base acts as the proton scavenger and also accounts for why basic conditions favour the chemisorption.

The deprotonation of the S-MWCNTs creates negatively charged sulphur centres which can easily exert a nucleophilic attack on the positively charged mercury ions resulting in the formation of Hg-S bonds.

The desorption process by thiourea can be explained by cleavage of Hg-S bonds on the CNTs by thiourea. This is achieved by competing sulphur centres and additional nitrogen centres for the chemisorption of mercury.

The regeneration of the S-MWCNTs is achieved in the presence of HCl in the thiourea mixture which supplies H^+ ions for the reprotonation of the S-MWCNTs.

5.4 Conclusion

S-MWCNTs and S-ACs have demonstrated an ability to remove mercury ions from solution. These adsorbents have shown a superior adsorption capability to that of unmodified activated carbon and unmodified MWCNTs due to the presence of sulphur. This is further correlated to the low pH_{pzc} values which make these adsorbents negatively charged over a wide pH range and facilitates the uptake of mercury cations. The uptake of mercury increases linearly with sulphur content. The maximum uptake of mercury corresponds to sulphur contents of 3.97% for S-MWCNTs and 2.87% for S-AC.

Both S-MWCNTs and S-ACs demonstrate high uptake capacities and high selectivities to the uptake of mercury. However, the advantage of using S-MWCNTs over S-ACs relates to mercury uptake in the presence of SO_2 . The results indicate that microporous supports should not be used for mercury removal in the presence of SO_2 .

The key process that seems to control the adsorption of mercury onto these adsorbents is a chemisorption process via Hg-S bond formation. The uptake of mercury by the sulphur-containing adsorbents obeys the Freundlich Isotherm. The maximum uptake capacities have been evaluated as 72.83 μg per g for S-MWCNTs and 44.67 μg per g for S-AC from the Freundlich Isotherm. The

adsorption is highly selective even in the presence of competing cations and excess chloride ions. This high degree of selectivity therefore suggests that the S-MWCNTs can selectively extract mercury from a mixture of competing ions and counter-ions.

CHAPTER 6

SULPHUR-CONTAINING MULTI-WALLED CARBON NANOTUBES FOR THE TREATMENT OF INDUSTRIAL WASTES CONTAINING MERCURY

6.1 Introduction

In Chapter 2 it was noted that competitive adsorption studies on the uptake of Hg from a complex matrix, such as an industrial effluent, are lacking. This chapter therefore presents a case study in which the ability of sulphur-containing multi-walled carbon nanotubes (S-MWCNTs) to selectively extract mercury from the complex chemical matrix of an industrial effluent is examined. The industrial effluent used in this study was a chlor-alkali effluent. The results of using these materials on an industrial scale was investigated in continuous flow studies where the S-MWCNTs are mixed into silicon carbide (SiC) and phosphorus pentasulphide matrices (P_2S_5 ; a source of additional sulphur centres for Hg uptake) respectively and the ability to regenerate these materials by the desorption of mercury is examined. Finally, recommendations for a good industrial practice are made.

6.2 Materials and Method

The silicon carbide was commercially obtained from Sigma Aldrich in the nanopowder form. The chemical characteristics including the particle size of the SiC are reported in **Appendix 1** (see **Table A1**). Synthesised unfunctionalised MWCNTs were tested for comparative purposes. However, to ensure that limited functional groups were present these were re-heated in a tube furnace under argon at 900°C . An IR spectrum (not shown) verified that no functional groups were present. Sulphur containing moieties were added to some of the unfunctionalised MWCNTs as per the method reported in Chapter 5 where S-

MWCNTs with a sulphur content of 3,78% were produced. The P_2S_5 was also commercially obtained from Sigma Aldrich.

6.2.1 Mixing of S-MWCNTs into P_2S_5 and Silicon Carbide

The S-MWCNTs were mixed into the P_2S_5 and silicon carbide matrices respectively by adding 1,00 g of the MWCNTs with 5,00 g of the P_2S_5 and silicon carbide respectively prior to packing in a column (60 mm long and 10 mm wide). This is similar to a method previously reported in Chapter 4 where unfunctionalised MWCNTs were mixed into silicon carbide for Cr(VI) removal.

6.2.2 Sampling of the Industrial Effluent

This study was conducted using a chlor-alkali effluent obtained from Durban, SA. The removal capacity was monitored as a function of contact time. The full chemical composition of the effluent was determined by ICP-MS and Gas Chromatography-Inductively Coupled Mass Spectroscopy (GC-ICP-MS) and is presented in **Table 6-1**. The samples of the industrial effluent were collected in polyethylene bottles and were refrigerated when not in use. The pH of the effluent was also measured and was found to be 11.5

6.2.3 Laboratory Scale Studies

The laboratory scale studies were conducted by keeping the unfunctionalised and S-MWCNTs in contact with the industrial effluent for contact times ranging from 10-240 minutes. After each contact time had elapsed, the MWCNT-SiC suspension was filtered through a 0.45 μm filter and the filtrates were collected and analysed for their mercury content by GC-ICP-MS.

6.2.4 Continuous Flow Studies

The continuous flow studies were conducted in a similar manner to that reported for the uptake of Cr(VI) from industrial effluents except that this time the primary toxin in the industrial effluent was mercury (see **Figure 4-2** in Chapter 4). The continuous flow studies included studies in which the S-MWCNTs were embedded into the P_2S_5 and silicon carbide matrices, respectively. However, control

experiments in which the S-MWCNTs, P_2S_5 and silicon carbide were used as sole adsorbents were also conducted.

6.2.5 The Effect of the Effluent Matrix

The effect of the effluent matrix was investigated by identifying potential metals in the industrial effluent that are likely to form cations which hinder the uptake of mercury. These metals were identified as iron, aluminium and sodium which can form the cations, Fe^{2+} , Fe^{3+} , Al^{3+} and Na^+ . These cations can potentially out-compete the mercury cations for the sulphur binding sites on the MWCNTs. This warrants their removal from the matrix of the industrial effluent.

Since aluminium and iron are known to form insoluble hydroxides, the hydroxides of these metals were precipitated by adding excess sodium hydroxide to the effluent. The precipitates were filtered off and the resulting filtrate was kept in contact with the unfunctionalised MWCNTs. Analysis of the filtrate by AAS and ICP-MS revealed that the concentrations of these metals were negligible (<0,002%) after precipitation.

The sodium ion, on the other hand, is not as easy to remove since it forms soluble compounds with most anions. However, it is believed these cations are unlikely to interfere with the uptake of mercury because of their ability to migrate in aqueous solution. This was confirmed by experiments in which the filtrate was spiked with 0.01, 0.5 and 1.00 M NaOH respectively. These results are shown in **Figure A2 (Appendix 1)** and indicate that the presence of the sodium ion does not hinder the uptake of Hg. The sodium cations are also considered to be hard acids and do not interact with sulphur-containing ligands.⁴⁶⁹ Thus, these do not interfere with the uptake of mercury.

6.2.6 Desorption and Recycling Experiments

The desorption and recycling experiments were conducted by pumping and keeping the effluent in contact with the adsorbents for 240 min. Thereafter the column was eluted and rinsed with distilled water. Any mercury that was retained on the adsorbent was washed with 0,5% thiourea in 0.05 M HCl. The washings were eluted from the column and analysed for mercury using GC-ICP-MS. These experiments were repeated for six cycles of adsorption and desorption.

6.2.7 Analysis

Since the speciation of Hg in industrial effluents can vary, all filtrates collected from the adsorption and desorption studies were analysed for their mercury content by Gas Chromatography-Inductively Coupled Plasma Spectroscopy (GC-ICP-MS). A known developed method was again employed.⁴⁶⁰ This method involved an initial treatment of the sample with concentrated HCl (1% v/v), followed by filtration and then analysis. In the case of the organomercury species, derivatisation was conducted to obtain volatile species. The pH was adjusted to between 3 and 4, by treating 3 mL of each sample with concentrated ammonium hydroxide and 5 mL of acetic acid–sodium acetate buffer (0.1-0.2 M). This was followed by the addition of 2 mL isooctane and 5 mL of 0.5 – 1% (w/w) sodium tetraethyl borate (NaBEt₄). The mixture was manually agitated in a sealed bottle for 5 minutes to extract the organic phase. The organic phase was then removed by syringe and stored at -18⁰C in a sample vial until measurement.

For the actual analysis, external calibration standards were prepared from stock solutions of CH₃HgCl and HgCl. The calibration levels used included ratios of inorganic mercury to organic mercury that varied from 0.1:0.2, 0.5:0.5 and 1:0.1 at the parts per billion (ppb) level. Both blanks and standards were analysed in the same manner.

An ICP-MS analysis (similar to that reported in Chapter 5) was also conducted to determine the total mercury content of the effluent. The elemental mercury concentration was thus determined from the difference between the total mercury concentration and the individual inorganic and organic mercury concentrations that were determined by GC-ICP-MS.

6.2.8 Statistical Analysis

All the adsorption and desorption experiments were conducted in duplicate and the average of two mercury concentrations is reported here. An allowance of 5% relative error was made. If the relative error exceeded 5% the analytical data was discarded and the experiment was repeated until the relative error was within 5%. The analytical data was found to be quite reproducible with a relative error of $\pm 2\%$. All data was validated using a Statcalc package (Statistica 9.0; a product of Statsoft).

6.3 Results and Discussion

6.3.1 Chemical Components in the Industrial Effluent

It is of interest to note that three forms of mercury are present in the effluent, namely elemental mercury, mercury(II) and phenyl mercury. The leachate originated from a sludge which was produced as a result of immobilising mercury via a sulphur stabilisation method. However, trace quantities of mercury prevail in the leachate after the stabilisation process. This can be due to incomplete precipitation where small amounts of fine precipitate escape into the effluent.⁴⁵⁸ The presence of chloride and nitrate ions suggests that the mercury(II) is present mostly as mercuric chloride and mercuric nitrate. The chloride ions are known to bind strongly to Hg(II) and are also likely to be present in wastewaters⁴⁷⁰ and therefore can also present some interference to the uptake of Hg(II).

Table 6-1 shows the full chemical composition of the effluent.

Table 6-1: The Full Chemical Composition of the Industrial Effluent

CHEMICAL COMPONENT	ANALYTICAL METHOD	CONC. (ppb) (±0,01 ppb)	CONC. (ppm) (±0,02 ppm)
Mercury (Total) Elemental ⁶	ICP-MS	472	
Mercury(II)	GC-ICP-MS	10.5	
Phenyl mercury	GC-ICP-MS	272	
		189	
Total Al	AAS		250
Total Fe	AAS		391
Total Na	AAS		504
Cl ⁻	Ion-Exchange Chromatography		333
NO ₃ ⁻	Ion-Exchange Chromatography		2291

The presence of other metals like aluminium, iron and sodium suggest that there could be chemical affinity competition between the cations of these metals and the mercury cations for the active sites on the MWCNTs.

6.3.2 Contact Time

Figure 6-1 shows that both types of MWCNTs (S-MWCNTs and unfunctionalised MWCNTs) have the ability to remove Hg(II) from the effluent. This ability also applies to the elemental and organic forms of mercury present in the effluent (see **Figures 6-2 and 6-3**). The origin of elemental mercury in the effluent is from its use as a cathode in the chlor-alkali process⁴⁷¹. Although efforts to remove mercury by a sulphide precipitation process have been made where elemental mercury is reacted with sulfides to produce cinnabar, HgS, one of the fundamental disadvantages of this process is the incomplete removal of mercury (see Chapter 2).⁷⁰ Thus, trace concentrations of elemental mercury can still prevail in the effluent.

⁶ Determined from difference between total mercury and inorganic and organic mercury concentrations

It is important to note here that the removal percentages have been calculated based on the concentrations of each form of mercury as reported in **Table 6-1**, In all cases the uptake of mercury increases with contact time until saturation is attained within 120 minutes of contact time. The saturation is accounted for in terms of limited active sites on both types of MWCNTs.

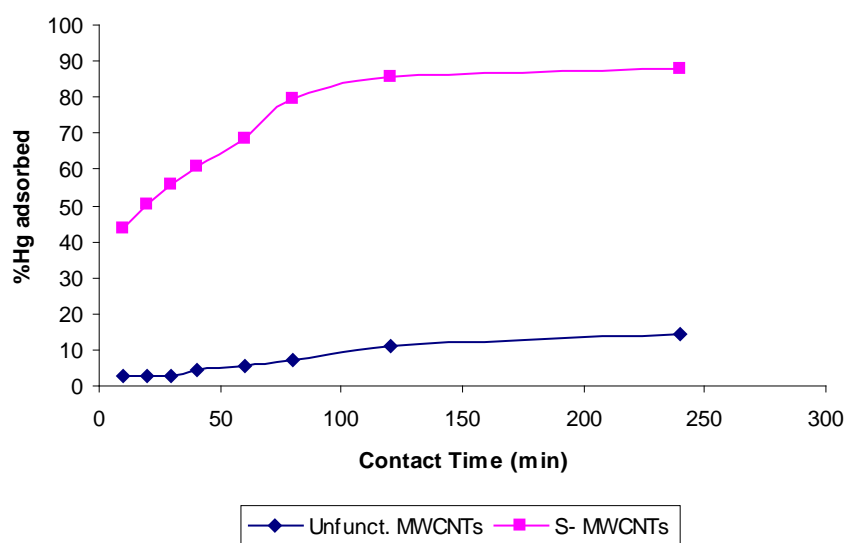


Figure 6-1: The effect of contact time on the uptake of Hg(II) from the effluent

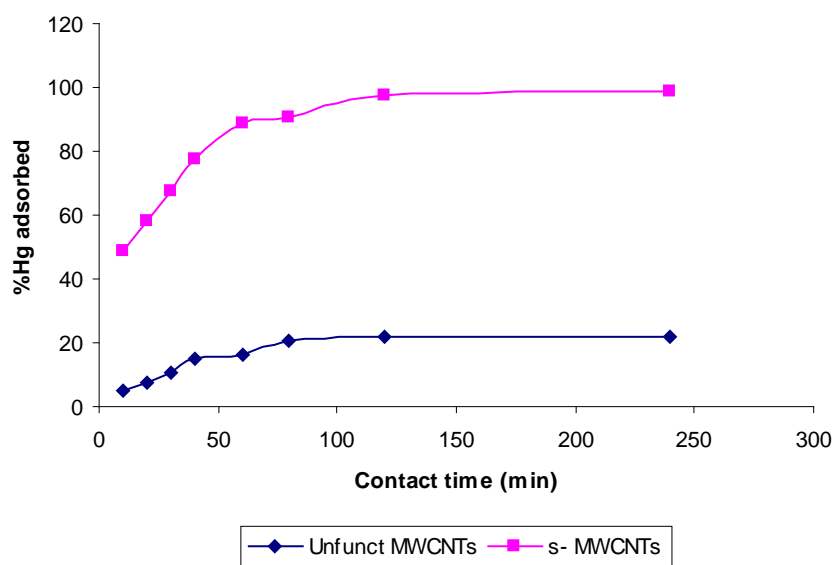


Figure 6-2: The effect of contact time on the uptake of elemental mercury

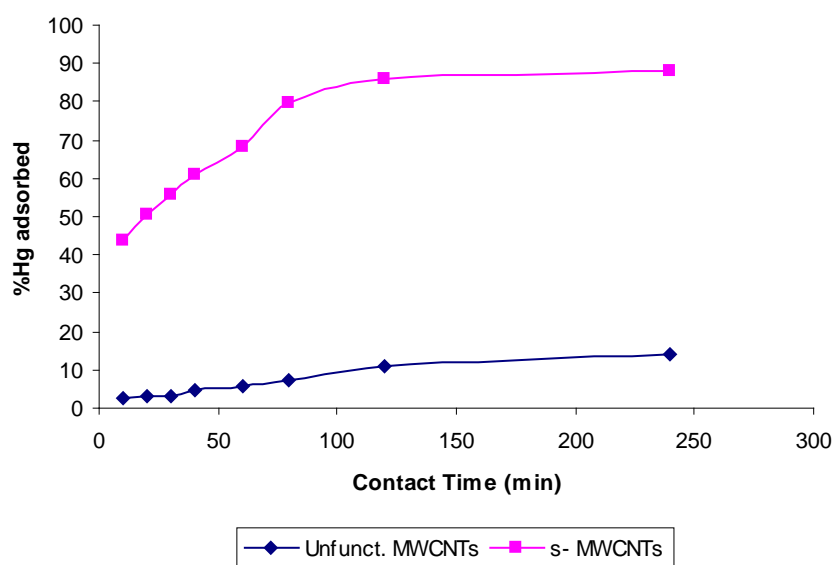


Figure 6-3: The effect of contact time on the uptake of phenyl mercury

However, it is noted that the S-MWCNTs are far more efficient at the uptake of all forms of mercury than the unfunctionalised MWCNTs. This is consistent with

previous observations for the uptake of mercury in a pure chemical matrix (see Chapter 5). Even the presence of chloride ions in the matrix of the industrial effluent does not seem to influence the uptake of mercury by the S-MWCNTs. The different degrees of efficiency have been accounted for in terms of the high affinity that mercury has for sulphur. This has been explained in terms of Hard and Soft Acid Base Theory (HSAB) where mercury is a soft acid and therefore has strong affinity for soft bases like sulphur.^{469, 472,473,474,475,476,477,478} The results in Chapter 5 have also presented evidence for chemisorption where there is a clear covalent bond formation between mercury and sulphur.

Further examination of the results reveals that the extent of adsorption of the S-MWCNTs are the same as those observed for the pure chemical systems but that those of the unfunctionalised MWCNTs are about 10-20% lower than those observed for the pure chemical systems. (see results in Chapter 5). This suggests that the S-MWCNTs are highly selective for the adsorption of mercury regardless of the matrix in which it is present. The unfunctionalised MWCNTs, on the other hand are not very selective for the adsorption of mercury and the uptake of mercury may thus be hindered by the presence of competing cations as previously demonstrated in Chapter 5. Further evidence of this is presented in Section 6.3.3.

6.3.3 Influence of the Effluent Matrix

As described in Section 6.2.5, Fe^{2+} , Fe^{3+} and Al^{3+} ions which are likely to present chemical affinity competition to the uptake of Hg(II) were removed by precipitation as hydroxides. **Figure 6-4** shows conclusively that the uptake of Hg(II) by the S-MWCNTs is unaffected by the removal of these competing cations. This confirms that these type of MWCNTs are highly selective for the uptake of Hg(II).

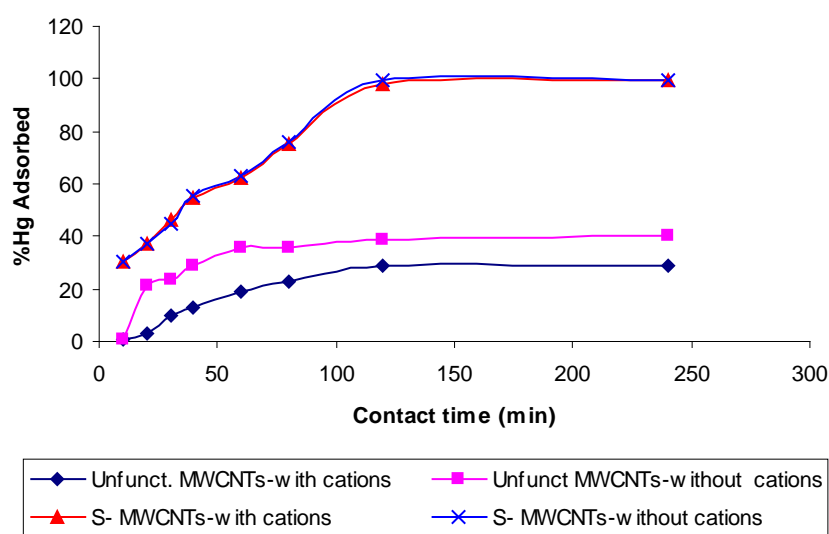


Figure 6-4: The effect of competing cations on the uptake of Hg(II)

The uptake by the unfunctionalised MWCNTs on the other hand increases by about 20% after the removal of these competing cations. This confirms that the reduced adsorption capacities by these types of MWCNTs are indeed due to chemical interferences by the cations of Fe and Al. **Figure A3 (Appendix 1)** on the other hand reveals that presence of sodium ions does not affect the uptake of Hg(II). Other workers have made the same observation for the uptake of Hg(II) by bacterial cells.⁴⁷⁹ This lack of interference can be explained in terms of the sodium ions ability to easily migrate into an aqueous phase and therefore they are not easily retained on a solid surface. The addition of excess NaOH also increases the pH which favours the uptake of Hg. As stated in Section 6.2.5 the lack of interference after the addition of excess NaOH was confirmed by spiking with excess NaOH (see **Figure A2- Appendix 1**).

However, the adsorption capacities of the unfunctionalised MWCNTs are still not as high as that of the S-MWCNTs. This reveals that the S-MWCNTs are indeed a better form of MWCNTs that can be used to treat industrial wastes that are rich in mercury and were the only type of MWCNTs used in the continuous flow studies discussed below.

6.3.4 Continuous Flow Studies

Figures 6-5 to 6-7 clearly show that the uptake of all forms of mercury is at its highest when the S-MWCNTs are either used as the sole adsorbents or when these are mixed into a silicon carbide matrix. The source of sulphur centres on the S-MWCNTs and mercury's strong affinity for sulphur again accounts for this observation. The rationale applied when mixing the S-MWCNTs into a P_2S_5 matrix, there are additional sulphur centres on P_2S_5 which are also available for the binding of mercury. Thus, the adsorption should be enhanced when both these adsorbents are used but the results obtained do not reveal this.

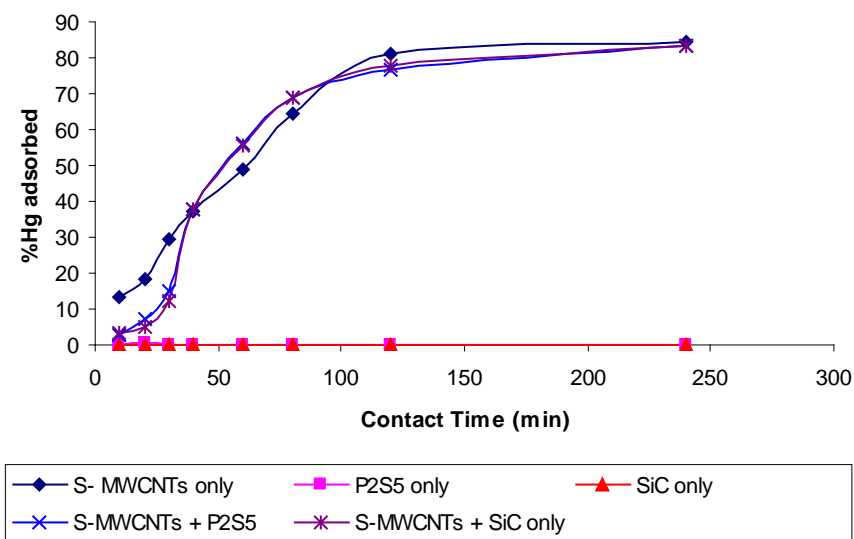


Figure 6-5: Continuous Flow studies on the uptake of Hg(II)

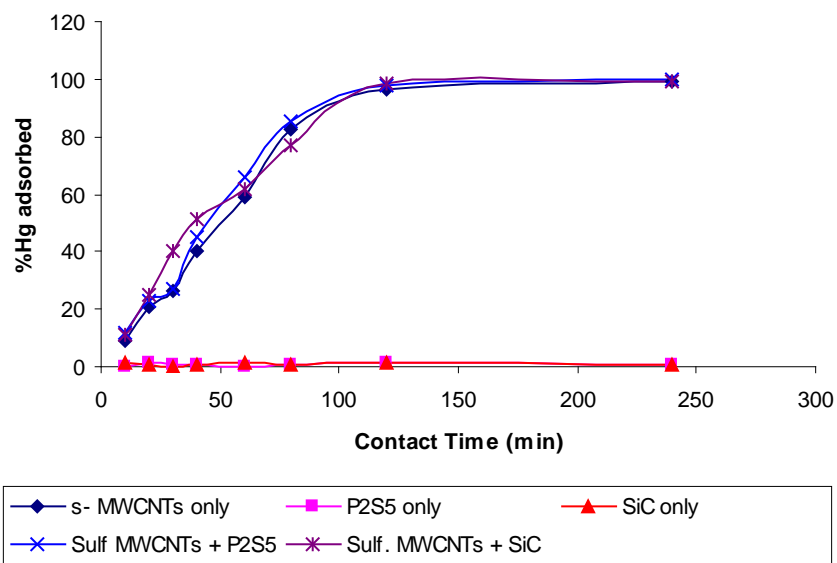


Figure 6-6: Continuous Flow Studies on the Uptake of Elemental Mercury

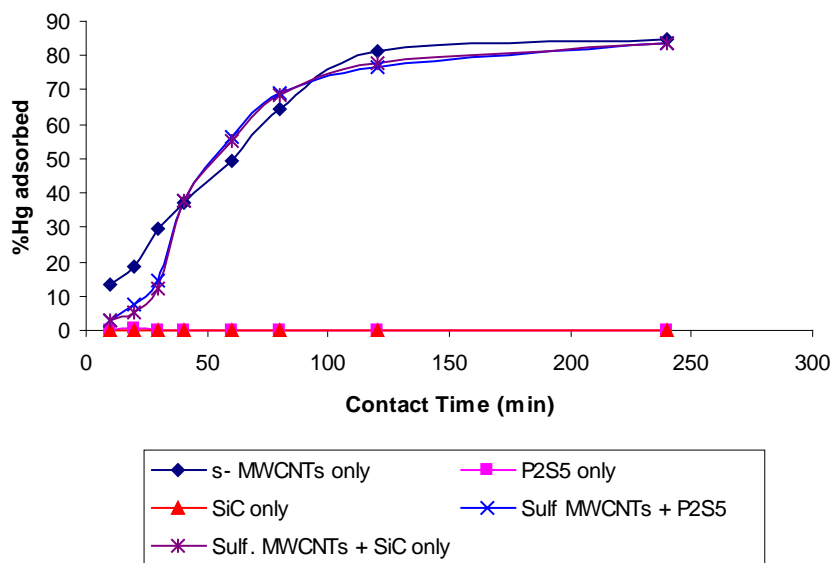


Figure 6-7: Continuous Flow Studies on the Uptake of Phenyl Mercury

This is evident in the results obtained from the control experiments where P_2S_5 was used as the only adsorbent which reveal that almost no adsorption of mercury is observed. Although P_2S_5 has sulphur centres which can selectively bind to mercury, it is known to be highly soluble in alkali media especially sodium hydroxide⁴⁸⁰. Thus, almost no adsorption is observed due to the P_2S_5 being lost upon dissolution in the alkaline effluent. To confirm this, 50,0 g of P_2S_5 were dissolved in 100 mL of effluent and were found to be completely soluble. The dissolution was observed as the effluent was pumped through the column containing P_2S_5 and even when pumped through the mixture of S-MWCNTs and P_2S_5 . Thus, the adsorption that is observed when the S-MWCNTs are mixed into P_2S_5 is mainly due to the action of the S-MWCNTs.

The same applies to the case where the S-MWCNTs are embedded into a silicon carbide matrix. All of the above figures clearly show that there is no uptake of mercury by silicon carbide. Thus, the S-MWCNTs are solely responsible for the adsorption that is taking place and the silicon carbide merely acts as an inert support for the S-MWCNTs.

6.3.5 Desorption and Recycling

In order to establish the viability of using the S-MWCNTs as part of a treatment technology for the removal of mercury from industrial effluents some desorption and recycling experiments were conducted by keeping the effluents in contact with the S-MWCNTs for a contact time of 240 min after which the adsorbed mercury was desorbed in 0,5% thiourea in 0,05 M HCl. These results are presented in **Figure 6-8 to 6-10**

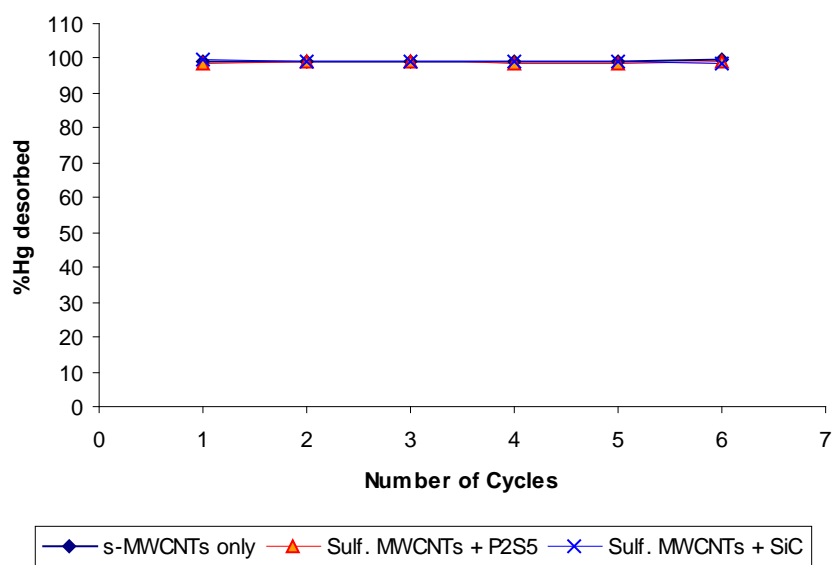


Figure 6-8: The extent of desorption of Hg(II)

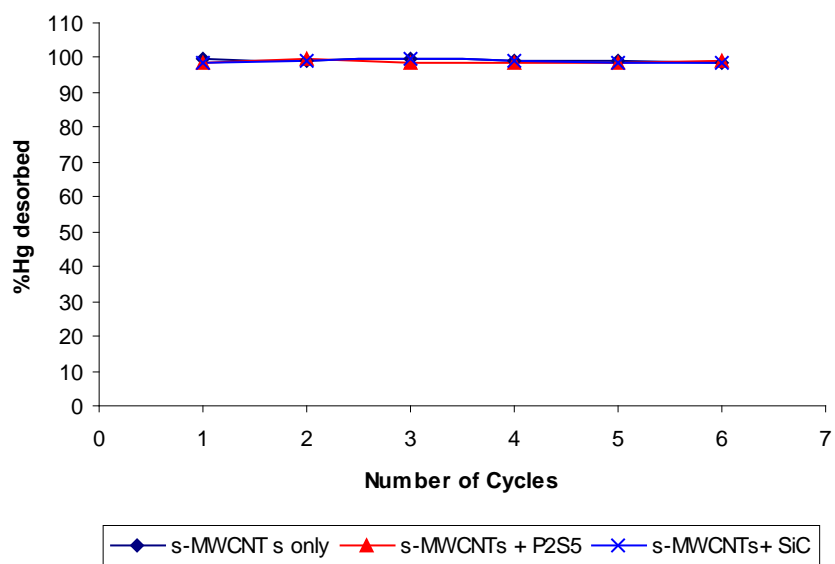


Figure 6-9: The extent of desorption of elemental mercury

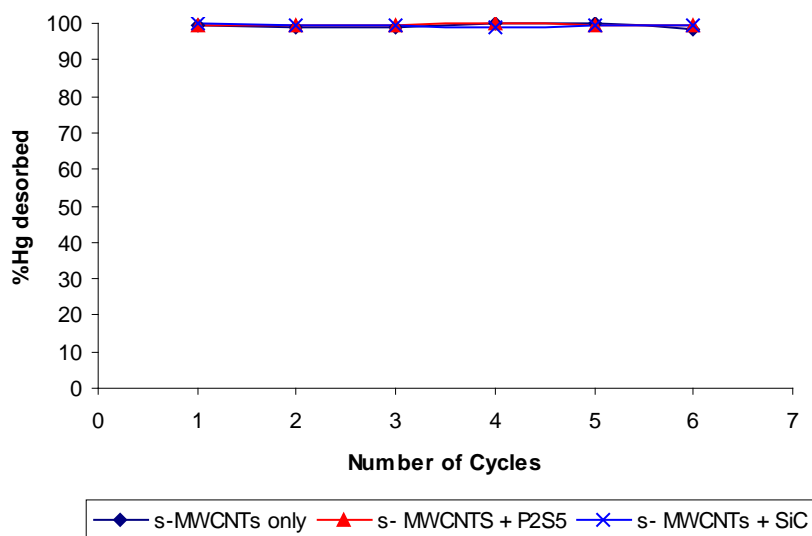


Figure 6-10: The extent of desorption of phenyl mercury

These figures present evidence that shows that all the forms of Hg readily desorb from all the adsorbents after six successive cycles of adsorption-desorption. The extent of desorption is in the 98-99% range. Furthermore, all adsorbents retain their structural integrity after the six cycles and the mass losses that occur are only in the 1-2% range.

This therefore suggests that it is viable to re-use all adsorbents for the treatment of industrial effluents containing Hg and the synthesis of large amounts of S-MWCNTs is therefore not necessary.

6.4 Conclusion

S-MWCNTs have been identified as excellent adsorbents for the uptake of both inorganic and organic forms of mercury from an industrial effluent. These adsorbents have not only demonstrated superior adsorption capacity to that of unfunctionalised MWCNTs but have also demonstrated high selectivity for Hg(II) from a complex chemical matrix. The adsorption capability of this material is unaffected by the presence of competing cations.

The continuous flow studies conducted have indicated that successful adsorption occurs when the S-MWCNTs are used alone or when mixed into a silicon carbide matrix. Silicon carbide is not effective when used as the sole adsorbent due to its inert nature. Although P_2S_5 has additional sulphur centres, it is highly soluble in alkaline media and is therefore not suitable for the treatment of alkaline waste.

All the adsorbents can also be easily regenerated and reused after six successive adsorption-desorption cycles. In this case 0,5% thiourea in 0,5 M HCl was an effective desorbing medium.

Based on the above observations it is recommended that S-MWCNTs can be used as the primary adsorbents for the treatment of wastes that are rich in mercury. These adsorbents are highly selective for mercury removal and therefore do not warrant any pre-treatment of the industrial effluent. The best industrial practice would be to support these onto a silicon carbide matrix. The adsorbent may also be regenerated and reused by frequent desorption but the desorption must be carefully conducted such that adsorbed mercury species are released into solutions where they can be collected.

CHAPTER 7

ANION AND CATION UPTAKE BY CARBON NANOMATERIALS

7.1 Introduction

The literature survey in Chapter 2 reported studies on the use of oxidised nitrogen doped carbon nanotubes for the uptake of cations.⁴¹³ However, suitable comparisons with unoxidised nitrogen doped CNTs were not made and the actual role played by nitrogen-doping in the metal ion uptake was unclear. Furthermore, studies on the effect of microwave-induced acid and base treatment on the CNTs are also scarce.

Thus, in this chapter the properties of surface modified carbon nanomaterials was studied and the impact of their surfaces were investigated by studying their influence on anion and cation uptake. These include microwave-induced acid and base surface reactions and nitrogen-doping of the carbons. Varying dopant contents and heat treatment of nitrogen-doped MWCNTs (N-MWCNTs) was also performed.

Similar studies on a different form of carbon namely carbon spheres (CSs) and nitrogen doped carbon spheres (N-CSs) were conducted in order to examine the effect of the form of the carbon materials (comparison of carbon spheres (CSs) and carbon nanotubes (CNTs)).

The effect of impurities such as amorphous carbon and excess catalyst impurities on the carbons was established. Three cations were selected for this study. These were the divalent metal cations, Hg^{2+} , Cd^{2+} and Pb^{2+} . The anions selected for this study included dichromates ($\text{Cr}_2\text{O}_7^{2-}$) and sulphates (SO_4^{2-}). Surface parameters such as point of zero charge (pH_{PZC}) were used to explain the results

7.2 Materials and Method

7.2.1 Chemicals

All reagents used in this study were of analytical grade. The source of Hg^{2+} , Cd^{2+} and Pb^{2+} were $\text{Hg}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, respectively. The source of $\text{Cr}_2\text{O}_7^{2-}$ and SO_4^{2-} were $\text{K}_2\text{Cr}_2\text{O}_7$ and Na_2SO_4 , respectively. Basically 1000 ppm of each of the solutions was prepared and diluted to 100 ppm for the batch adsorption studies.

7.2.2 Synthesis of MWCNTs and Carbon Spheres (CSs)

Pristine MWCNTs were synthesized by a nebulised spray pyrolysis method as outlined in Chapter 4. Studies on the unpurified materials (which contained catalyst and amorphous carbon impurities) and purified materials (impurities removed by thermal annealing and soxhlet extraction) were undertaken.

The N-MWCNTs and N-CSs were synthesised at the University of the Witwatersrand and supplied for this study. The undoped precursors used to make these materials were also supplied. These precursors were synthesized by a method employed by Mhlanga et. al.⁴⁸¹ For the synthesis of the nitrogen-doped materials this method was modified by bubbling N_2 and C_2H_2 over acetonitrile which acted as the nitrogen source.⁴⁸²

Details on the BET data (surface area and pore volume) and the pore sizes of these nanomaterials are supplied in **Appendix 1-Table A2**). The nitrogen contents of the nitrogen doped materials were also determined on a C,H,O,N analyzer and the details of this analysis are supplied in **Section 7.2.6**.

7.2.3 Microwave-induced Acid and Base-Treatment of Pristine MWCNTs

To study the effects of surface functional groups introduced by acid treatment of the pristine MWCNTs (2,00 g), the MWCNTs were heated under microwave (1000 W) for 2 hours using a mixture of strong acids (98% H_2SO_4 (60 mL) and 55

% HNO₃ (30 mL)). For comparative purposes, these MWCNTs were also heated under microwave using a mixture of weak acids (98% CH₃COOH (60 mL) and 98% H₃PO₄ (30 mL)). Similarly, base treatment was conducted by treating the MWCNTs in a strong base (0,1 M KOH (90 mL)) and a weak base (0,1 M aqueous NH₃ (90 mL)), respectively. After the 2 hour microwave treatment the mixtures were cooled to room temperature, filtered through a 0,45 µm filter and washed with distilled water as per a method described by Chao et. al.⁴⁸³. The acid and base treated MWCNTs were subsequently dried in an oven at 80⁰C for one hour and vacuum dessicated for 24 hours.

7.2.4 Heat Treatment of N-MWCNTs and N-CSs

Heat treatment of the nitrogen doped materials was conducted by heating the carbons under argon at 1273 K. This is similar to a method used by Yang and Kaneko.⁴⁸⁴ for the heat treatment of nitrogen doped activated carbon fibres.

7.2.5 Characterisation of Acid and Base Treated MWCNTs

Surface functional groups formed by the acid and base treatment (conducted by heating 2,00 g MWCNTs under microwave (1000 W) for 2 hours in 90 mL of 0,1 M KOH and later by heating a separate 2,00 g sample of MWCNTs under the same conditions in 90 mL of 0,1 M aqueous NH₃) of the pristine MWCNTs were identified by means of Fourier Transform Infrared Spectroscopy (FTIR). The method employed to conduct this functional group analysis included the preparation of a KBr pellet, (prepared by mixing 2,00 mg sample with 200 mg KBr). Thorough mixing of the KBr-sample mixture using a pestle and mortar was required for the analysis. The pellet was pressed in a pellet press at a pressure of 6 tonne per 13 mm² for 5 minutes. The pellet was then mounted onto a sample holder and placed into a MIDAC FTIR (model 4000) for analysis. Sixteen scans were conducted at a resolution of 4 cm⁻¹. Details of the major functional groups observed from this analysis are given in **Table 7-1**.

7.2.6 Oxygen and Nitrogen Content Determination

The oxygen content of the acid and base-treated MWCNTs and the nitrogen content of the N-MWCNTs and N-CSs were determined on a Perkin-Elmer C,H,O,N,S analyzer. The basic experimental protocol that was followed to conduct this analysis involved weighing approximately 2 mg of each sample into a tin capsule. The capsule was then folded and placed into a reaction chamber (housed inside the instrument) where combustion occurs and the nitrogen and oxygen contents were measured from the masses of NO_2 and CO_2 that form. Prior to analysis the instrument was calibrated using known standards. Blank measurements using empty tin capsules were conducted. These results are summarized in **Tables 7-2 and 7-6**.

7.2.7 Determination of Point of Zero Charge (pH_{PZC})

As described in Chapters 3 and 5 the pH_{pzc} of the acid and base treated MWCNTs and N-MWCNTs and N-CSs was measured on a Malvern Zetasizer by varying the Zeta potential as a function of pH. This was conducted by suspending 2,00 mg of sample into 5,00 mL n-hexane and adjusting the pH to the desired value using either 0,1 M HCl or 0,1 M NaOH. After pH adjustment, the suspension was transferred into a cuvette, which was placed into the Zetasizer for measurement of the Zeta potential at the specific pH value. Typically the pH was varied between 2-14 and the Zeta potential at each pH value was measured. The Zeta potential was plotted as a function of pH. The point at which the graph crosses the X-axis was determined as the point of zero charge of the material. These pH_{pzc} values are shown in **Table 7-2**.

7.2.8 X-ray Photo Electron Spectroscopy (XPS) Studies

This study was conducted on the nitrogen doped materials and the NH_3 -treated MWCNTs with the main purpose of identifying the form in which nitrogen is present in these sample. This study also aimed at establishing the elemental composition (both qualitative and quantitative) of these materials.

In order to conduct these studies the samples were prepared by placing a thin layer of sample on a grid with an area of $500 \mu\text{m}^2$ for surface analysis. These samples were subsequently placed into a Physical Electronics Quantum 2000 instrument for analysis. The details of the experimental parameters employed for this study are provided in **Appendix 3**. The analysis was conducted at room temperature ($25^\circ\text{C} \pm 5^\circ\text{C}$) and at a relative humidity of $50\% \pm 25\%$.

7.2.9 Batch Adsorption Studies

All batch adsorption studies were conducted as previously described by keeping each type of carbon in contact with each type of solution for contact times ranging from 10 to 240 minutes. After each contact time was completed, the carbon-solution suspension was filtered through a $0,45 \mu\text{m}$ filter and the filtrate was analysed for its metal ion content. The following parameters were examined in these studies:

- The effect of microwave induced (1000 W; heating for 2 hours) acid-base treatment on anion and cation uptake
- The effect of nitrogen doping on anion and cation uptake including the effect of heat treated nitrogen doped materials and the effect of dopant content.
- The effect of impurities such as catalyst and amorphous carbon impurities on cation and anion uptake

7.2.10 Analysis of Anions and Cations

The cations Hg^{2+} , Cd^{2+} and Pb^{2+} were analysed by Atomic Absorption spectroscopy (AAS). The $\text{Cr}_2\text{O}_7^{2-}$ was determined by UV-visible spectroscopy using diphenyl carbazide as the colorimetric agent⁴⁸⁵. Finally, the SO_4^{2-} ion was determined by UV-visible spectroscopy (Turbidometry). Further details of the analysis are provided in **Appendix 2**.

7.2.11 Quality Assurance and Validation of the Analytical Data

As reported in the previous chapters all batch adsorption studies were conducted in duplicate and an average of two results is reported here. Any analytical data which exceeded a relative error of 5% was not used in the interpretation of the results. The data was validated using Statistica 3.0. The analytical results were found to be reproducible within $\pm 2\%$.

7.3 Results and Discussion

7.3.1 The Effect of Microwave Induced Acid-Base Treatment

As mentioned earlier, the acid-treatment of the MWCNTs was conducted by heating 2,00 g of the MWCNTs firstly in a strong acid mixture (consisting of 98% H_2SO_4 (60 mL) and 55 % HNO_3 (30 mL)) under microwave (1000 W) for 2 hours. Similarly, a separate 2,00 g sample was heated in a weak acid mixture consisting of 98% CH_3COOH (60 mL) and 98% H_3PO_4 (30 mL) under the same conditions.

The base-treatment was also conducted under the same conditions where a separate 2,00 g sample of MWCNTs was heated in 90 mL of 0,1 M KOH to examine the effect of strong base treatment. On the other hand, the effect of weak base treatment was also studied by heating a 2,00 g sample of MWCNTs under microwave for 2 hours in 90 mL of 0,1 M aqueous ammonia.

Table 7-1 summarises the functional groups present on both the acid and base treated MWCNTs as identified by FTIR spectroscopy (detailed spectra shown in **Appendix 3 (See Figure A4)**).

Table 7-1: The Primary Functional Groups Present on Microwave-Induced Acid and Base –Treated CNTs

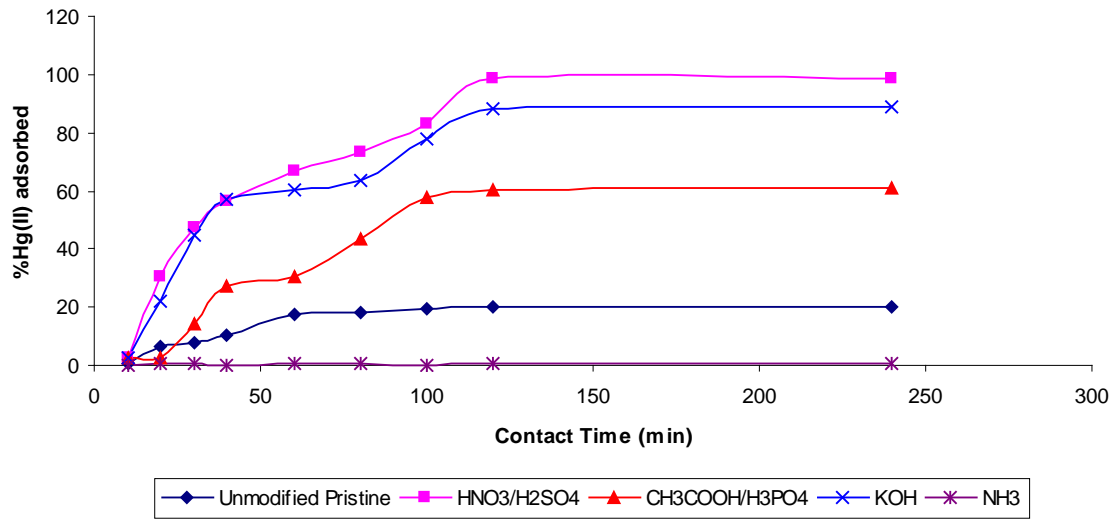
Acid/Base	Major Functional Groups	Wavenumbers (cm ⁻¹)
H ₂ SO ₄ /HNO ₃	C=O	1747
	O-H	3416
CH ₃ COOH/H ₃ PO ₄	C=O	1762
	O-H	3429
KOH	O-H	3475
NH ₃	N-H	3389

From this table it is clear that microwave-induced acid treatment results primarily in the formation of carboxyl functional groups which is evident from the carbonyl and hydroxyl groups that are observed after treatment with both the strong and weak acid mixtures.

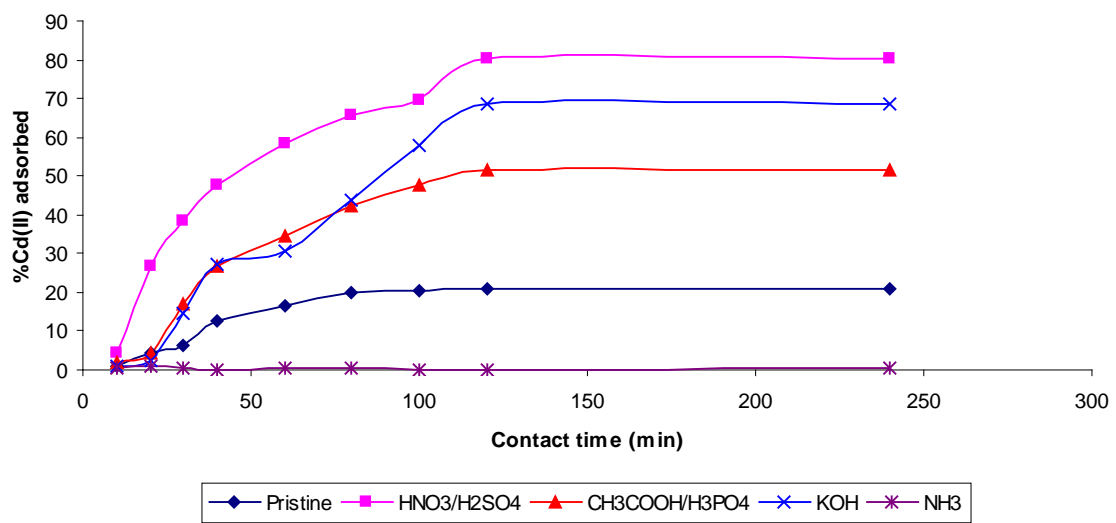
By contrast the treatment with strong base resulted primarily in the formation of hydroxyl functional groups while the treatment with a weak base resulted in the formation of amine bands. There are therefore adequate binding sites for cation and anion uptake on these materials.

Figures 7-1 and 7-2 show the adsorption performance of these materials for cation and anion uptake.

a)



b)



c)

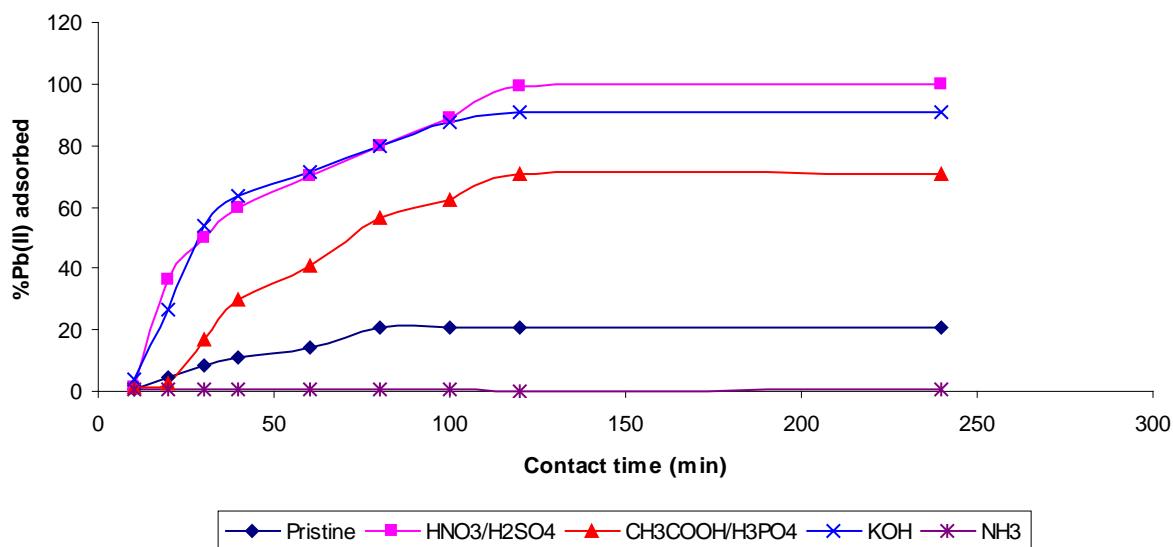


Figure 7-1: The influence of microwave-induced acid-base treatment on the uptake of a) Hg(II), b) Cd(II) and c) Pb(II) by MWCNTs

From **Figure 7-1** it is evident that the MWCNTs that were treated with the strong acid mixture and the strong base KOH achieved the highest extents of adsorption. This is attributed mainly to the functional groups introduced by these types of treatments. As stated earlier the oxygen-containing functional groups provide good binding sites for the cations via a chemisorption process. This observation is therefore consistent with the literature reports outlined in Chapter 2 where it has been stated that oxygen-containing functional groups improve the cation exchange capacity of CNTs by rendering these more hydrophilic.⁴¹¹ Further evidence of this phenomenon is presented in **Table 7-2** where it is clearly shown that the MWCNTs with the highest oxygen content namely those oxidized in the strong acid mixture achieved the highest extents of adsorption.

Table 7-2: The Effect of Point of Zero Charge and Oxygen Contents on the Optimum Cation Exchange Removal of Each Type of MWCNT

TYPE OF MWCNT	Oxygen Content (%) ⁷	Highest % Cation removal achieved	Point of Zero Charge (pH _{PZC})
Pristine	Not Detected	20%	9,92
NH ₃ -treated	Not Detected	0%	8,87
CH ₃ COOH/ H ₃ PO ₄ treated	2,57	60%	6,39
KOH treated	3,98	80%	3,47
HNO ₃ /H ₂ SO ₄	5,25	99%	2,89

By contrast the MWCNTs in which no oxygen was detected show little or no cation uptake. Thus, the strong acid mixture simply results in generating more oxygen binding sites for cation uptake. However, other parameters such as the point of zero charge need to be examined before any definite conclusions are drawn.

The pH_{pzc} data reveal that the treatment of the MWCNTs with the strong acid mixture or the strong base give materials with low points of zero charge. This indicates that MWCNT surfaces are negatively charged over a wide pH range. This renders them more favourable for cation uptake by electrostatic interactions. Treatment with the weak acid mixture results in a slightly higher pH_{PZC} which imparts a slightly more positive surface charge to the MWCNTs which renders them less favourable for cation uptake due to increased electrostatic repulsions. Hence, the cation uptake by these MWCNTs is 20-40% lower than that of the MWCNTs treated with the strong acid mixture and the strong base. By contrast, the unmodified pristine MWCNTs and the MWCNTs which were treated with the weak

⁷ Determined on a C,H,O,N analyser

base NH_3 have the highest points of zero charge which renders them positively charged over a wide pH range. This clearly does not favour cation uptake due to stronger electrostatic repulsions. Hence these materials show the lowest extents of cation uptake. It has also been reported in the literature that the introduction of hydrophilic amine groups impart a high pH_{PZC} to CNTs.³⁹¹ The nitrogen content of this material was also determined as 4,89%.

There are therefore two factors that are playing a role here. The first of these is the strength of the interactions where a lower point of zero charge results in stronger electrostatic interactions between the cations and the predominate negative surface charge of the CNTs. The second factor relates to the number of interactions where a higher oxygen content results in more binding sites for the cations on the CNT surface. This becomes more evident when the oxygen content and pH_{PZC} data of the KOH treated MWCNTs and the $\text{HNO}_3/\text{H}_2\text{SO}_4$ treated MWCNTs are compared.

Here it is noted that there is not much of a difference in the pH_{PZC} of the materials but there is a marked difference in the oxygen content. So, in this case the higher cation uptake by the $\text{HNO}_3/\text{H}_2\text{SO}_4$ -treated MWCNTs is due mainly to the higher oxygen content where there are more binding sites available for the cations.

The results for anion uptake (shown in **Figure 7-2**) seem to be counter-intuitive as far as the uptake of $\text{Cr}_2\text{O}_7^{2-}$ is concerned. Here it is observed that despite the low pH_{PZC} the acid-treated MWCNTs still adsorb $\text{Cr}_2\text{O}_7^{2-}$ to an appreciable extent. The surface pH induced by the acid treatment appears to influence the speciation of chromium. It is well known that at low pH Cr(III) predominates as a result of the reduction of Cr(VI) to Cr(III) (See **Figure 2-1** in Chapter 2). It is therefore postulated that the low surface pH induced by the acid treatment impacts on the reduction of Cr(VI) to Cr(III) and it is actually the trivalent cation which is undergoing adsorption either by binding to the oxygen sites on the MWCNTs or by electrostatic attraction onto the surface of the acid-treated MWCNTs. This postulate is supported by the results of Hu et. al.⁴²⁰ and verified by UV-vis spectroscopy analysis in which Cr(III) was detected. **Table 7-3** compares the relative concentrations of Cr(III) and Cr(VI)

adsorbed as determined by UV-visible spectroscopy. The adsorbed chromium was desorbed using distilled water prior to the analysis by UV-visible spectroscopy.

Table 7-3: The Relative Concentrations of Cr(III) and Cr(VI) as determined by UV Visible Spectroscopy

TYPE OF MWCNT	CONTACT TIME (MIN)	Cr(III) conc. (ppm) adsorbed ($\pm 0,01$ ppm)	Cr(VI) conc. (ppm) ($\pm 0,01$ ppm)
HNO ₃ /H ₂ SO ₄ -treated	10	5,26	0,01
	20	40,6	0,05
	30	57,3	0,03
	40	66,3	0,04
	60	77,1	0,02
	80	83,2	0,08
	100	93,0	0,07
	120	99,4	0,02
	240	99,9	0,04
CH ₃ COOH/H ₃ PO ₄ -treated	10	2,63	0,05
	20	3,78	0,03
	30	14,5	0,01
	40	27,0	0,06
	60	30,4	0,07
	80	43,5	0,01
	100	57,7	0,05
	120	60,5	0,02
	240	60,8	0,03

The analytical data was also validated by subtracting the Cr(VI) concentrations from total chromium concentrations determined by AAS. Thus, it is clear that the concentration of Cr(VI) adsorbed relative to that of Cr(III) was negligible and the postulate that it was predominantly Cr(III) that underwent adsorption is valid.

On the other hand adsorption by the base-treated MWCNTs is as expected. The KOH-treated MWCNTs show no appreciable uptake of Cr₂O₇²⁻ due to the low pH_{pzc} which results in an electrostatic repulsion of the oxyanions. In general Cr₂O₇²⁻ and

CrO_4^{2-} predominate at high pH (See **Figure 2-1**) but any Cr(III) that exists at high pH is most likely to precipitate as $\text{Cr}(\text{OH})_3$. Therefore it is highly possible that anionic Cr(VI) is undergoing adsorption onto these materials. The uptake of $\text{Cr}_2\text{O}_7^{2-}$ by the NH_3 treated MWCNTs is in fact the highest, which is not surprising if the high pH_{PZC} of these materials is considered. Similarly, the unmodified pristine MWCNTs also shows a high anion uptake due to a relatively high pH_{PZC} .

The uptake of SO_4^{2-} seems to be in line with what is expected for anion uptake. The acid-treated and KOH-treated MWCNTs show little or no uptake of SO_4^{2-} . The Eh-pH diagram of sulfur reveals that the bisulphate ion (HSO_4^-) predominates at low pH. However, this species is still negatively charged so electrostatic repulsion is expected and the uptake of the anion therefore is restricted. On the other hand SO_4^{2-} predominates at high pH and this explains why the uptake of this anion by the KOH-treated MWCNTs is so low. Conversely, the uptake of this anion by the unmodified pristine MWCNTs and NH_3 -treated MWCNTs is quite high and almost complete removal occurs when the MWCNTs are treated with the weak base due to the high point of zero charge of these materials

Another noteworthy observation from **Figure 7-2** is that the uptake of chromates relative to that of the sulphates by MWCNTs that were treated with a $\text{CH}_3\text{COOH}/\text{H}_3\text{PO}_4$ mixture was much higher. As explained earlier, the chromium ion adsorbed in this case was predominantly Cr(III) (see **Table 7-3**) so the point of zero charge of these materials clearly favours the uptake of the cation (Cr(III)) over the anion (SO_4^{2-}).

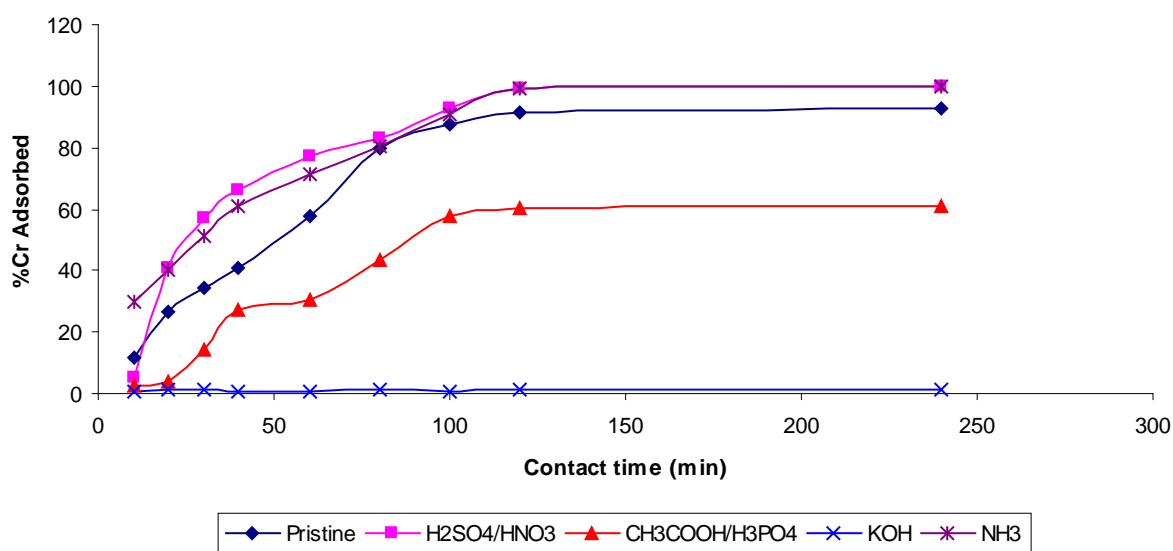
The effect of acid and base treatment on the uptake of anions therefore varies depending on the type of anion undergoing adsorption. Nevertheless the results in **Table 7-1** and **Figures 7-1** and **7-2** reveal that treatment with both strong and weak acid mixtures resulted in oxygen containing functional groups which lower the point of zero charge of the MWCNTs and favour cation uptake. This also applies to treatment with a strong base such as KOH. However, treatment with a weak base like NH_3 results in the generation of nitrogen containing functional groups which increase the point of zero charge and favour anion uptake. This is confirmed by

the FTIR data shown in **Table 7-1**. These results also shed some light on the effect that the introduction of heteroatoms such as nitrogen and oxygen can have on the adsorption capacities of MWCNTs. This is examined further in Section 7.3.2 where the effect of nitrogen-doping is discussed.

7.3.2 The Effect of Nitrogen Doping and the Dopant Content

Figures 7-3 and 7-4 compare the adsorption capabilities of both nitrogen doped MWCNTs and CSs and their undoped counterparts for both cation and anion uptake.

a)



b)

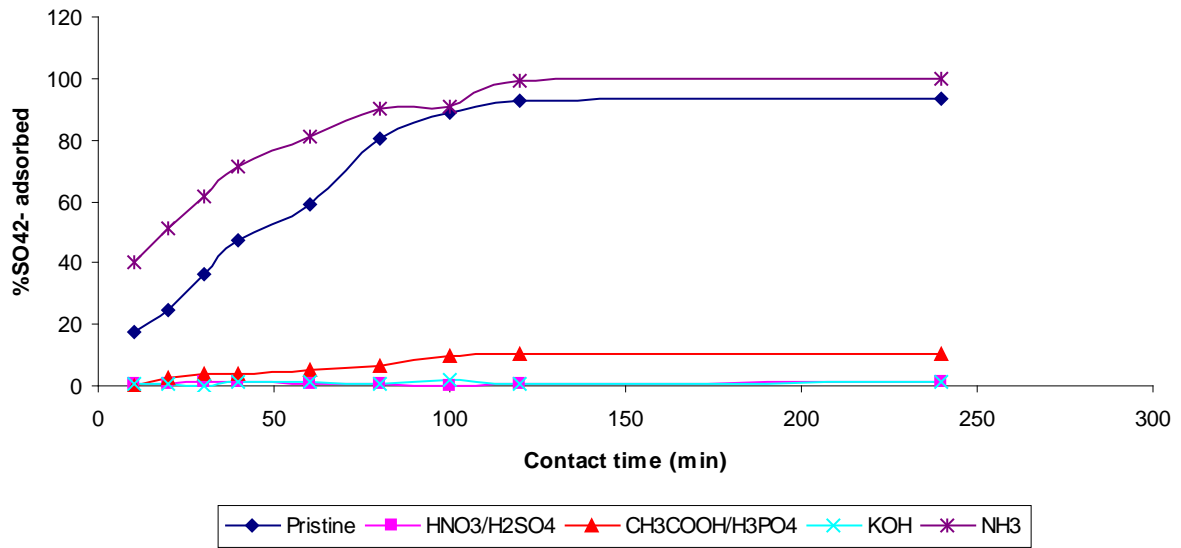
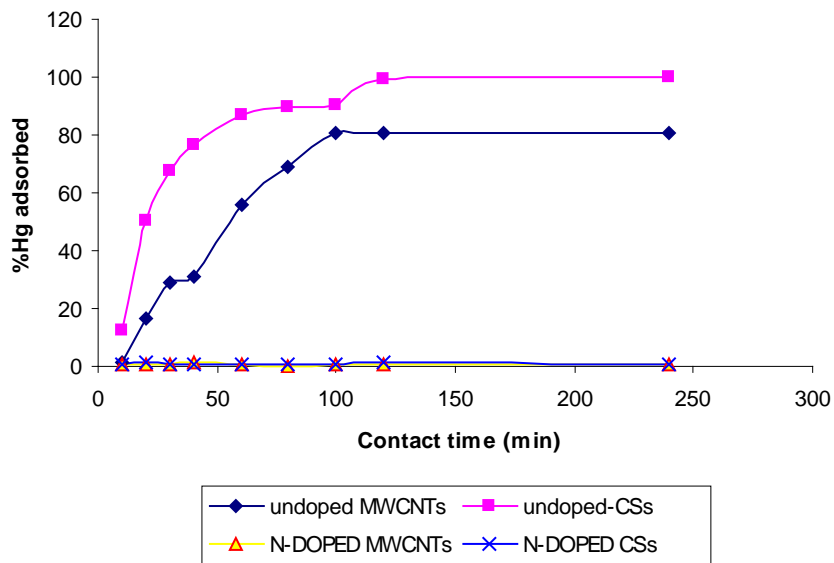
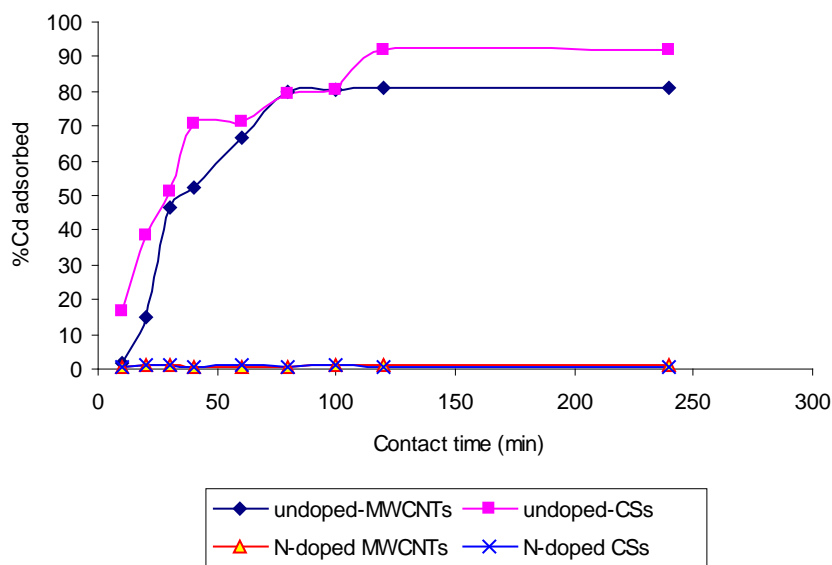


Figure 7-2: The influence of microwave-induced acid-base treatment on the uptake of a) $\text{Cr}_2\text{O}_7^{2-}$ and b) SO_4^{2-} by MWCNTs

a)



b)



c)

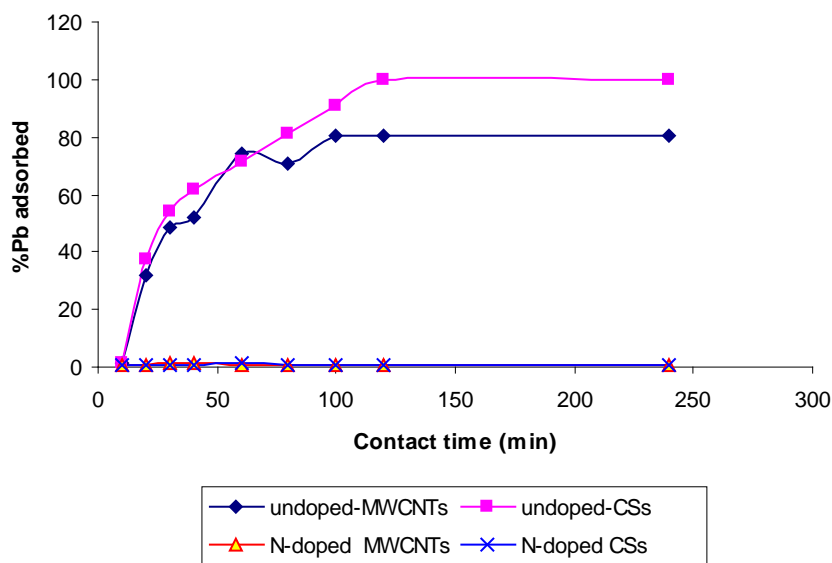


Figure 7-3: The effect of nitrogen-doping on the uptake of a) Hg(II), b) Cd(II) and c) Pb(II)

Figure 7-3 reveals that the undoped carbon nanomaterials have a higher uptake capacity for the cations Hg^{2+} , Pb^{2+} and Cd^{2+} than the nitrogen doped carbon nanomaterials. The opposite is observed in **Figure 7-4** where the nitrogen doped carbon nanomaterials adsorb the anions ($\text{Cr}_2\text{O}_7^{2-}$ and SO_4^{2-}) to a better extent

than the undoped materials. This is readily understood when the point of zero charge data for these materials (shown in **Table 7-4**) is examined.

Table 7-4: The Point of Zero (pH_{pzc}) Charge Data for Undoped and Nitrogen Doped Carbon Nanomaterials

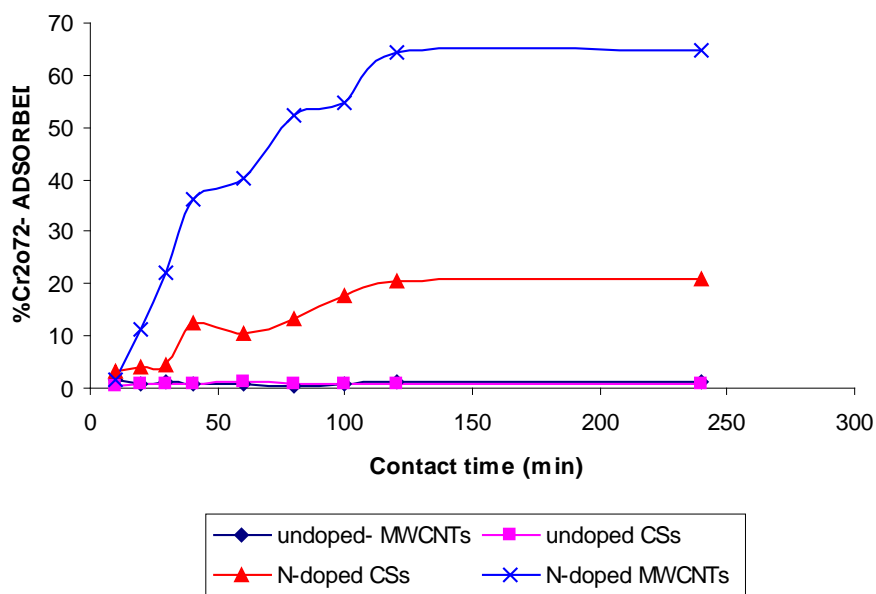
TYPE OF CARBON NANOMATERIAL	pH_{pzc}
Undoped MWCNTs	3,59
Undoped CSs	2,89
N-MWCNTs	10,89
N-CSs	8,39
Heat-treated N-MWCNTs ⁸	12,95
Heat-treated N-CSSs ⁹	10,15

From this data it is noted that the undoped materials have low points of zero charge implying that these materials are negatively charged over a wide pH range which renders them suitable and effective for cation uptake. This data also correlates well with the data presented in Section 7.3.1. where it was noted that the introduction of the nitrogen-containing functional groups by treatment in aqueous ammonia resulted in a predominately positive surface charge which favours the uptake of anions.

⁸ Studied for the effect of heat treatment (see Figure 7-6)

⁹ Studied for the effect of heat treatment (see Figure 7-6)

a)



b)

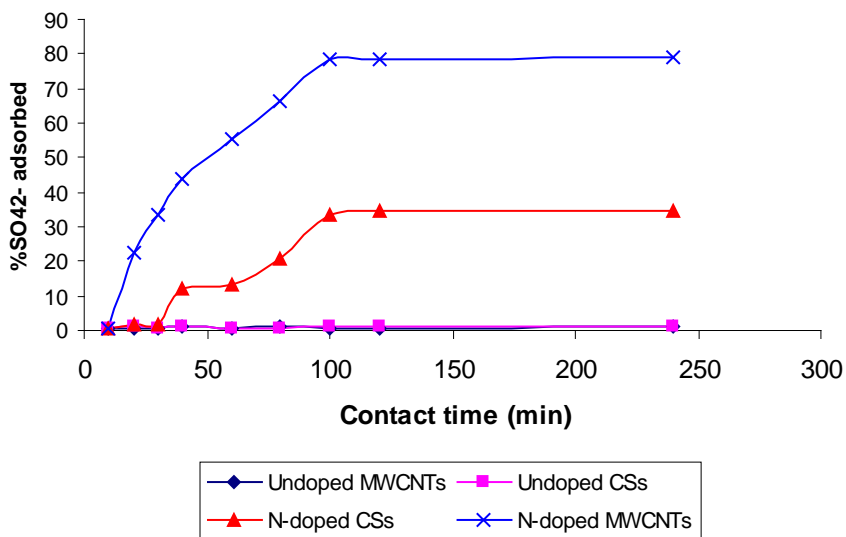


Figure 7-4: The effect of nitrogen doping on the uptake of a) $\text{Cr}_2\text{O}_7^{2-}$ b) SO_4^{2-}

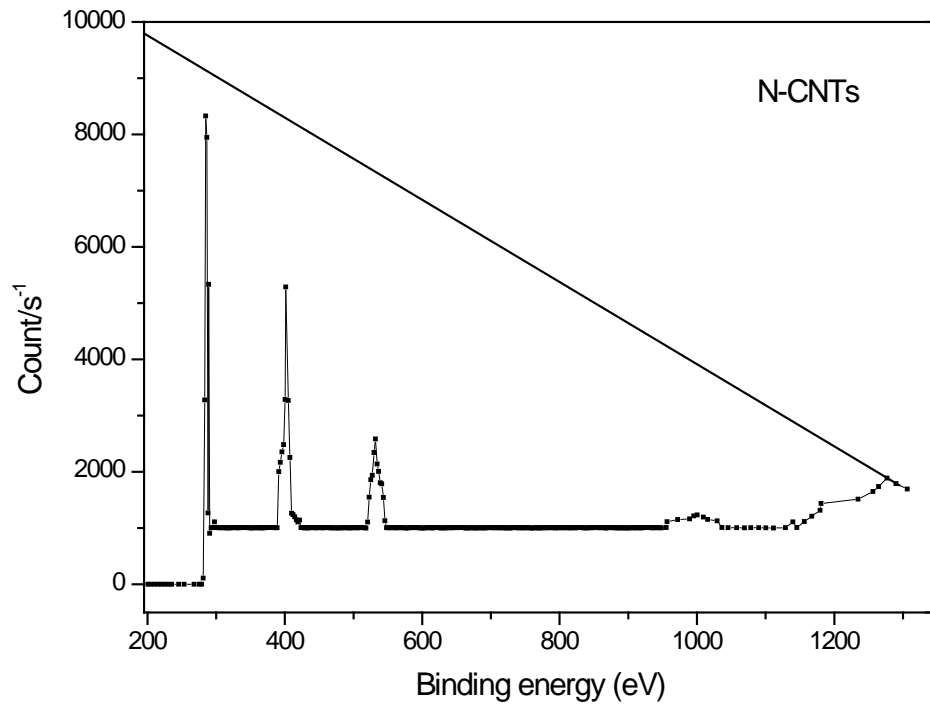
The form in which nitrogen is present on these nitrogen doped carbon nanomaterials helps to explain why the introduction of the heteroatom nitrogen can induce a positive surface charge onto these materials. It is possible that the initial acid-treatment conducted to purify the nanomaterials could have protonated

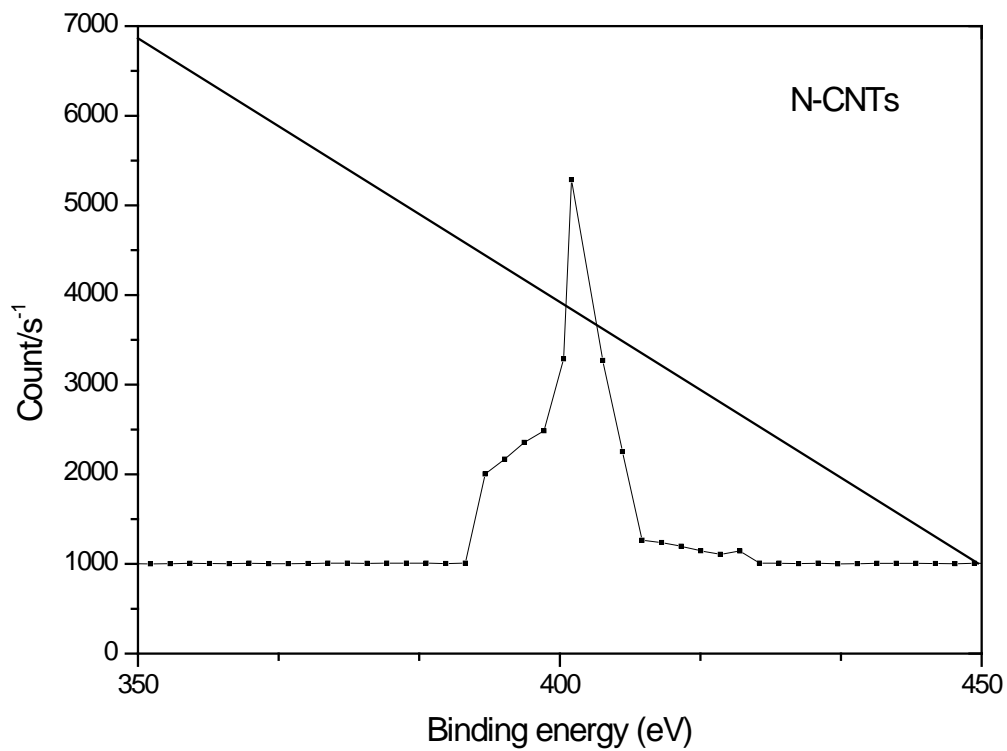
the nitrogen atoms of these materials. **Table 7-4** and **Figure 7-5** show the XPS results of both types of N-doped nanomaterials and the MWCNTs treated with NH_3 (used earlier in studies on the effect of acid-base treatment on anion and cation uptake—see Section 7.3.1)

Table 7-6: The Deconvoluted XPS results for the adsorbents NH_3 treated-MWCNTs, N-MWCNTs and N-CSs,

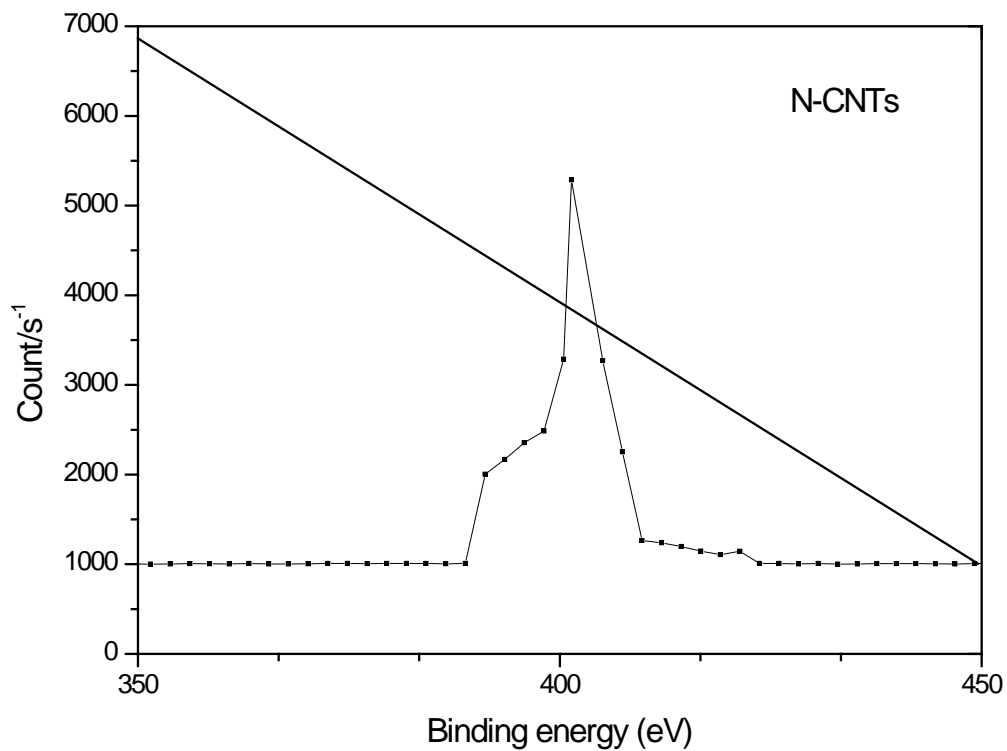
Adsorbent	Elemental Composition	Atomic Concentration (%)	Binding Energy (eV)	Identification
NH ₃ -treated MWCNTs	C	95,15	284.8	C-C
	N	4,85	401,3	Quaternary nitrogen
N-MWCNTs	C	87.9	284.9 (95%) 286.6 (3%) 289.11 (2%)	C-C C-O O-C=O
	O	4.93	532.17	O-C, O-H,
	N	7,17	401,4	Quaternary nitrogen
N-CSs	C	92,36	284.8 (92%) 286.5 (6%) 289.0 (2%)	C-C C-O O-C=O
	O	5.04	532.4	O-C, O-H,
	N	2.6	401,4	Quaternary nitrogen

a)

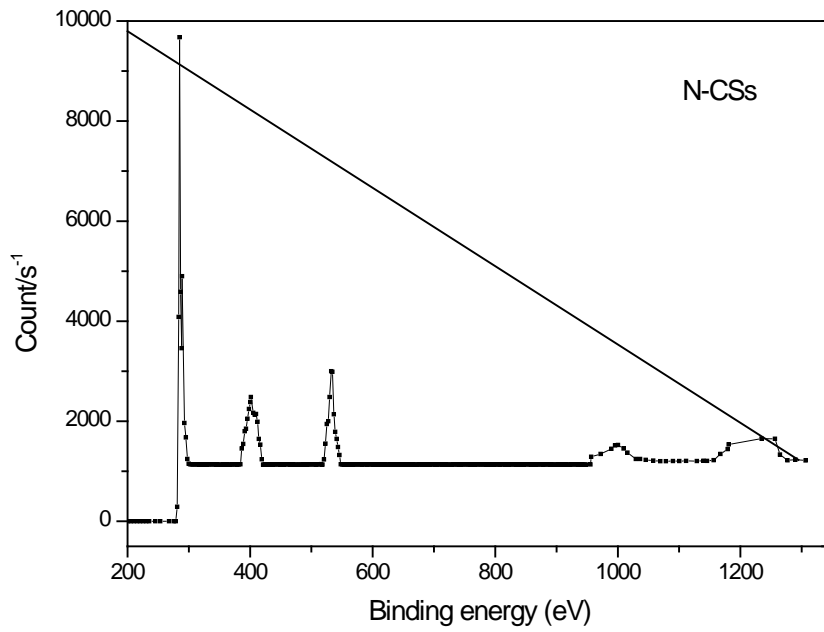




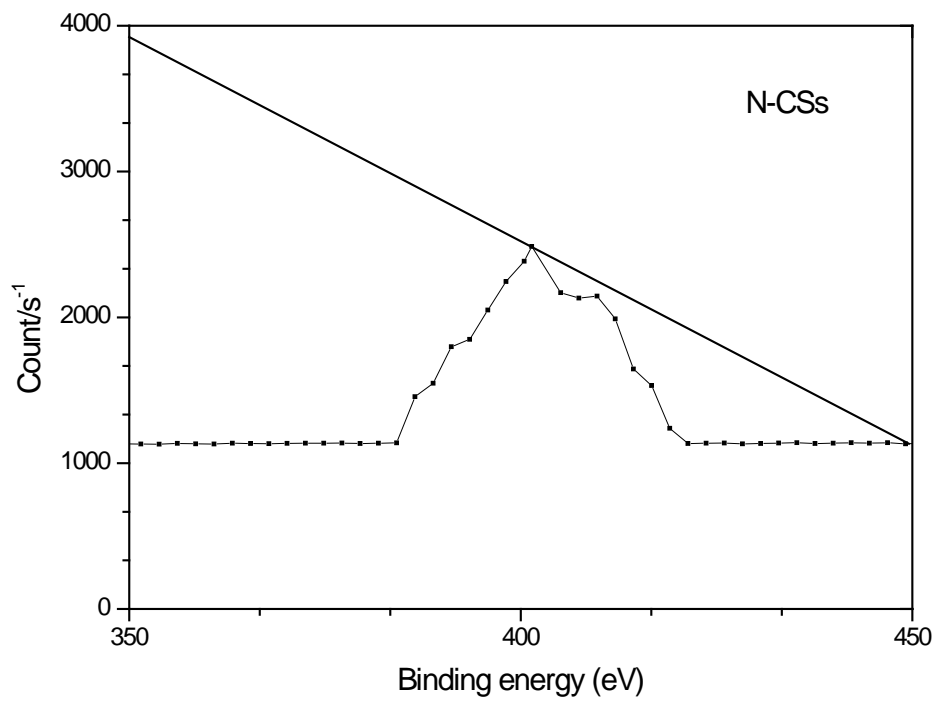
b)



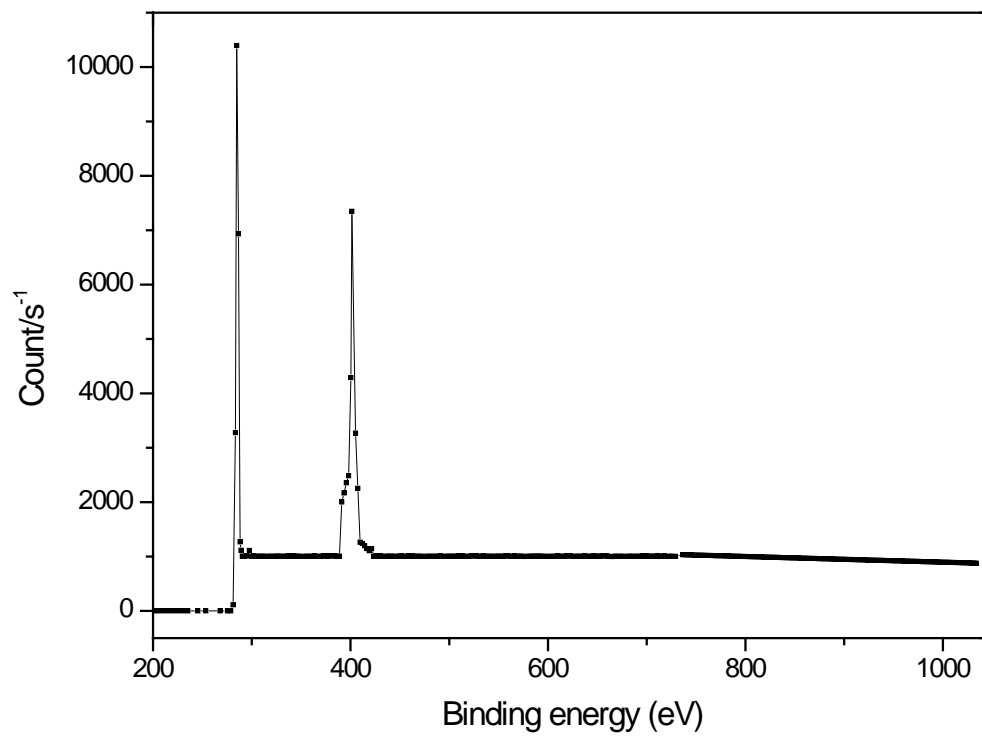
c)



d)



e)



f)

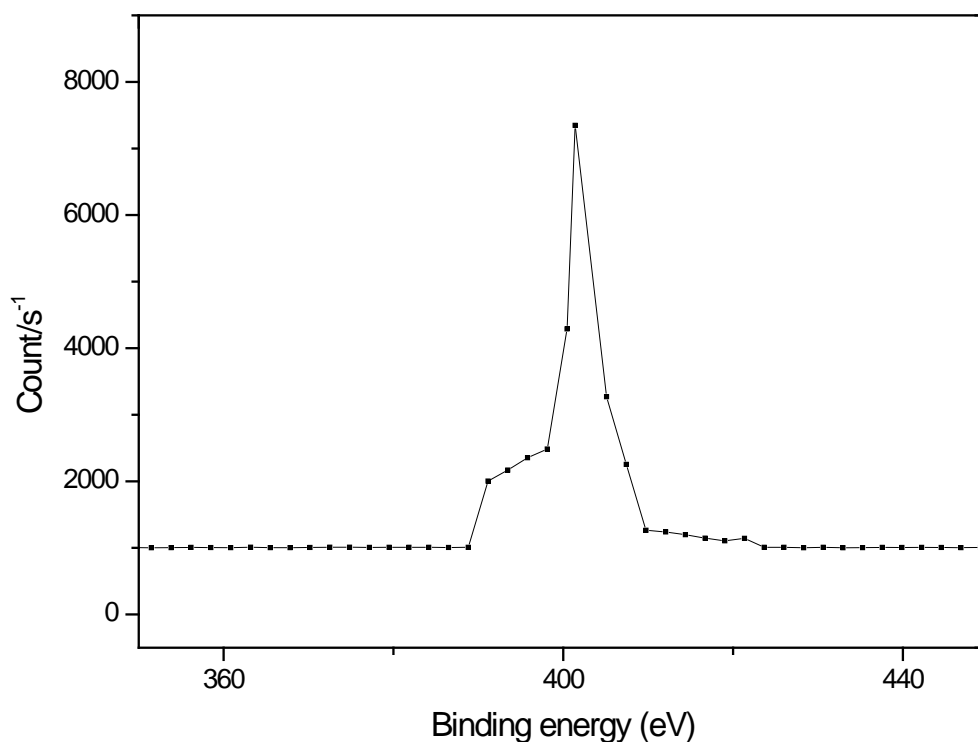


Figure 7-5: XPS Spectra of a) N-CNTs b) Nitrogen peak on N-CNTs c) NCSs a d) Nitrogen peak on NCSs e) NH₃-treated MWCNTs and f) Nitrogen peak on NH₃-treated MWCNTs

It is of interest to note here that apart from the predominant nitrogen peak at 401 eV, there are other minor peaks between 400 and 402 eV. These can correspond to pyridinic oxide (402-405 eV), pyrrolic nitrogen (400,5 eV) and pyridinic nitrogen (398,6 eV).⁴⁸⁶ However, the predominant peak at 401,3-401,4 eV has been identified as that of quaternary nitrogen.^{484,486} This verifies that the nitrogen atoms are indeed protonated thereby carrying a positive charge which renders these materials favourable for anion uptake by electrostatic attractions.

Another important feature of these results is that oxygen is present in both the N-doped samples. This is probably due to the initial acid-treatment of the materials.

Once again, no oxygen was detected in the NH₃-treated samples. This correlates well with the results in **Table 7-2** where no oxygen was detected by a C,H,O, N analyzer. It is also important to note that the results obtained for nitrogen content correlate well with that determined by the C,H,O,N analyzer.

7.3.3 The Effect of the Carbon Materials

The results in **Figures 7-3** and **7-4** also show that MWCNTs and CSs have different adsorption capabilities for anion and cation uptake. In the undoped form the CSs show a higher capacity for cation uptake than MWCNTs. The slightly higher point of zero charge of the MWCNTs could account for this.

However, when doped with nitrogen the MWCNTs show a better uptake capacity for anion removal than the CSs. Although the higher point of zero charge of N-MWCNTs (**Table 7-3**) can account for this other factors including the actual nitrogen content of the materials can also explain these observations

Table 7-7: The Nitrogen Contents of N-MWCNTs and N-CSs (determined by C,H,O,N analyzer)

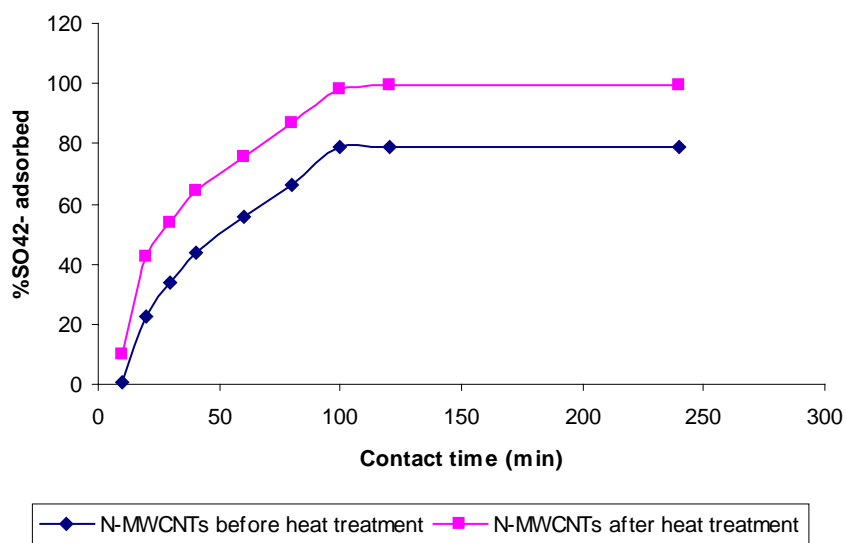
TYPE OF NANOMATERIAL	NITROGEN CONTENT (%)
N-MWCNTs	7.12
N-CSs	2.67

The data reveals that the N-MWCNTs had a nitrogen content that was about 2,6 times higher than that of N-CSs. This correlates with the XPS data shown in **Table 7-4**. Thus the anion uptake capacity of N-CSs is poorer due to a lower nitrogen content which results in less active positively charged nitrogen centres (predominantly quaternary nitrogen) to electrostatically attract the anions.

7.3.4 The Effect of Heat-Treatment on the Uptake Capacities of N-MWCNTs and N-CSs

Figure 7-6 shows the effect that nitrogen-doped materials (heat treated at 1273K) have on the uptake of sulphates. .

a)



b)

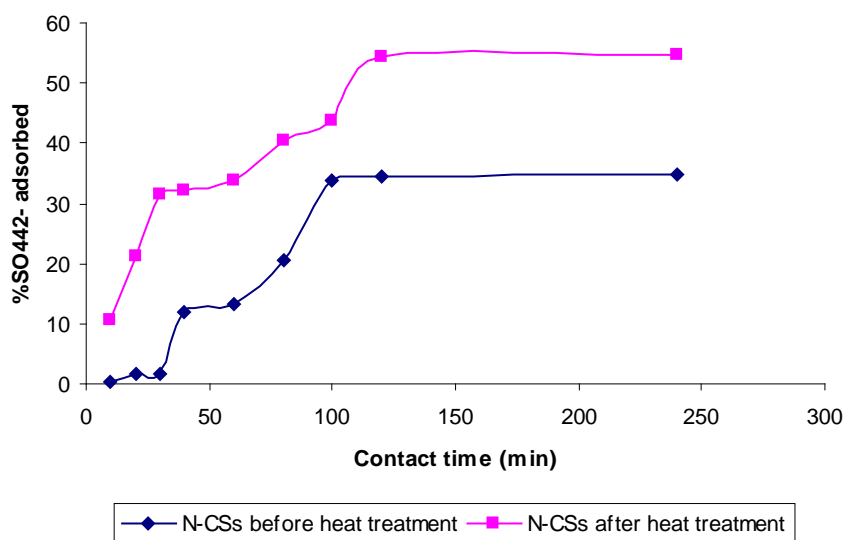


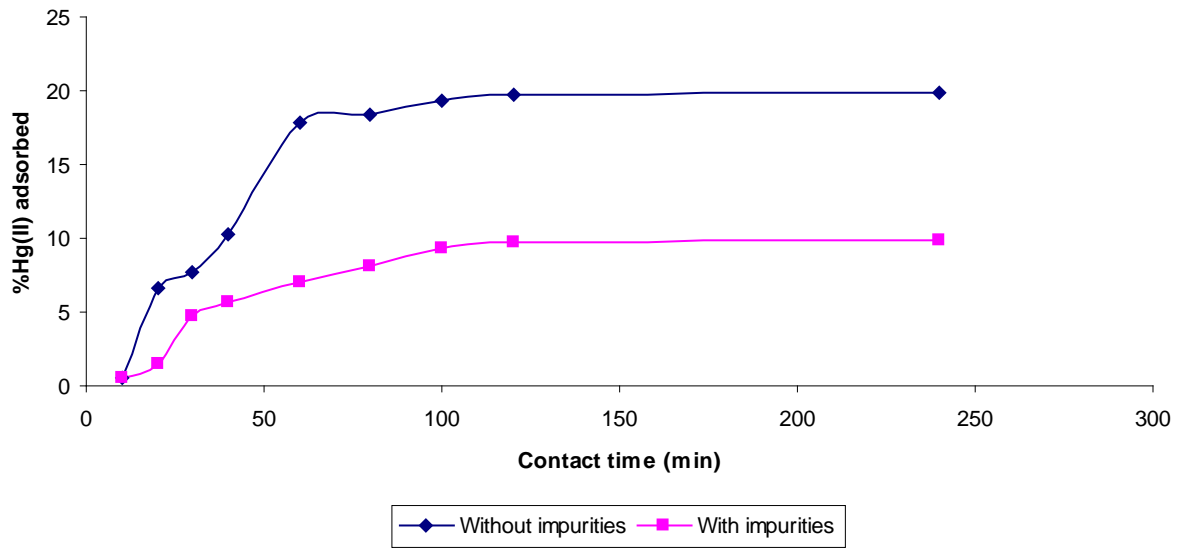
Figure 7-6: The effect of heat treatment on the adsorption performance of a) N-MWCNTs and b) N-CSs for the uptake of SO_4^{2-}

Here it is noted that heat treatment of both N-doped materials enhances the adsorption performance for sulphate uptake by about 20%. The Ph_{PZC} of both materials was determined according to the method outlined in Section 7.2.7. These are also reported in **Table 7-3** together with the pH_{pZC} data for the materials before heat treatment. A comparison of the data in **Table 7-3** reveals that the point of zero charge of both types of N-doped materials increases by about two units after heat treatment. Hence, there is an alteration in the surface charge where the surfaces charges become positively charged over a wide pH range. This results in more favourable conditions for anion uptake by electrostatic attractions. The increase in pH_{PZC} after heat treatment could be due to the removal of surface oxygen functional groups which have a tendency to lower the pH_{pZC} . This was verified by a C,H,O,N analysis where no oxygen could be detected after the heat treatment was carried out.

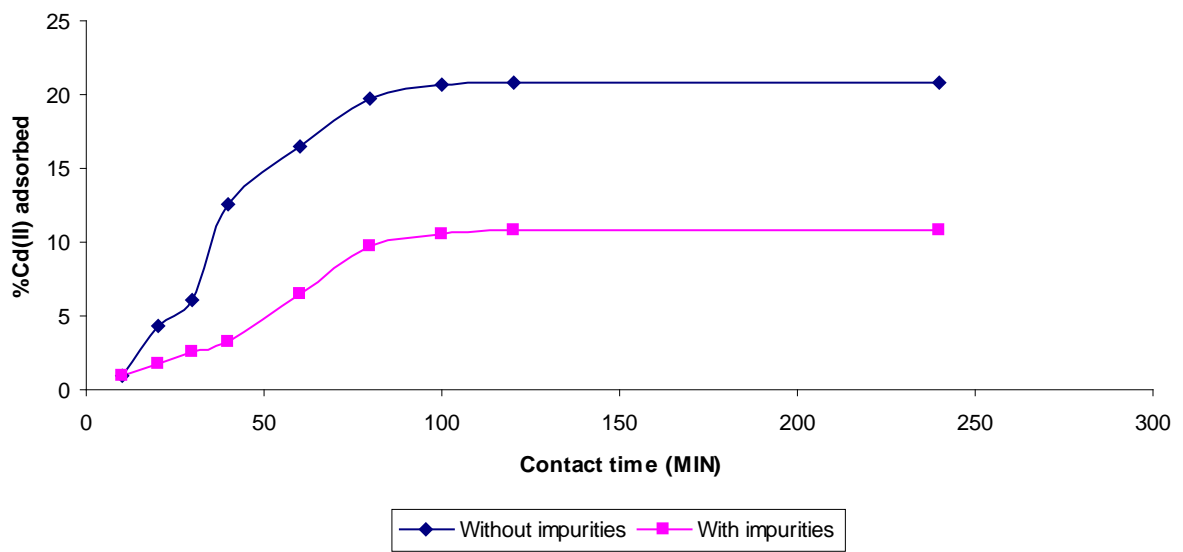
7.3.6. The Effect of Catalyst and Amorphous Carbon Impurities on Cation and Anion Uptake by Pristine MWCNTs

As indicated in Section 7.2.2 MWCNTs synthesized by nebulised spray pyrolysis can contain impurities such as amorphous carbon and catalyst impurities. Such impurities may be removed by thermal annealing and a soxhlet extraction process. In order to examine the effect of these impurities on anion and cation uptake, some of MWCNTs were left in the unpurified form (no thermal annealing or soxhlet extraction) and used in batch adsorption studies for anion and cation uptake. **Figures 7-7 and 7-8** compares the adsorption capabilities of pristine MWCNTs (for cation and anion uptake) both in the presence and absence of impurities which mainly include catalyst impurities and amorphous carbons.

a)



b)



c)

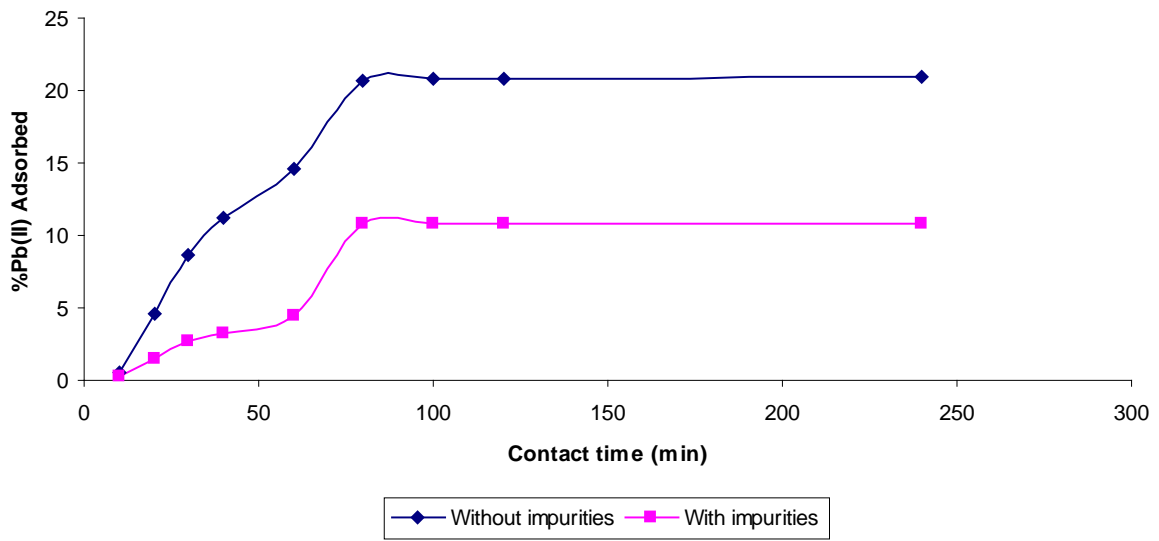
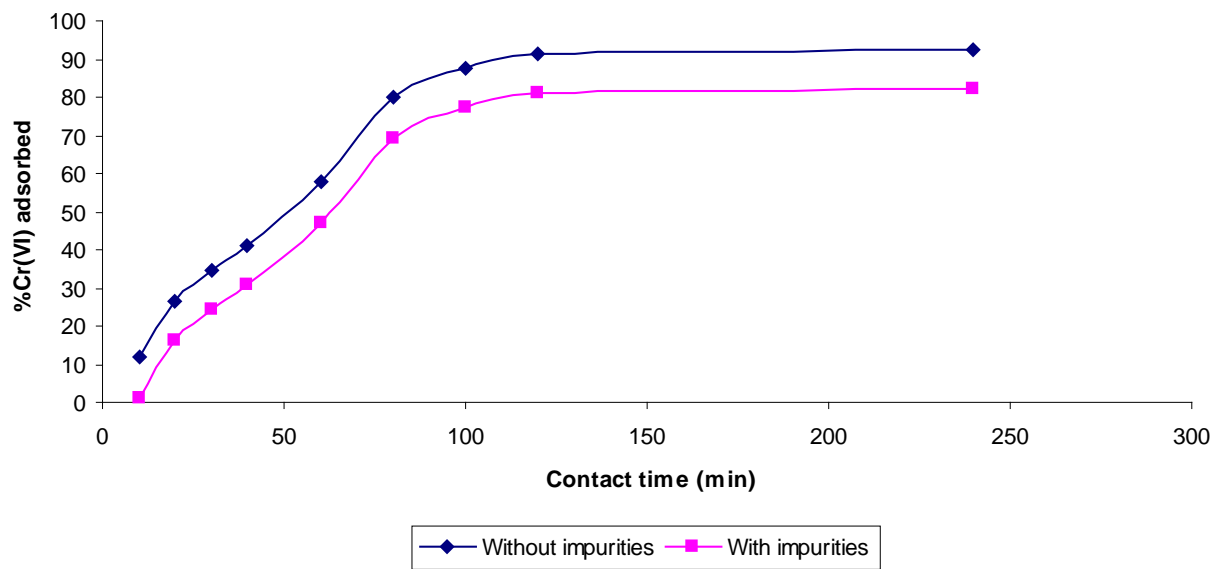


Figure 7-7: The effect of catalyst and amorphous carbon impurities on the uptake of a) Hg(II) b) Cd(II) and c) Pb(II) by pristine MWCNTs

a)



b)

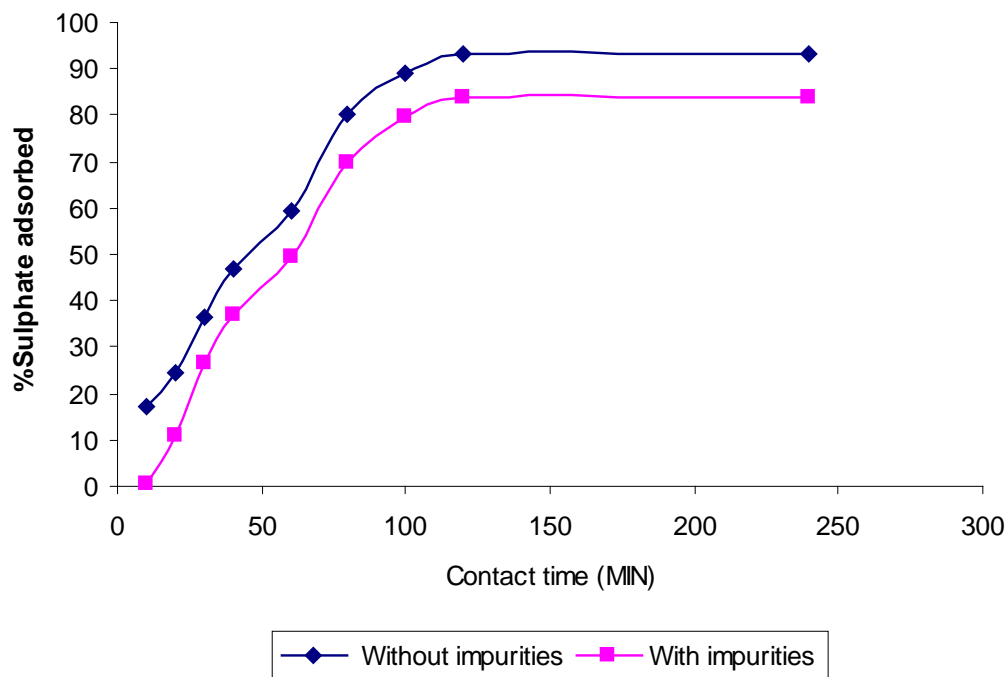


Figure 7-8: The effect of catalyst and amorphous carbon impurities on the uptake of a) $\text{Cr}_2\text{O}_7^{2-}$ and b) SO_4^{2-} by Pristine MWCNTs

These figures reveal that the uptake of both anions and cations is reduced by about 10% in the presence of impurities. According to the literature⁴⁴⁵ this could be due to an increase in the effective surface area where thermal annealing not only removes the impurities but also increases the effective surface area of the CNTs. This is verified by the results obtained from a BET analysis shown in **Table 7-8**

Table 7-8: BET Analysis of Pristine MWCNTs before and after Purification Treatment

Condition	Surface Area (m ² /g)	Average Pore Volume (cm ³)
Before thermal annealing	27,4	0,13
After thermal annealing	39,2	0,22

This data reveals that both the surface area and pore volume increased after purification thereby resulting not only in a larger surface for adsorption but also in large pores into which the anions and cations may be physisorbed. The increase in pore size after purification also suggests that impurities could be hindering the uptake of anions and cations by blocking or filling the pores (active adsorption sites).

7.4 Conclusion

The results presented in this chapter have revealed that the key surface properties which influence the uptake of anions and cations by MWCNTs and CSs include the presence of surface functional groups and in particular the types and forms of heteroatoms that are present and the point of zero charge which results from the introduction of these heteroatoms. The results have clearly shown that the introduction of oxygen-containing surface functional groups via acid/base treatment lowers the pH_{PZC} of the MWCNTs and CSs thereby favouring cation uptake by these materials. On the other hand, the introduction of nitrogen via treatment with aqueous ammonia or by nitrogen doping increases the pH_{pzc} thereby making these materials more suitable for anion uptake. Nitrogen doping in particular seems to enhance anion uptake via the introduction of positively charged nitrogen centres resulting from protonation of the nitrogen atoms during acid-treatment of the materials. This is confirmed by the predominant presence of quaternary nitrogen identified by XPS analysis.

The fact that heteroatoms play a key role in enhancing the uptake capacities is also supported by the observation that increasing concentrations of these heteroatoms enhance anion and cation uptake respectively.

The morphology of the carbon materials only appears to play a role in the unmodified form where unmodified CSs showed a better uptake capacity for cations than unmodified MWCNTs. However, when heteroatoms are introduced the adsorption capacity of the materials appears to be more dependent on the heteroatom content than on the morphology of the materials.

The presence of impurities on the MWCNTs also lowers the adsorption performance of these materials possibly by blocking pores (active adsorption sites) and reducing the effective surface area for adsorption. This is evident from the results which show that the presence of catalyst and amorphous carbon impurities on pristine MWCNTs reduces the uptake capacities for both anions and cations by 10% (**Figure 7-7 and 7-8**) and the BET results shown in **Table 7-8**.

Heat treatment of the nitrogen doped materials resulted in a higher point of zero charge which enhanced anion uptake by electrostatic attraction. The role played by nitrogen doping depends largely on the form in which nitrogen is present. In this case quaternary nitrogen was identified as the predominant form of nitrogen (positively charged centres) and this had a better impact on anion uptake.

As far as acid and base treatment are concerned MWCNTs treated with a strong acid mixture and MWCNTs treated with aqueous ammonia show a huge potential for cation and anion uptake respectively. In Chapter 8, the adsorption capacities of these materials are exploited to selectively extract oxyanions and oxycations from binary and ternary systems and the possibility of using these materials in trace analytical applications is also explored.

CHAPTER 8

SELECTIVE EXTRACTION AND DETERMINATION OF OXYANIONS AND OXYCATIONS BY ACID AND BASE TREATED MULTI-WALLED CARBON NANOTUBES

8.1 Introduction

Although MWCNTs have been previously used to determine the concentration of arsenates in water,⁴²⁶ studies in multi-component systems where competing oxyanions exist have been scarce. There are also to date no reports on the uptake of oxycations by MWCNTs both in single component and multi-component systems.

This chapter therefore focuses on using the adsorption capabilities of MWCNTs that have been treated with a strong acid mixture ($\text{HNO}_3/\text{H}_2\text{SO}_4$) and with the weak base (ammonia) for the selective solid phase extraction of oxyanions and oxycations from binary and ternary mixtures. The MWCNTs that were treated with a strong acid mixture and that demonstrated a high uptake capacity for cations as shown in Chapter 7, were used in the studies for the selective extraction of oxycations. On the other hand, the MWCNTs that were treated with the weak base (ammonia) demonstrated a high uptake capacity for anions and were therefore used in this study for the selective extraction of oxyanions. The model oxyanions used in this study were chromates (CrO_4^{2-}), arsenates (AsO_4^{3-}) and selenates (SeO_4^{2-}). The model oxycations used in this study were the vanadyl (VO_2^+) and the uranyl ions (UO_2^{2+}). The selection of these ions was based on their chemical similarities with respect to the sizes of the central atoms and the charges on the ions. Micro-column studies were conducted to establish the selectivity of MWCNTs for the oxyanions and oxycations. Lastly, the results from the solid phase extraction experiments were used to develop an off-line analytical method

for the sequential and selective determination of these oxyanions and oxycations from binary and ternary mixtures.

8.2 Materials and Methods

8.2.1 Chemicals

All chemicals used in this study were of analytical grade. The source of chromate ions was Na_2CrO_4 (Merck). Likewise, the sources of arsenate and selenate ions were $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Merck) and Na_2SeO_4 (Fluka), respectively. For the studies on oxycation uptake the sources of the uranyl and vanadyl ions were $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) and $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck), respectively. Stock solutions of 1000 ppm were prepared using deionised water and then diluted to 100 ppb for the micro-column studies.

8.2.2 Solid Phase Extractants

As outlined in the introduction to this chapter acid-treated MWCNTs were used as the solid phase extractants for the oxycation uptake and base-treated MWCNTs were used for the study on the uptake of oxyanions. The details of the preparation of these MWCNTs have already been described in Chapter 7.

8.2.3 Micro-column Studies and Column Preparation

A microcolumn was set up as described in Chapter 4 (see **Figure 4-2**). This involved a system in which the solutions were pumped (via a peristaltic pump) from a 200 mL glass vessel into a micro-column (60 mm long and 10 mm wide) pre-packed with the respective type of MWCNTs (ca. 2,00 g; packing density $3,3 \times 10^{-3} \text{ g mm}^{-3}$) and eluted with a suitable eluting agent for analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The micro-column was precleaned with 0,1 M HNO_3 and deionized water. pH Preconditioning of the column was conducted by washing the column with either 0,1 M HCl or 0,1 M NaOH. The column was also washed with deionised water before a new solution was pumped through to avoid contamination.

8.2.4 The Effect of Different Eluting Agents

A study on the effect of different eluting agents was conducted firstly by loading the column with the solutions of oxyanions and oxycations for a contact time of 240 min and then eluting them with different eluting agents. The different types of eluting agents used included 0,1 M of the following solutions: HCl, NaOH, $(\text{NH}_4)_2\text{CO}_3$, CH_3COOH and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and 100 mL of each eluting agent was used. The results from these experiments are presented in **Table 8-1**.

8.2.5 The Uptake of Oxyanions and Oxycations In Single Component Systems.

This investigation was conducted by pumping the chromate, arsenate, selenate, vanadyl and uranyl solutions in separate experiments through the microcolumn for contact times ranging from 10-240 min. After each contact time had expired, the solution was eluted and analysed by ICP-MS. The eluting solutions used were 0,1 M NaOH for the oxyanions and 0,1 M HCl for the oxycations. These results are reported in **Figures 8-2 and 8-6**.

8.2.6 The Uptake of Oxyanions and Oxycations in Binary Systems

8.2.6.1 The Uptake of Oxycations

A binary mixture of the oxycations was prepared by mixing 100 mL of 100 ppb uranyl and vanadyl solutions, and this solution was eluted through the column with 0,1 M HCl. The results from these studies are reported in **Figure 8-5**.

8.2.6.2 The Uptake of Oxyanions

This study was conducted in a similar manner to the oxycation study where a binary mixture of oxyanions was prepared and passed through the microcolumn. Since three oxyanions were studied in this instance, the following binary mixtures were prepared:

- i) 100 mL of 100 ppb CrO_4^{2-} and 100 mL of 100 ppb AsO_4^{3-}
- ii) 100 mL of 100 ppb CrO_4^{2-} and 100 mL of 100 ppb SeO_4^{2-}
- iii) 100 mL of 100 ppb SeO_4^{2-} and 100 mL of 100 ppb AsO_4^{3-}

Each binary mixture was eluted from the column using 0,1 M NaOH. The results from this study are reported in **Figure 8-3**.

8.2.7 The Uptake of Oxyanions from a Ternary System

These studies were conducted by preparing a mixture of three oxyanions and passing the solutions through the column for contact times ranging from 10-240 min and eluting after each contact time with 0,1 M NaOH. The ternary mixture was prepared by mixing 67 mL of 100 ppb chromate, arsenate and selenate solutions respectively to obtain a total volume of 200 mL. These results are shown in **Figure 8-4**.

8.2.8 Development of a Method for the Selective and Sequential extraction of the oxyanions by Solid Phase Extraction onto NH_3 -treated MWCNTs.

A method of quantitatively separating the arsenates, and chromates prior to adsorption of selenates onto the NH_3 -treated MWCNTs and quantitative determination of selenates by elution in 0,1 M NaOH was investigated. This method involved using the known chemical properties of arsenic and chromium to sequentially separate these from the ternary mixture.⁴⁸⁷

Arsenic is known to form stable complexes with Fe(III) polyions⁴⁸⁷ Therefore in this study, iron(III) perchlorate monohydrate (excess of a 0,1 M solution) was added to the ternary mixture to immobilise the arsenates and the pH was adjusted to approximately 4 using a 0,1 M HCl solution. Ferric arsenate is known to precipitate in the pH range of 2,5-6,2.⁴⁸⁷ This proved to be successful in the sense that a pale yellow precipitate, identified as FeAsO_4 as reported in the literature⁴⁸⁷ formed, and was removed by filtration. The filtrate was then pumped

through the micro-column for adsorption of the chromate and selenate ions. After approximately 240 min of contact time the column was pre-conditioned and eluted with 100 mL of 0,1 M HCl to release all chromates that were reduced to Cr(III) and the eluent was analysed for its chromium content using ICP-MS. The column was subsequently washed with deionised water to remove any excess acid and then eluted with 0,1 M NaOH to release the selenates. The eluant collected was analysed for selenates by ICP-MS. The FeAsO_4 precipitate was dissolved in a 0,1 M citric acid (100 mL) since citric acid is known to mobilise both Fe(III) and arsenates from the precipitate⁴⁸⁷. The solution was then pumped through the column. After 240 min of contact time, the column was eluted with 0,1 M NaOH to release the arsenates for analysis by ICP-MS. This methodology is summarised in **Figure 8-1** and the results for the determination of the oxyanions by ICP-MS shown in **Table 8-2**.

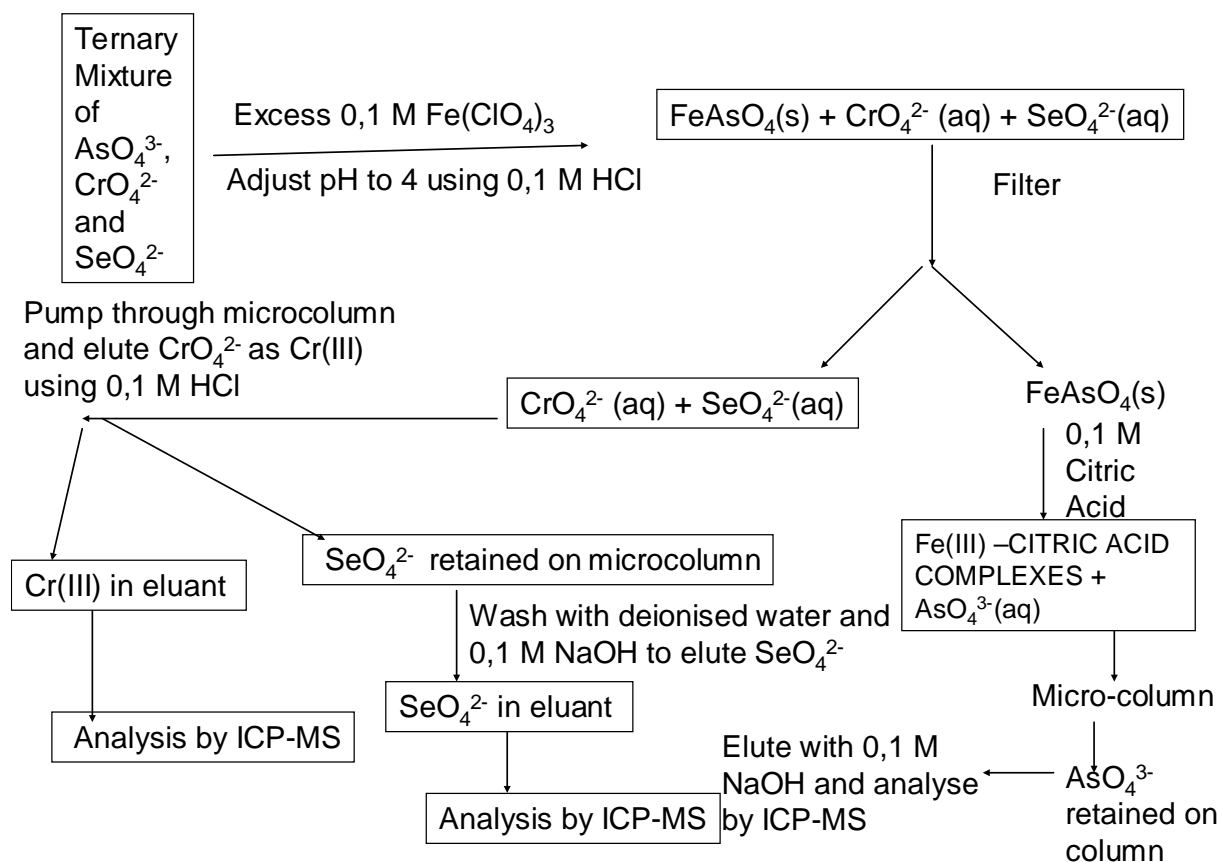


Figure 8-1: Experimental protocol followed for the sequential and selective extraction and determination of the oxyanions from a ternary system

8.2.9 Development of a Method for the Selective and Sequential Extraction of Uranyl and Vanadyl ions from a Binary Mixture using Acid-treated MWCNTs as the Solid-Phase Extractants

A method to separate a binary mixture of uranyl and vanadyl ions was developed to eliminate the effects of chemical affinity competition. This method involved adjusting the pH of the mixture to 8 using 0,1 M NaOH and then adding 100 mL of 0,1 M ammonium carbonate in an attempt to separate the uranyl ions from the vanadyl ions. The mixture was then passed through the column and eluted with 0,1 M ammonium carbonate. Thereafter, the column was eluted with 0,1 M HCl to extract any vanadyl ions that might have been retained. Both the ammonium carbonate and the HCl eluants were analysed for their uranium and vanadium

contents using ICP-MS. The results from the recoveries of these elements are presented in **Table 8-3**.

8.2.10 Analysis of Eluents

All the eluents from the microcolumn studies were analysed for their respective metal ion content by ICP-MS (Spectromass 2000). The software package used for the data analysis was Smart Analyzer supplied by Spectro. The instrument was calibrated using standards with concentrations of 5, 10, 20, 50 and 100 ppb respectively. The standards were prepared from a 1000 ppb stock solution. The details of each standard analytical procedure (optimised instrumental parameters) are provided in **Appendix 2**.

8.2.11 Quality Assurance and Validation of the Analytical Data

All microcolumn experiments were conducted in duplicate to ensure the reproducibility of the analytical data and an average of two results is reported. Any result which exceeded 5% relative error was discarded and not used in the interpretation of the results. Statistically, three replicate analyses were performed and the results were found to be reproducible within $\pm 2\%$. Statistical evaluations of the analytical data e.g. determination of the relative standard deviations were also conducted. The linear range (calibration) varied from 10-100 ppb and the correlation coefficient was found 0,9996. The detection limits of the three oxyanions were also calculated from three times the standard deviation (3σ) of the blank as 0,01 ppb, 0,04 ppb and 0,02 ppb for CrO_4^{2-} , AsO_4^{3-} and SeO_4^{2-} respectively. The relative standard deviations (RSD) were 2%, 4% and 1% for CrO_4^{2-} , AsO_4^{3-} and SeO_4^{2-} respectively.

The analytical results for the oxyanion determination were found to be reproducible within $\pm 1\%$. A correlation coefficient of 0.9999 was also observed for the linear calibration. The detection limits calculated at three times the standard deviation of blank was found to 0,05 ppb for UO_2^+ and 0,03 ppb for VO_2^+

respectively. Statistical analyses also revealed that the relative standard deviations (RSD) were 2% and 1% for uranyl and vanadyl respectively).

8.3 Results and Discussion

8.3.1 The Effect of Various Eluting agents

As described in Section 8.2.4, the micro-column was first loaded with each type of oxyanion and oxycation in separate experiments for a contact time of 240 min. Thereafter the column was eluted with different types of eluting agents in separate experiments.

Table 8-1 summarises the key results obtained by using various eluting agents for the oxyanions and oxycations respectively.

Table 8-1: The Effect of the Various Eluting agents on the Recoveries of the Oxyanions and Oxycations

Oxyanion or Oxycation	% Recovery				
	NaOH	HCl	CH ₃ COOH	(NH ₄) ₂ CO ₃	(NH ₄) ₂ C ₂ O ₄
CrO ₄ ²⁻	99.9	99.6	0.08	99.9	99.9
AsO ₄ ³⁻	99.9	0.03	0.05	99.9	99.9
SeO ₄ ²⁻	99.9	0.01	0.09	99.9	99.9
UO ₂ ²⁺	0.05	99.9	0.02	99.9	0.04
VO ₂ ⁺	0,01	99.9	0.09	0,02	0.01

These results show that all three oxyanions can be almost quantitatively eluted in 0,1 M NaOH. This is not surprising as the strong base acts as a source of hydroxyl ions which can out-compete the oxyanions for active sites on the NH₃-treated MWCNTs. As discussed in Chapter 7, the point of zero charge of the base-treated MWCNTs favours anion uptake so competing anions can displace the oxyanions from the adsorption sites on the MWCNTs. This observation also supports the data presented in Chapter 3 where it was shown that dichromate ions can be quantitatively desorbed from unfunctionalised MWCNTs using 0,1 M NaOH as the desorbent.

Conversely, the arsenate and selenate ions are not quantitatively eluted by 0,1 M HCl. This suggests that the chloride ions do not out-compete the oxyanions for active adsorption sites. The Eh-pH diagrams of arsenic and selenium also reveal that their respective oxyanions only become protonated at low pH. Thus, the protonated forms of these oxyanions which still carry a negative charge are retained on the base-treated MWCNTs which were shown to contain protonated nitrogen centres (Chapter 7).

However, the chromate ions behave differently from the arsenate and selenate ions when HCl is employed as the eluting agent. In this case, almost complete recovery of the chromate ions is observed. To understand this result the speciation of chromium needs to be considered. As noted in Chapters 3 and 7, chromium is predominantly present as Cr(III) at low pH even though protonated forms of the chromate ion can exist at low pH (See **Figure 2-1**). This is because Cr(VI) is reduced to Cr(III) at low pH. It is therefore postulated that the chromate ions are reduced to Cr(III) upon addition of the acidic eluting agent. The trivalent cation is unsuitable for retention by the MWCNTs which carry a positive surface charge and are thus eluted in the acidic medium. This postulate was verified by analysing the eluents for Cr(III) by UV-visible Spectroscopy (details of analysis provided in **Appendix 2**). The concentration of Cr(III) was measured as 99,49 ppb ($\pm 0,02$ ppb) which is actually a recovery of 99,49% Cr(III). There is thus a 0,09% difference between this concentration and that reported for total chromium

by ICP-MS. This verifies that most of the chromates had indeed been reduced to Cr(III).

By contrast, the elution of the oxyanions in the weak acid (CH_3COOH) is poor. The acetate ions are too large and bulky (4,16 angstroms) to present any chemical affinity competition for the retention of the oxyanions. CH_3COOH is also a weak acid and thus the concentration of these ions in solution was also low and therefore could not adequately present any chemical affinity competition. The charge on the acetate ion is also lower than those of the oxyanions. On the other hand, all three oxyanions readily elute in 0,1 M $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ respectively because the carbonate and oxalate ions can outcompete the oxyanions for active adsorption sites on the base-treated MWCNTs.

Thus the eluting agent which shows any selectivity for an oxyanion is HCl which selectively elutes the chromate ions by reduction of Cr(VI) to Cr(III) in acidic media.

The oxycations on the other hand do not successfully elute in 0,1 M NaOH. This suggests that the Na^+ ions do not outcompete the uranyl and vanadyl ions for active adsorption sites on the acid-treated MWCNTs which carry a negative surface charge as discussed in Chapter 7. However, the recovery of these oxycations in 0,1 M HCl is high due to competition between H^+ ions and these oxycations for active adsorption sites. By contrast, the percentage recoveries of both oxycations were much lower in 0,1 M CH_3COOH because this is a weak acid and does not generate enough H^+ ions to compete with the oxycations for active adsorption sites.

The eluting agent that shows selectivity for an oxycation is $(\text{NH}_4)_2\text{CO}_3$ which is able to elute the uranyl ion almost completely. This is because the uranyl ion is known to form stable complexes with carbonate ions.⁴⁸⁸ In alkaline media (pH 6-11) the complexes, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ predominate.⁴⁸⁸ The pH of the uranyl solution that was passed through the microcolumn was found to be 7,56. Thus, it is highly likely that these carbonate complexes form upon contact with the

ammonium carbonate solution thereby causing the uranyl ions to elute. These findings are also supported by a study which showed that U(VI) can be successfully eluted with an ammonium carbonate solution.⁴⁸⁹ Surprisingly though, the ammonium ions do not present any chemical affinity competition for the oxyanions.

8.3.2 Solid phase Extraction of Oxyanions in Single Component Systems

Figure 8-2 shows the results obtained when standard solutions (100 ppb) of the three oxyanions were passed through the micro-column as a single component system (ie. a solution containing only one oxyanion (ie. arsenates only, selenates only and chromates only). The MWCNTs used for this study were those that were treated with aqueous ammonia as described in Chapter 7.

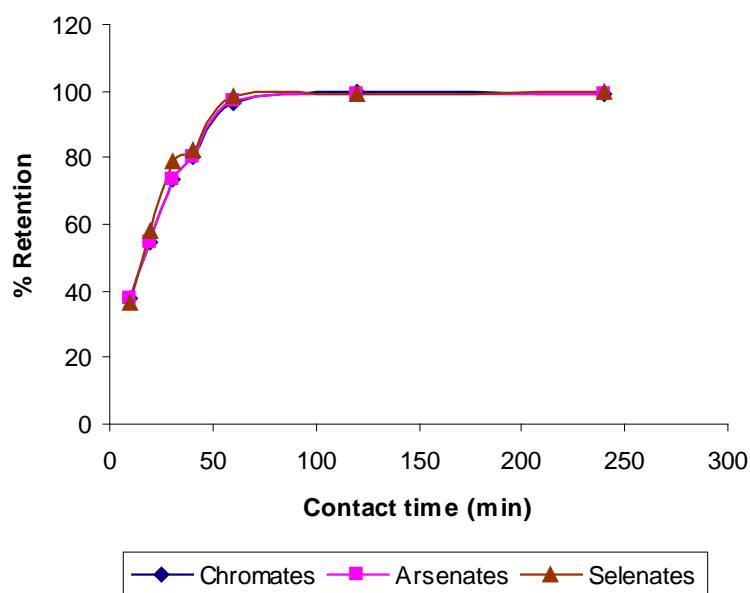


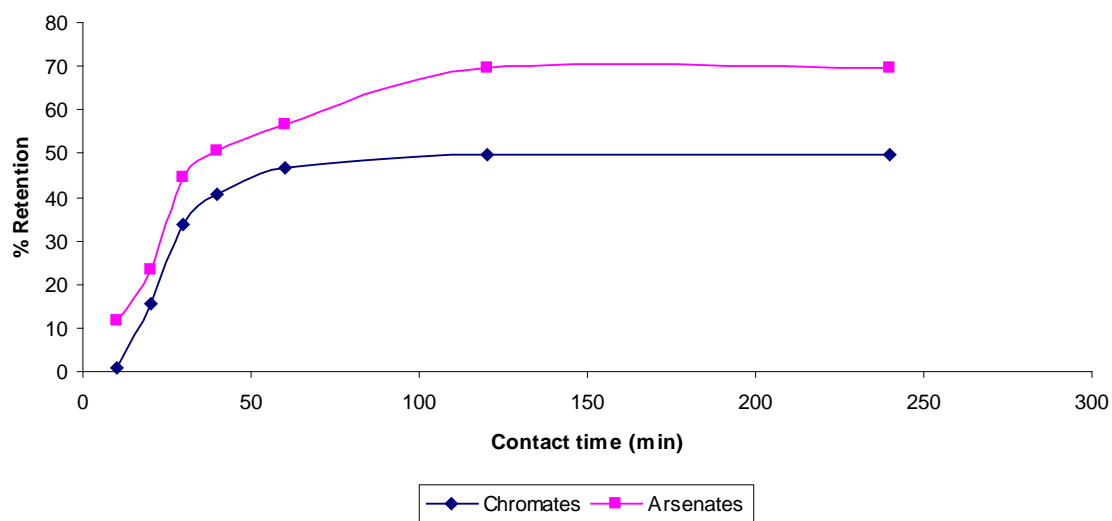
Figure 8-2: The uptake of chromates, arsenates and selenates in single – component systems

This figure reveals that the MWCNTs treated with the weak base NH_3 have an equal retention capacity for all three oxyanions in the single component systems and a complete removal of all three oxyanions is observed. This is consistent with the data presented in Chapter 7 where it was noted that these MWCNTs have a high point of zero charge (8,87) and therefore are favourable for anion uptake by electrostatic attractions.

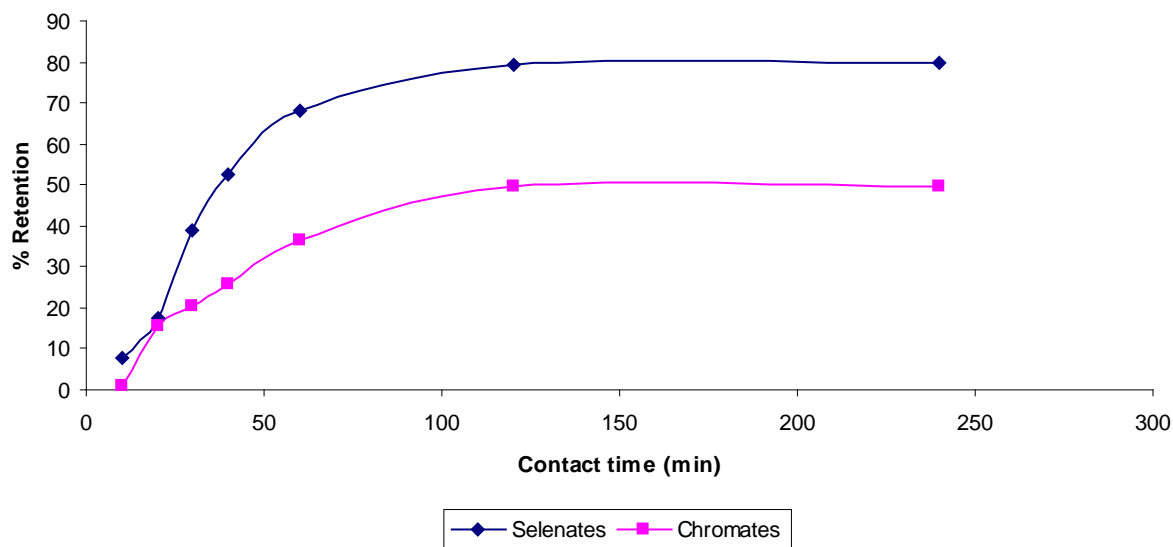
8.3.3 Solid phase Extraction of Oxyanions in Binary and Ternary Systems

Figure 8-3 reports the retention capacities of the base-treated MWCNTs for the respective oxyanions in each of the binary systems studied.

a)



b)



c)

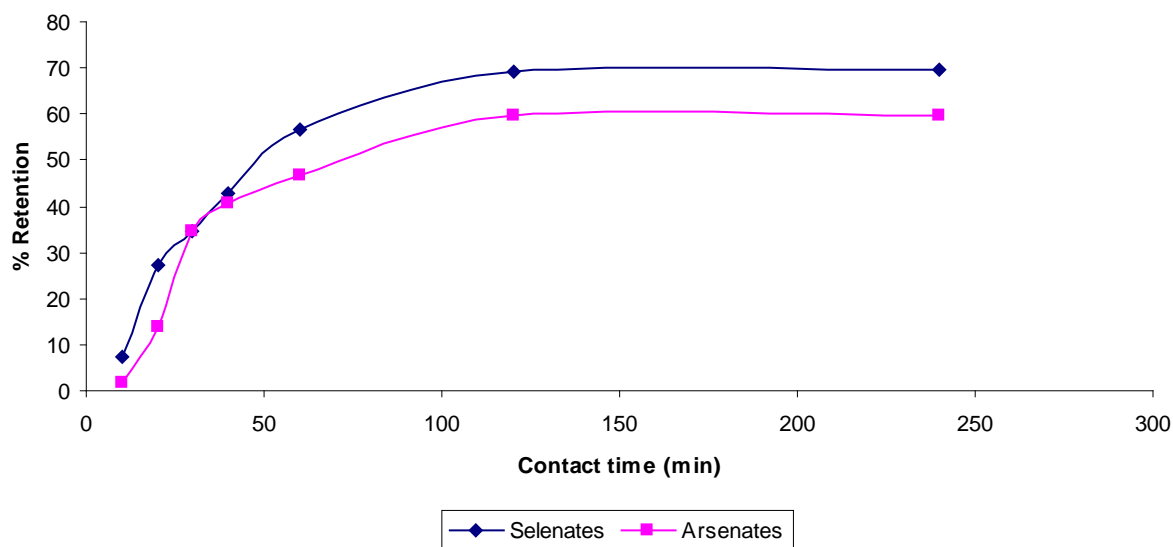


Figure 8-3: The retention capacities of oxyanions in binary systems containing a) arsenates and chromates b) selenates and chromates and c) selenates

The results show that the retention capacities for all oxyanions are below 100% in all binary systems because chemical affinity competition arises where the oxyanions compete for active adsorption sites on the MWCNTs. However, the

retention capacities for selenates are higher than those of arsenates and chromates. This is also supported by the results in **Figure 8-4** where it is again shown that the retention capacities of all oxyanions are reduced due to chemical affinity competition and the retention capacities for the selenates are superior. Clearly, the different chemical properties of the central atoms on the oxyanions are playing a role here. It is of interest to note that the order of chemical affinity is namely $\text{SeO}_4^{2-} > \text{AsO}_4^{3-} > \text{CrO}_4^{2-}$ corresponds to the order of covalent radii of the central atoms where Se has the smallest covalent radius (116 pm)⁴⁹⁰, chromium has the largest covalent radius (140 pm)¹ and the radius of arsenic is intermediate between that of selenium and chromium (120 pm)⁴⁹¹. If the covalent radius of oxygen (66 pm)⁴⁹² is considered this implies that the lengths of the Se-O, As-O and Cr-O bonds are 182 pm, 186 pm and 200 pm respectively. Thus, the chromate ion is the largest of the three oxyanions hence it is adsorbed to the least extent where size selectivity occurs. The arsenate ion is also slightly larger than the selenate ion which results lower retention of this ion.

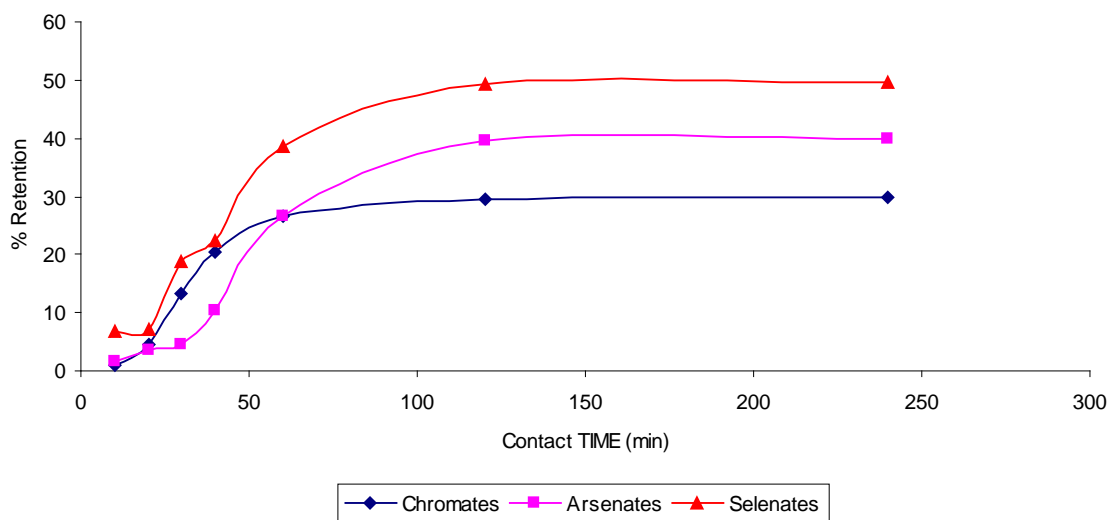


Figure 8-4: The uptake of chromates, arsenates and selenates in a ternary system

The chemical affinity competition is also supported by the data presented in Chapters 3 and 4 where it was shown that the retention of dichromates and chromates by unfunctionalised MWCNTs was hindered by the presence of competing anions. It is acknowledged that the reduced retention capacities could be due to the saturation of adsorption sites. However, this is not ideal for the quantitative determination of these oxyanions from ternary mixtures by solid phase extraction onto the MWCNTs. A way of sequentially separating these prior to analysis needs to be devised.

8.3.4 Development of a Proposed Method for the Selective and Sequential Extraction of the Oxyanions by Solid Phase Extraction onto NH₃-treated MWCNTs.

As described in **Figure 8-1** the chemical properties of arsenates and chromates were used to devise a method to sequentially extract and determine the concentrations of these oxyanions in ternary systems. Since arsenates are known to precipitate in the presence of Fe(III) in acidic media, the pH of the ternary mixture was adjusted to 4 and Fe(III) was added to precipitate all the arsenates as FeAsO₄. The precipitate was then filtered off and the mixture of selenates and arsenates was then pumped through the micro-column which was preconditioned with acid to reduce the chromates to Cr(III). This led to selective retention of the selenates which were eluted with 0,1 M NaOH and analysed by ICP-MS. The Cr(III) fraction was also analysed by ICP-MS and by UV-vis spectroscopy to verify the complete reduction of chromates to Cr(III). The arsenates were subsequently released from the FeAsO₄ precipitate by adding citric acid, pumped through the micro-column, eluted with NaOH and analysed by ICP-MS. These results are shown in **Table 8-2**.

Table 8-2: Results from the Selective Extraction and Determination of Oxyanions in a Ternary System

Oxyanion	Concentration added to ternary mixture (ppb)	Concentration found by ICP-MS after separation (ppb) (% Recovery)	Adsorption Condition	Eluant
CrO_4^{2-}	100	99,9	Not adsorbed –reduced to Cr(III) and eluted	0,1 M HCl
AsO_4^{3-}	100	99,7	Adsorbed after release from FeAsO_4	0,1 M NaOH
SeO_4^{2-}	100	99,8	Adsorbed onto microcolumn without any pre-treatment	0,1 M NaOH

The results in Table 8-2 reveal that almost quantitative recovery of all three oxyanions is achieved via the proposed extraction method. Thus, this method is effective at separating these oxyanions for quantitative determination by ICP-MS.

8.3.5 The Solid phase Extraction of Oxycations in Single Component Systems

Figure 8-5 shows the results obtained for the solid phase extraction of the uranyl and vanadyl ions from single component systems by MWCNTs treated with a strong acid mixture.

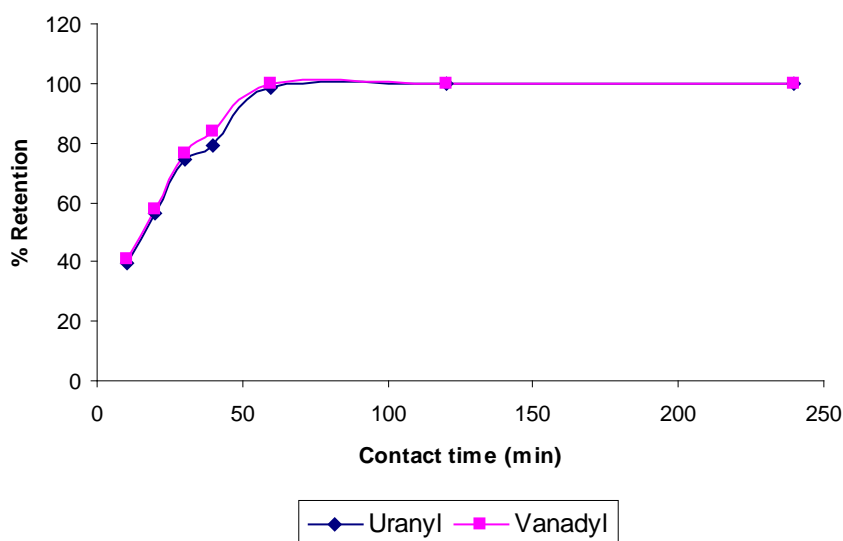


Figure 8-5: The retention of uranyl and vanadyl ions on acid-treated-MWCNTs in single component systems

This figure reveals that retention capacity of the acid-treated MWCNTs is good for both oxycations in single component systems where complete removal of both oxycations from aqueous solution is observed. This is in accordance with the observations made in Chapter 7 where it was noted that these MWCNTs have a low point of zero charge (2,89) and consequently are favourable for cation uptake by electrostatic attractions.

8.3.6 The Retention of Oxycations in Binary Systems

Figure 8-6 shows the results obtained when a binary mixture of uranyl and vanadyl ions was pumped through the microcolumn.

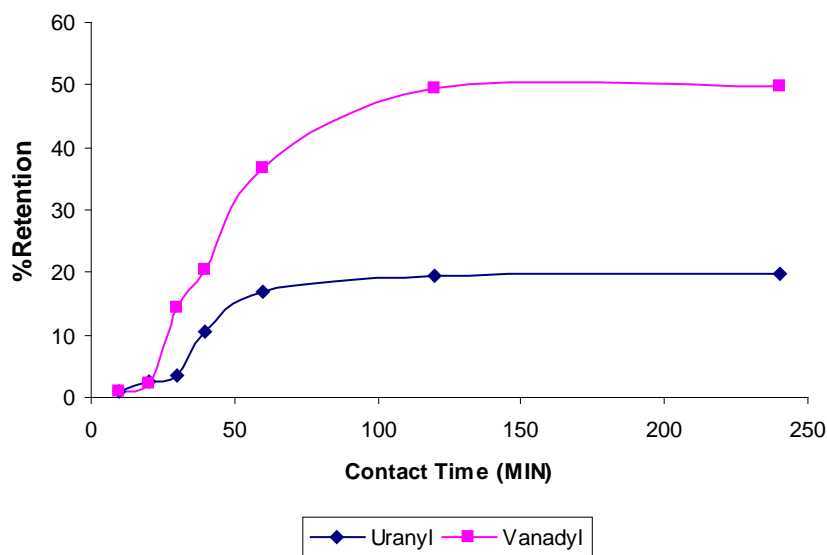


Figure 8-6: The retention of oxycations in a binary system.

This figure shows that the retention capacities for both oxycations is reduced in a binary system. This suggests that a chemical affinity competition between both oxycations for active adsorption sites is prevalent. The acid-treated MWCNTs also demonstrate a higher retention capacity for the vanadyl ion where the percentage retention is about 30% higher than that of the uranyl ions. This once again correlates with the different covalent radii of the central atoms where the covalent radius of uranium is 142 pm^{493} and that of vanadium is 125 pm^{494} . Again, if the covalent radius of oxygen (66 pm^{492}) is considered, the lengths of the U-O and V-O bond are 208 pm and 191 pm respectively. This implies that the vanadyl ion is slightly smaller than the uranyl ion which enables it to be more readily retained in a binary system where size selectivity occurs.

Pre-treatment of the mixture is essential for the quantitative determination of these oxycations in a binary mixture.

8.3.7 The Selective Extraction and Sequential Determination of Oxycations by ICP-MS

As indicated in Section 8.3.2, the selective extraction of the oxycations was achieved by treating the binary mixture with 0,1 M $(\text{NH}_4)_2\text{CO}_3$ so that the uranyl ions can form complexes with the carbonate ions and could be easily eluted and separated from the vanadyl ions. The vanadyl ions which were selectively retained on the microcolumn were then eluted from the microcolumn using 0,1 M HCl and the concentrations of both oxycations were determined using ICP-MS. These results are reported in **Table 8-3**.

Table 8-3: Results from the selective extraction and determination of oxycations in a binary system

Oxycation	Concentration added to the binary mixture (ppb)	Concentration determined by ICP-MS after selective extraction (%) (Recovery)	Adsorption Mechanism	Eluant
UO_2^{2+}	100	99,9	Not retained on Microcolumn – pre-treatment with ammonium carbonate for desorption	0,1 M $(\text{NH}_4)_2\text{CO}_3$
VO_2^{2+}	100	99,9	Selectively retained on column after pre-treatment with $(\text{NH}_4)_2\text{CO}_3$	0,1 M HCl

These results show that the selective extraction of the vanadyl ion can be achieved when the binary mixture is pretreated with ammonium carbonate in alkali medium. This is due to the formation of uranylcarbonate complexes which elute easily. The results also reveal that this extraction method is successful in terms of quantitative recovery of the oxycations.

8.4 Conclusion

The results presented in this chapter have revealed that NH_3 -treated MWCNTs and acid-treated MWCNTs are very effective for the removal of oxyanions and oxycations respectively from single component aqueous media by virtue of their high and low values for point of zero charge respectively. However, the selectivity for oxyanions and oxycations in binary and ternary systems is poor since chemical affinity competition sets in. Pre-treatment of binary and ternary mixtures are therefore essential to promote good recoveries of oxyanions and oxycations. For the oxyanions the order of chemical affinity competition was established as $\text{SeO}_4^{2-} > \text{AsO}_4^{3-} > \text{CrO}_4^{2-}$ for the oxyanions and as $\text{VO}_2^+ > \text{UO}_2^{2+}$ for the oxycations. This correlates well with the order of covalent radii of the central atoms of the oxyanions and oxycations. These trends imply that the smallest ions are retained more readily and size selectivity occurs.

Eluting agents which are species sensitive can also be used to promote selective retention. Acid and base-treated MWCNTs are therefore only effective in the trace analysis of complex mixtures of oxycations and oxyanions if the samples are pre-treated beforehand. More research on improving the selectivity of these materials for this purpose is therefore essential.

CHAPTER 9

CONCLUSION

9.1 Introduction

This chapter summarises the major findings of the study conducted. Much attention is paid to the extent to which the specific objectives of the study were achieved and the overall issue of whether MWCNTs can be utilised for the treatment of industrial effluents containing ions such as Cr(VI) and Hg are addressed. Other aspects of the study such as the effect of surface modified MWCNTs and the selectivities of these ions for metal ion uptake were discussed. The chapter concludes with some recommendations for further studies.

9.2 The Adsorption Performance of MWCNTs for ppb levels of Cr(VI) and Hg

This study clearly demonstrated that MWCNTs are very efficient at adsorbing trace (ppb levels) of Cr(VI) and Hg (both inorganic and organic forms) where an adsorption capacity of up to 100% has been observed. The specific type of MWCNTs used however depends on the type of metal ion under investigation. In this study it was noted that unfunctionalised MWCNTs worked best for the uptake of Cr(VI) which exists in the anionic form. The high pH_{pzc} of these MWCNTs clearly favour the uptake of the negatively charged chromium ions. Functionalised MWCNTs on the other hand are not as efficient due to electron rich atoms on the functional groups and a low pH_{pzc} which repels the negatively charged chromate and dichromate ions. Functionalised MWCNTs favour the uptake of Hg mainly due to a low pH_{pzc} and mercury's affinity for sulphur.

9.3 Comparison of the Adsorption Performances of MWCNTs and Activated Carbon

For the uptake of Cr(VI) the adsorption capacities of MWCNTs (both functionalised and unfunctionalised) was clearly superior to that of activated carbon (see Chapter 3). This could mainly be due to the known hygroscopic nature of activated carbon^{206,207} which poses problems for the adsorption of the hydrophilic substances like Cr(VI) and the low pH_{pzc} which do not favour the uptake of anions.

Care must however be exercised when comparing the adsorption capacities of MWCNTs and activated carbon for the uptake of mercury. Although both unmodified MWCNTs and S-MWCNTs show a superior adsorption capacity to unmodified activated carbon and S-AC respectively it must be borne in mind that the sulphur content of S-AC was lower than that S-MWCNTs (see Chapter 5). Thus, it can be argued that if the sulphur contents of these adsorbents were equal their adsorption capabilities would also be equal. The distinctive advantage that S-MWCNTs present over S-AC is greater selectivity for the uptake of mercury in the presence of SO_2 . In general, the adsorption performance of activated carbon is better for the uptake of mercury than for the uptake of Cr(VI) (Chapter 3). This is due mainly to the presence of $-OH$ (hydroxyl) binding sites for the chemisorption of mercury. Studies by other workers have also demonstrated high uptake capacities of activated carbon for mercury both when unmodified and functionalised with sulphur.¹⁴⁹

Based on the advantages that MWNCTs present over activated carbon (better adsorption capacities and greater selectivity for mercury uptake in the presence of SO_2) it is therefore concluded that these adsorbents could replace activated carbon for the uptake of Cr(VI) and Hg.

9.4 The Key Parameters influencing the uptake of Cr(VI) and Hg

Chapters 3 and 5 have demonstrated that two common key parameters are instrumental in influencing the uptake of Cr(VI) and Hg. The first of these is

contact time. For both the adsorptions of Cr(VI) and Hg it is seen that the uptake capacities increase with contact time due to a greater accessibility to the active adsorption sites but saturation eventually sets in due to the depletion of these adsorption sites.

The second key parameter that is common to both the uptake of Cr(VI) and Hg is the initial solution pH. This is definitely an important parameter since this also influences the speciation of the respective metal ions. In Chapter 3 it was noted that the uptake of Cr(VI) is higher at low pH than that at higher pH. At very low pH (< 3) Cr(III) predominates and it is the uptake of this form of chromium that was observed. The converse was noted for the uptake of mercury (Chapter 5) which increased with increasing pH. These observations were explained in terms of surface charge effects where H^+ ions predominate at low pH thereby favouring the uptake of anions (Cr(VI)) and OH^- ions predominate at high pH thereby favouring the uptake of cations (Hg^{2+} , CH_3Hg^+).

The point of zero charge (pH_{pzc}) of the adsorbents also influences the uptake of Cr(VI) and Hg as seen in Chapters 3 and 5. In general, it has been observed that adsorbents with a low pH_{pzc} which are negatively charged over a wide pH range favour the uptake of mercury cations and adsorbents with a high pH_{pzc} which are positively charged over a wide pH range favour the uptake of Cr(VI) which occurs in anionic form. These observations are consistent with that expected from theory and relate to electrostatic interactions between the charge of the adsorbent and the charge of the specific metal ion.

Another parameter that is influential in the uptake of Cr(VI) is the chemical affinity competition presented by other anions. Chapters 3 and 4 have presented results which clearly demonstrate that the uptake of Cr(VI) is hindered in the presence of competing anions such as chlorides, sulphates and sulphites and the selectivity of unfunctionalised MWCNTs for Cr(VI) removal improves in the absence of these competing anions. S-MWCNTs on the other hand are highly selective to the uptake of mercury even in the presence of other ions and pollutants like SO_2 (see Chapter 5 and 6).

The uptake of Hg by S-MWCNTs is also highly dependent on the sulphur content of the S-MWCNTs. Chapter 5 has presented results which show a linear increase in mercury uptake with increasing sulphur content.

9.5 The Mechanisms of Adsorption and Desorption

This study has revealed that the mechanism of adsorption by MWCNTs is highly dependent on the specific metal ion that is adsorbed. Although a number of mechanisms including a redox mechanism have been proposed for Cr(VI) removal in Chapter 3, the experimental evidence indicates that an ion-exchange mechanism predominates where Cr(VI) is physisorbed onto active adsorption sites on the MWCNTs and can be subsequently desorbed by introducing competing anions (like OH⁻ from base) which displace Cr(VI) from the adsorption sites.

The adsorption of Hg on the other hand proceeds via a chemisorption process. Experimental evidence (see Raman spectra in Chapter 5) for Hg-S (for adsorption by S-MWCNTs) and Hg-O (for adsorption by unmodified MWCNTs) bond formation have been presented in Chapter 5. However, while the Hg-O chemisorption is easily reversed by HCl addition, the reversibility of the Hg-S chemisorption is not easily achieved and is only possible if a desorbing agent with alternate sulphur centres like thiourea is used.

The fact that the adsorption processes can be reversed suggests that regeneration and reusability of the adsorbents is possible. The use of MWCNTs as adsorbents can therefore be cost-effective.

9.6 Adsorption Isotherm Models

Adsorption isotherm models have been applied to describe the equilibrium adsorption process (Chapters 3 and 5). The specific type of adsorption isotherm model which can be applied depends on the metal ion undergoing adsorption. The uptake of Cr(VI) obeyed both the Langmuir and Freundlich Isotherms. The

calculation of certain parameters from these isotherms revealed that the adsorption process is to some extent restricted by intraparticle diffusion.

The adsorption of mercury on the other hand obeyed the Freundlich Isotherm (Chapter 5) and the maximum adsorption capacity by S-MWCNTs was calculated as 72.83 μg per g S-MWCNTs from this isotherm.

9.7 The Practical Use of MWCNTs for the Industrial Scale Treatment of Industrial Effluents containing Cr(VI) and Hg.

Chapters 4 and 6 have presented detailed case studies in which the practical aspects of using MWCNTs for the treatment of industrial effluents containing Cr(VI) and mercury were investigated. These studies have revealed that MWCNTs can extract Cr(VI) and Hg from industrial effluents. However, the unfunctionalised MWCNTs used for Cr(VI) adsorption in Chapter 4 are not very selective to the uptake of Cr(VI) in the presence of competing anions namely sulphite ions and pre-treatment procedures involving the removal of these competing anions are therefore necessary. Adsorption of mercury by S-MWCNTs (Chapter 6) is highly selective even in the presence of chloride ions and no pre-treatment is required.

The results from the continuous flow studies have revealed that mixing the MWCNTs into a silicon carbide matrix and regenerating by desorption is a good industrial practice.

9.8 The Influence of Surface Modified MWCNTs and CSs

Chapter 7 presented some important results for the ability of surface modified MWCNTs and CSs to extract anions and cations from aqueous solution. Here it was noted that acid-treatment of MWCNTs particularly treatment in a strong acid mixture results in the introduction of oxygen-containing surface functional groups which lower the pH_{pzc} of the MWCNTs thereby making these materials more favourable for cation uptake by electrostatic attraction. On the other hand, the effect of base-treatment seems to depend largely on the type of base used and

type of functional groups introduced by this type of treatment. For instance it was shown in Chapter 7 that MWCNTs treated with the strong base KOH generated surfaces that contained hydroxyl groups and therefore had the same effect on cation uptake as the treatment with a strong acid mixture. Conversely, treatment with the weak base NH_3 resulted in nitrogen-containing functional groups (mainly quaternary nitrogen) which increased the pH_{pzc} thereby making the MWCNTs surface positively charged over a wider pH range and favoring the uptake of anions. Similar observations were made with nitrogen-doped materials (N-MWCNTs and N-CSs).

However, care must be exercised when drawing definite conclusions about the effect of nitrogen doping. This depends largely on the form in which nitrogen is present. In this case quaternary nitrogen atoms were predominantly present due to protonation of the nitrogen atoms by acid-treatment. It is acknowledged that different effects on anion and cation uptake could be observed if a different form of nitrogen (e.g. trivalent nitrogen which does not carry a positive charge) is present.⁴⁸⁶

Heat-treatment of nitrogen doped MWCNTs and CSs seems to improve the uptake capacities by increasing the pH_{pzc} . This increase in pH_{pzc} was accounted for in terms of removal of some oxygen-containing functional groups which lowered the point of zero charge (oxygen could not be detected by C,H,O,N analysis). The removal of catalyst and amorphous carbon impurities from pristine MWCNTs also results in better uptake capacities by increasing the surface area and pore volume of these materials.

9.9 The Selectivity of Carbon Nanomaterials for Metal Ion Uptake

The only study conducted thus far which demonstrated any selectivity of MWCNTs for a specific metal ion was the study on the uptake of Hg where it was noted that S-MWCNTs showed superior selectivity in the presence of other competing ions and even in the presence of SO_2 (see Chapters 5 and 6). However, in the case of the uptake of Cr(VI) and other competing anions and

oxy-anions the selectivity is poor due to chemical affinity competition (Chapters 3, 4 and 8). This was also evident in studies conducted on a binary mixture of oxycations (see Chapter 8). Thus, although carbon nanomaterials surpass other conventional adsorbents like activated carbon with their superior uptake capacities, these still need to achieve better selectivities for specific metal ions.

9.10 Recommendations for Further Studies

9.10.1 Further Studies on Nitrogen Doped Nanomaterials

Preliminary data has demonstrated that nanomaterials doped with nitrogen (mainly quaternary nitrogen) have good uptake capacities for anions due to a high pH_{pzc} . It has been noted that other forms of nitrogen could have different effects on anion and cation uptake. It is therefore proposed that further studies on nanomaterials which contain other forms of nitrogen (e.g. trivalent nitrogen) need to be undertaken. These may be extended to other types of nanomaterials e.g. nanorods and nanowires and the effect of introducing other heteroatoms such as boron may be investigated.

9.10.2 Selectivity Studies

This study has shown that MWCNTs demonstrate a poor selectivity for oxyanions and oxycations in binary and ternary mixtures even when competing anions are present. Although pre-treatment procedures which help to improve the selectivity have been proposed and developed in this study, more studies on improving the selectivity of these materials for specific metal ions are needed. This may include incorporating specific ligands into the MWCNTs for the selective uptake of a specific metal ion. As an example, the carbonate ions may be incorporated to selectively extract uranyl ions and Fe(III) can be introduced to selectively extract arsenate ions.

9.10.3 Studies on the Nanocomposites with Low Cost Adsorbents

Although this study has demonstrated that mixing the MWCNTs onto an inert support and desorption and reuse could be a cost-effective means of using MWCNTs on an industrial scale, studies on combining these and other nanomaterials with conventional low cost sorbents need to be initiated. A few studies of this nature have been discussed in Chapter 2. However, the effects of nanocomposites or nanopolymers formed with other low cost adsorbents such as chitosan and other biosorbents need to be explored.

APPENDIX 1

Supplementary Figures, Tables and Other Information

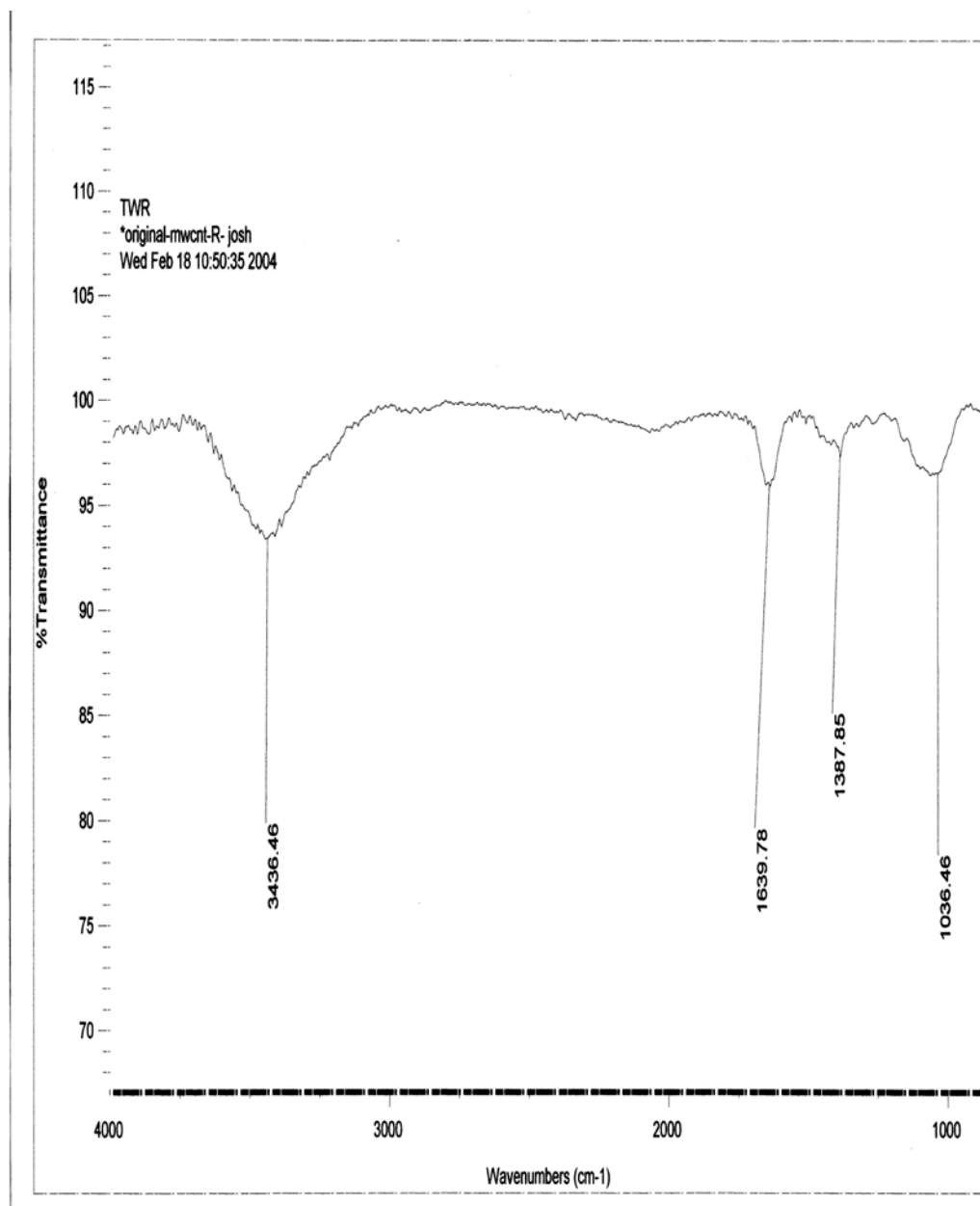


Figure A1: The IR spectrum of the functionalised MWCNTs

Table A1: A Summary of all the Physical Characteristics of the Silicon Carbide used in this Study

Form	Nanopowder
Particle Size	90-100 nm
Surface Area	70-90 m ² /g
Melting point	2700°C
Density	3.22 g/mL
Bulk Density	0.069 g/cm ³

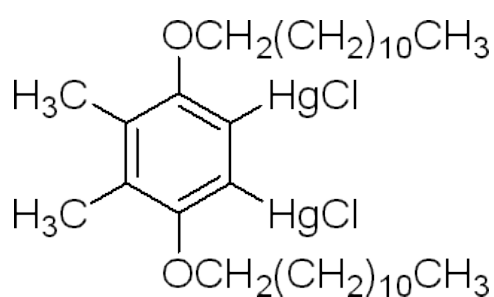


Figure A2: The structure of 3,6-didodecyloxy-4,5-dimethyl-o-phenylene-bis(mercury chloride (from: www.sigmaaldrich.com ⁴⁹⁵))

Table A2: BET Data for N-MWCNTs and N-CSs

TYPE OF NANOMATERIAL	SURFACE AREA (m²/g)	PORE VOLUME (cm³/g)	PORE SIZE (nm)
N-MWCNTs	24,7	0.0966	15,6
N-CSs	1,81	8,22 x 10 ⁻³	18,2

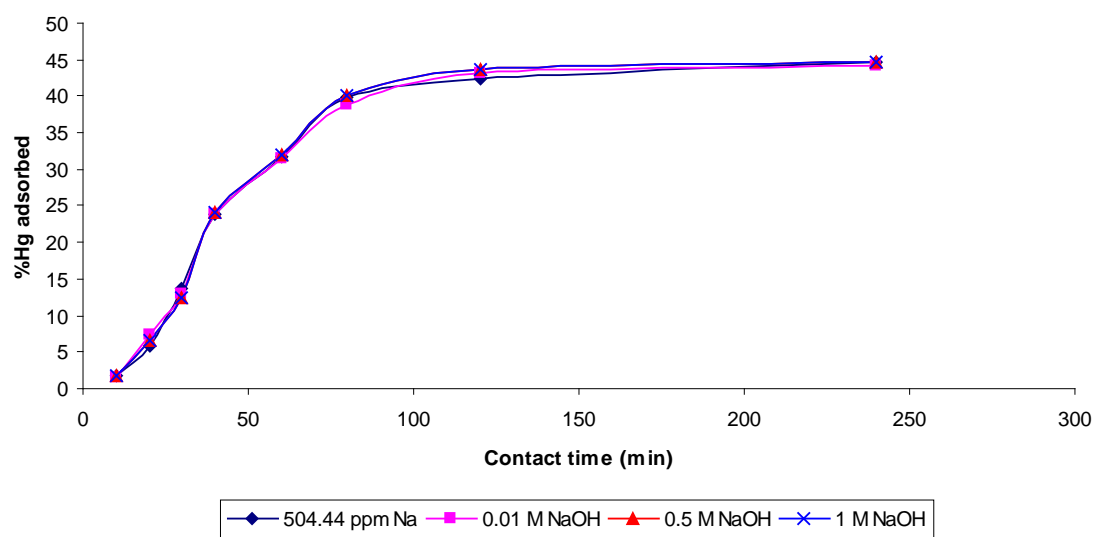


Figure A3: The effect of Na concentration on the uptake of Hg(II) by Unfunctionalised MWCNTs

APPENDIX 2

Details of Analytical Procedures

Optimised Parameters for ICP-MS determination of Hg in Chapter 5

RF power	1350 W
Nebulizer gas flow	1000 ml min ⁻¹
Coolant gas flow	3 scale units
Auxiliary gas flow	1 scale units
Pump speed	2
Nebulizer step	1
Default dwell time	1s
Sampler	Nickel
Skimmer	Nickel
p Interface	2.013 mbar
p Quadrupole	5.46 x 10 ⁻⁶ mbar
Detection mode	SEM
Data analysis	Smart analyzer software

Optimised Instrumental Parameters for Chromium, Arsenic and Selenium Determination by ICP-MS in Chapter 8 from Mulugeta et. al.⁴⁹⁶

RF power	1000 W
Nebulizer gas flow (Ar)	850 -1000 mL min ⁻¹ (optimized daily)
Auxillary flow rate (Ar)	1,0 L min ⁻¹
Plasma flow rate (Ar)	15 L min ⁻¹
Sample uptake rate	1,0 mL min ⁻¹

Data acquisition parameters:

Data Acquisition Mode	Signal versus Intensity
Dwell time per unit	10 ms
Sweeps per reading	1
Estimated replicate time	40 ms
Number of Replicates	2
Isotopes Monitored	As(75), Cr(52), Se(82)
Detection mode	SEM
Data analysis	Smart analyzer software

**Optimised Instrumental Parameters for Vanadium Determination by ICP-MS
in Chapter 8 from Nonose et. al.⁴⁹⁷**

RF power	1100 W
Nebulizer gas flow (Ar)	960 mL min ⁻¹
Auxillary flow rate (Ar)	1,5 L min ⁻¹
Plasma flow rate (Ar)	15 L min ⁻¹

Data acquisition parameters:

Data Acquisition Mode	Signal versus Intensity
Dwell time per unit	40 ms
Sweeps per reading	3
Detector dead time	40 ns
Settling time	0,2 ms
Accumulation	1,50 times
Detection mode	SEM
Data analysis	Smart analyzer software

Optimised Instrumental Parameters for Uranium Determination by ICP-MS in Chapter 8 adapted from Rozmaric et. al.⁴⁹⁸

RF power	1200 W
Nebulizer gas flow (Ar)	1004 mL min ⁻¹
Auxillary flow rate (Ar)	1,5 L min ⁻¹
Plasma flow rate (Ar)	15,5 L min ⁻¹

Data acquisition parameters:

Data Acquisition Mode	Signal versus Intensity
Dwell time per unit	40 ms
Sweeps per reading	3
Sample uptake	1mL min ⁻¹
Resolution	300
Detection mode	SEM
Data analysis	Smart analyzer software

Determination of Cr(III) by UV-visible Spectroscopy (used in Chapters 7 and 8)

The Cr(III) concentration was determined by UV visible spectroscopy according to a method developed by Kumar and Muthuselvi.⁴⁹⁹ This method involved using 2-nitrobenzaldiminoglycine (HBIG) as the complexing agent. This reagent was prepared according to the method described by Kumar and Muthuselvi.⁴⁹⁹ Typically 2 mL of sample solution were added to 2 mL HBIG prior to measurement on a Varian Cary UV-visible spectrophotometer at 565 nm against a reagent blank. The instrument was also calibrated using standard solutions of CrCl₃ ranging from 10-100 ppm (Chapter 7) and 10-100 ppb (Chapter 8) respectively.

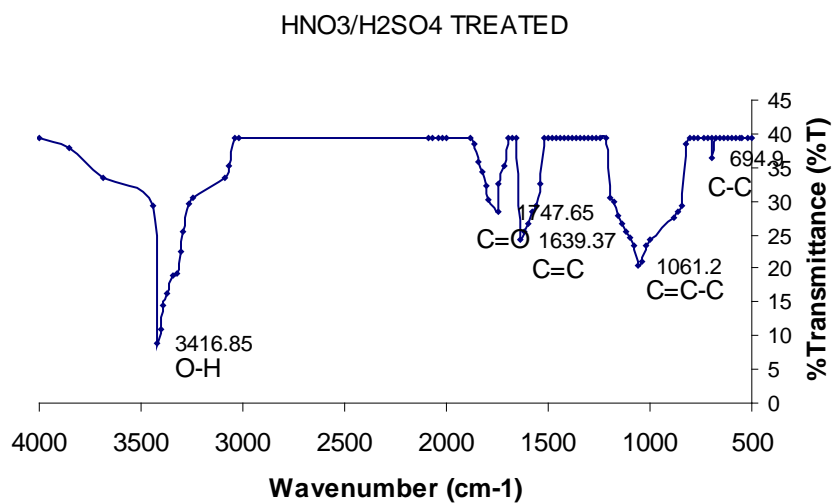
Determination of Sulphates (SO_4^{2-}) by UV-visible Spectroscopy (Chapter 7)

This involved a turbidimetric method whereby 2 mL sample was added 5 mL of 0,1 M CH_3COOH solution. Excess barium chloride was then added to this solution to precipitate all the sulphate in the sample as BaSO_4 . The sulphate concentration was subsequently measured on a Perkin-Elmer UV-visible spectrophotometer (Turbidometer) at 420 nm. To eliminate interferences from other ions in solution, the precipitate was first separated by filtration. The instrument was again calibrated with standard sulphate suspensions with sulphate concentrations ranging from 10 -100 ppm. Reagent blanks were also used.

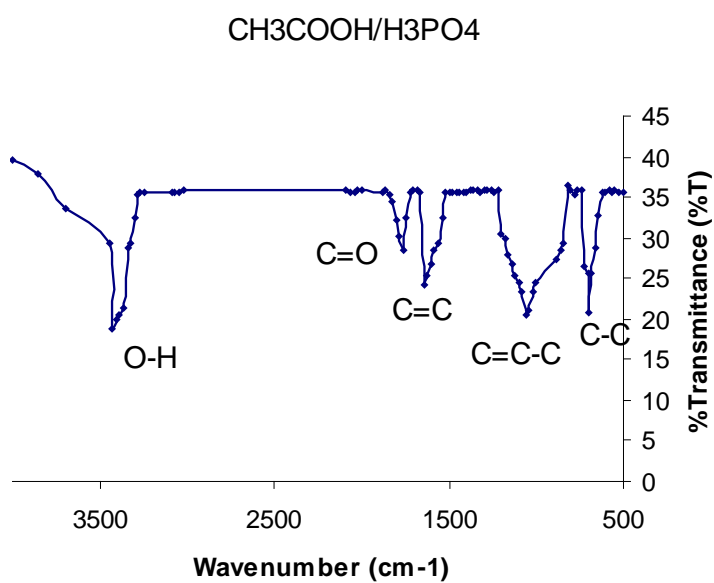
APPENDIX 3

Additional Spectra

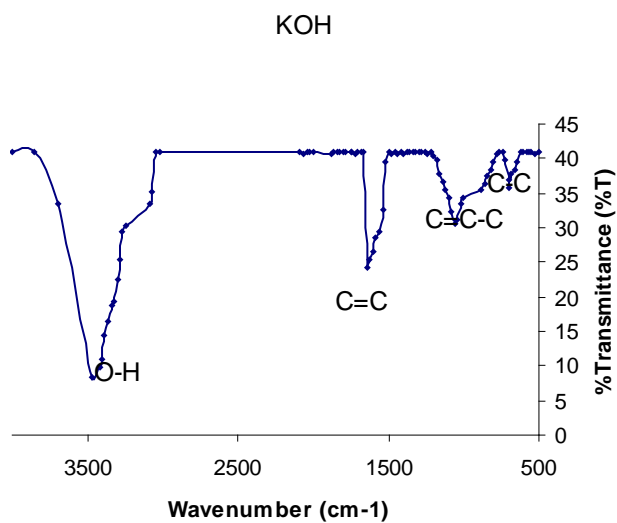
a)



b)



c)



d)

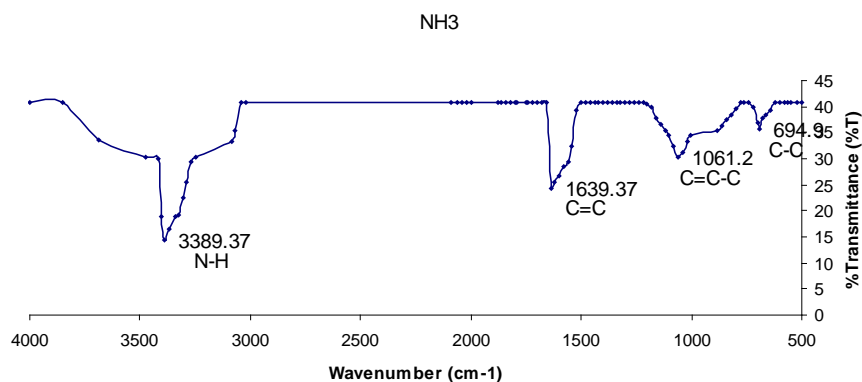


Figure A4: FTIR Spectra of a) HNO₃-H₂SO₄ b) CH₃COOH-H₃PO₄ c)KOH and d) NH₃-treated MWCNTs

Further details (parameters) of XPS analysis

X-ray source: Al K α (1486.6 eV)

X-ray power: 20W

Beam diameter: 100 μ m

Band pass: 117,4 eV for wide and 29,4 eV for narrow

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