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Phosphorylated multiwalled carbon nanotube-cyclodextrin polymer: Synthesis, characterisation and potential application in water purification

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ABSTRACT

Multiwalled carbon nanotubes were synthesised by the nebulised spray pyrolysis method and purified to remove amorphous carbon and fullerenes. The purified multiwalled carbon nanotubes were oxidised using a 3:1 H_2SO_4/HNO_3 mixture to introduce carboxylic groups and to a smaller extent hydroxyl groups on the walls of the carbon nanotubes. Subsequently, the oxidised carbon nanotubes were chlorinated using oxalyl chloride to generate acyl chloride groups through which phosphorylation took place. 4-Aminophenyl methylphosphonate was attached to the multiwalled carbon nanotubes *via* an amidation reaction. FT-IR and XPS confirmed the presence of P═O, P—O and P—C—P functional groups in the phosphorylated carbon nanotubes. Polymerisation of the phosphorylated carbon nanotubes with cyclodextrins was achieved using hexamethylene diisocyanate as a bifunctional linker. Surface morphology of the polymer was investigated by SEM while FT-IR was used to confirm the polymerisation reaction. Moreover, the thermal stability of the polymer was probed using TGA while BET was employed to determine the surface area and pore volume of the polymer. Furthermore, the polymer was tested for the removal of cobalt and 4-chlorophenol from synthetic aqueous solutions of the pollutants. The polymer displayed potential as an adsorbent for both cobalt and 4-chlorophenol.

1. Introduction

Cyclodextrin (CD) technology has attracted numerous interests from various industrial sectors. These include pharmaceutical, food processing, cosmetics, agricultural, chemical, adhesives and coatings and polymer industries (Martin Del Valle, 2004). Extensive work has been done in our laboratory on the synthesis and application of CD based polymers in water purification (Mamba et al., 2007; Mhlanga, Mamba, Krause, & Malefetse, 2007; Nxumalo, 2007). However, CDs are soluble in water; therefore they need to be made insoluble before application in water purification. This problem has been eradicated by polymerising CDs with compounds that alter their solubility in water. Diisocyanates such as hexamethylene diisocyanate (HMDI) and toluene diisocyanate (TDI) are the most prominently used in order to form highly cross-linked CD nanoporous polymers which are water insoluble (Ma & Li, 1999, 2000). Excess of the diisocyanate relative to the CD (8:1) is usually added to ensure maximum cross-linking of the polymer.

Oxidised MWCNTs though being a new class of adsorbents have demonstrated good adsorption capacity for various heavy metals and other inorganic pollutants as well as some organic pollutants from water (Li et al., 2003; Long & Yang, 2001; Lu, Chung, & Chang, 2005; Rao, Lu, & Su, 2007). In our previous work CDs were copolymerised with oxidised multiwalled carbon nanotubes (MWCNTs) and the resultant polymer (MWCNT-CD) was evaluated for the removal of lead and cobalt from synthetic aqueous solutions of the metal ions. The MWCNT-CD polymer was found to perform better at low concentration (10 ppm) beyond which its absorption efficiency drops drastically. Moreover, the MWCNT-CD polymer showed better absorption for lead than cobalt, under competitive conditions (Mamba, Mbianda, Govender, Mamba, & Krause, 2010). In the present work, oxidised MWCNTs were modified with an amino-phosphonate and an amino-alcohol concomitantly to yield phosphorylated MWCNTs (pMWCNTs). The pMWCNTs were polymerised with CDs using HMDI as a linker. Addition of the amino-alcohol on the MWCNTs provided possible sites whereby polymerisation and cross-linking took place. Phosphonates have a rich history as effective chelating agents for di and trivalent cations from aqueous media (Gumienna-Kontecka et al., 2002; Nowack, 2003; Regel-Rosocka, Rozenblat, Nowaczyk, & Wisniewski, 2005). Consequently, the incorporation of pMWCNTs into the polymer is anticipated not only to give it, improved structural integrity and thermal stability but also, a dual function for removing both organic and inorganic pollutants.

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The polymer was tested in order to evaluate its ability to remove 4-chlorophenol (4-CP) and cobalt from contaminated water solutions. Phenol and its derivatives are documented to have devastating health effects to humans even at low concentrations (Kuleyin, 2007; Rawajfih & Nsour, 2006). Cobalt has also been linked to various harmful health effects to humans when it accumulates above certain concentrations. Moreover both 4-CP and cobalt have also been labelled as potential carcinogens (De Boeck, Kirsch-Volders, & Lison, 2003; Rawajfih & Nsour, 2006). The ability of the polymer to quantitatively remove 4-CP and cobalt as a function of initial metal concentration and contact time was investigated.

2. Experimental

All chemicals and reagents used in this study were of high purity and were used without further purification. All solvents were dried and distilled according to standard procedures and were stored under anhydrous conditions (Armarego & Perrin, 2002). Reactions were carried out in an inert atmosphere with either argon or nitrogen gas.

2.1. Preparation of adsorbent

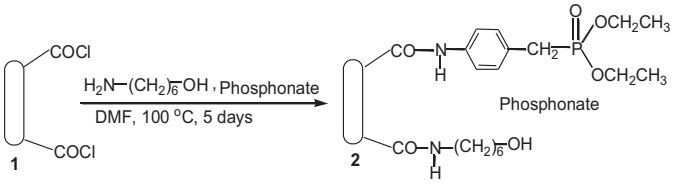
2.1.1. Synthesis, purification and functionalisation of MWCNTs

MWCNTs were synthesised in our laboratory from a solution of ferrocene (2.0 g) in toluene (50 mL), using the nebulised spray pyrolysis method as described in the literature (Salipira, Mamba, Krause, Malefetse, & Durbach, 2008; Vivekchand, Cele, Deepack, Raju, & Govindaraj, 2004). The produced MWCNTs were then purified by removing amorphous carbon and fullerenes. Purified MWCNTs were oxidised using a 3:1 H_2SO_4:HNO_3 mixture. The oxidised MWCNTs were filtered and washed until a neutral pH was achieved and then dried in an oven to remove the water.

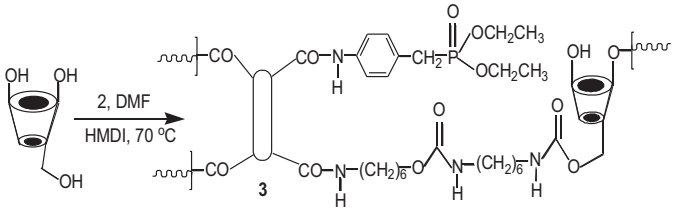
The oxidised MWCNTs were chlorinated and subsequently phosphorylated *via* an amidation reaction as described in the literature (Ndzimandze, 2006; Shen, Huang, Wu, Hu, & Ye, 2007), with some modifications. Typically oxidised MWCNTs (0.8 g) were sonicated in DMF (50 mL) and chlorinated using excess of oxalyl chloride at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and at room temperature for another 2 h. The temperature was raised to 70 °C and the reaction stirred overnight to remove the excess oxalyl chloride. This was followed by the simultaneous addition of 4-Aminophenyl methylphosphonate (8 g, 0.038 mol) in 10 mL DMF and 6-Amino-hexanol (2 g, 0.017 mol) in 5 ml DMF using dropping funnels. The amino alcohol was introduced to provide possible sites whereby polymerisation of the cyclodextrin and the pMWCNTs would take place. The mixture was stirred at 100 °C for 5 days. Finally, the product (pMWCNTs (**2**)) was filtered, washed with portions of ethanol and DMF and dried in an oven for 24 h at 80 °C. The phosphorylation of the acyl chlorinated MWCNTs (**1**) was anticipated to proceed as illustrated in Scheme 1.

2.1.2. Polymerisation of 2 with cyclodextrins

A literature procedure was adopted for the polymerisation reaction (Salipira, Krause, Mamba, et al., 2008). Typically, β-CD solution (8 g in DMF 50 mL) was polymerised with **2** (0.4 g) previously



Scheme 1. Concomitant phosphorylation and hydroxylation of acylated MWCNTs.



Scheme 2. Polymerisation of 2 and CDs.

sonicated in DMF (10 mL) under argon at 70 °C. HMDI (8 mL) was added dropwise with stirring. The reaction was complete after 24 h and the polymer (pMWCNT-CD (**3**)) was precipitated in acetone, filtered, washed and dried in an oven at 80 °C for 24 h. This gave a 5% MWCNT-CD polymer in terms of the mass of **2** relative to the mass of the CDs. The percentage of the **2** relative to the mass of CDs was kept at 5% which is the maximum percentage composition that has been used in the literature (Salipira, Krause, Mamba, et al., 2008). The polymerisation reaction was anticipated to proceed as depicted in Scheme 2.

2.2. Adsorption experiments

Stock solutions (1000 ppm) of Co^{2+} and 4-CP were prepared by dissolving $Co(NO_3)_2{\cdot}6H_2O$ (4.938 g) and 4-CP (1.0 g) respectively, in 100 mL of deionised water in 1 L volumetric flasks. The flasks were then made up to the mark using deionised water. From each of the stock solutions, 2.5, 5, 7.5, 10 and 12.5 mL was pipetted into 250 mL volumetric flasks then diluted to the mark to make solutions of 10, 20, 30, 40 and 50 ppm of Co^{2+} and 4-CP. In all the adsorption experiments 0.05 g of the adsorbent and 30 mL of the pollutant solution was used. The adsorption of 4-CP and Co^{2+} ions as affected by the initial pollutant concentration and contact time was investigated. The adsorption experiments were all done at room temperature with the pH of the pollutant solutions kept between values 5 and 6. This was the pH range of the drinking tap water.

2.3. Analytical instruments

An FT-IR spectrometer (MIDAC, model 400) was used to confirm the polymerisation reaction and functionalisation of the MWCNTs. Furthermore XPS (Physical Electronics, Quantum 2000 XPS) was used to investigate the functional groups present in the pMWCNTs and to determine the degree of phosphorylation of the MWCNTs. To investigate the purity and surface morphologies of the adsorbent a scanning electron microscope (JEOL, model 5600 SEM) was used. The surface area of the adsorbent was determined by an automated gas adsorption analyser (TriStar, model 3000). The concentrations of Co^{2+} and 4-CP were determined after adsorption using an atomic absorption spectrometer (Varian AAS, model SpectrAA 200) and UV–vis spectrophotometer (Shimadzu 2450 UV-Visible Spectrophotometer), respectively. The thermal stability of the polymer was probed using a PerkinElmer, TGA 4000 Thermogravimetric Analyser.

3. Results and discussion

3.1. Characterisation of unfunctionalised and functionalised MWCNTs

The SEM image of unfunctionalised MWCNTs is shown in Fig. 1(A) and it illustrates relatively clean and well graphitised MWCNTs. Moreover, the unfunctionalised MWCNTs were in the form of bundles consisting of numerous individual strands of MWCNTs. However, after oxidation Fig. 1(B) the MWCNTs lost

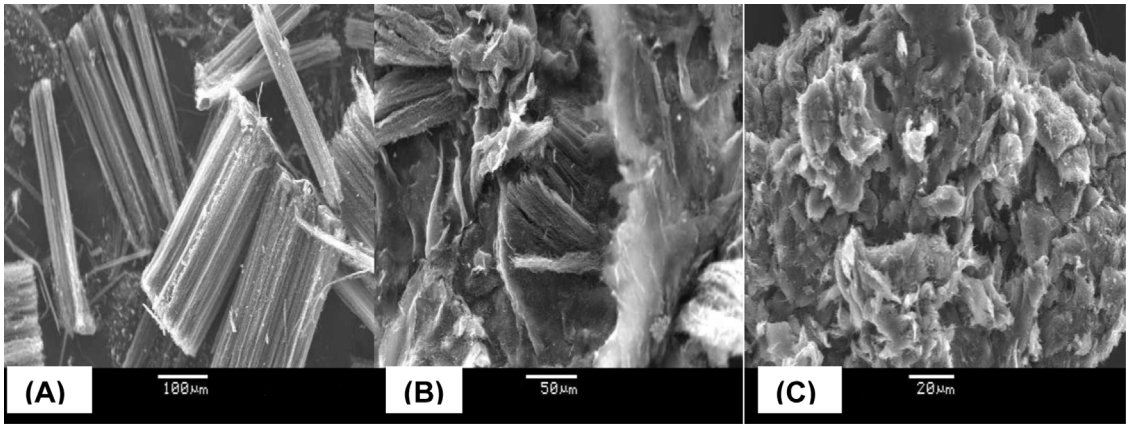


Fig. 1. SEM images of (A) pristine MWCNTs (B) oxidised MWCNTs and (C) pMWCNTs.

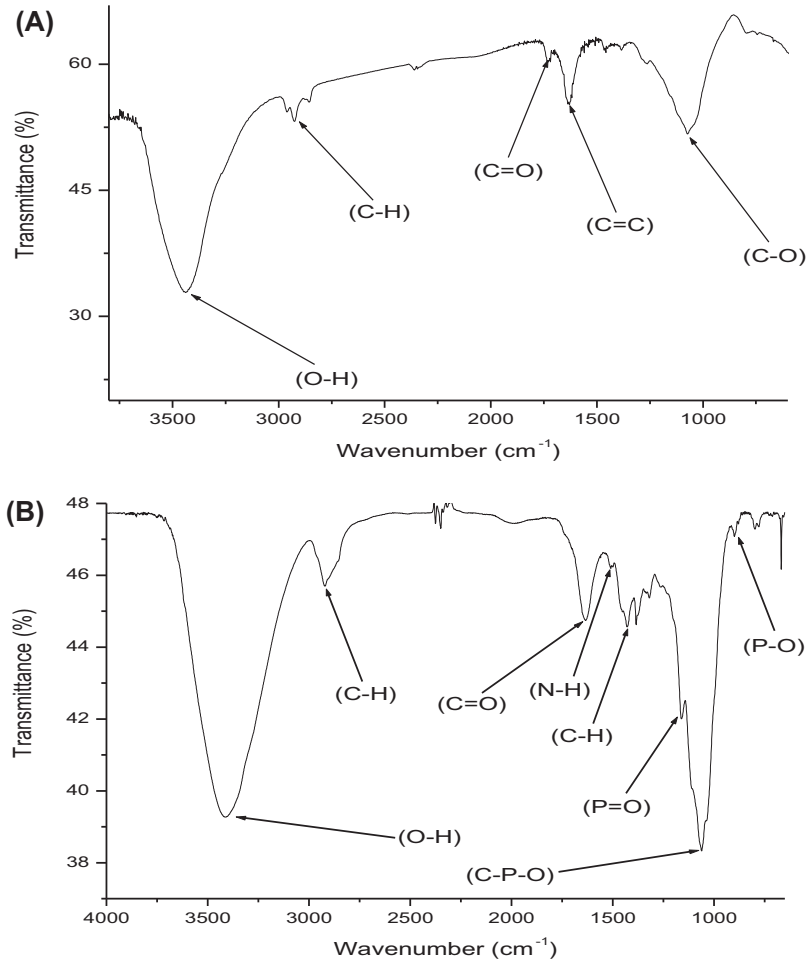


Fig. 2. FT-IR spectrum of (A) oxidised MWCNTs and (B) pMWCNTs.

their well aligned structure and displayed a distorted orientation with no definite pattern. This observation was also made for the pMWCNTs (Fig. 1(C)) which displayed more distortion compared to the oxidised MWCNTs. In comparison to the unfunctionalised MWCNTs, the SEM images of the oxidised and phosphorylated MWCNTs suggested that surface modifications have taken place.

FT-IR spectrum of unfunctionalised MWCNTs did not show any distinctive functional groups. The spectrum of the oxidised MWCNTs (Fig. 2(A)) showed the emergence of C=O (1724 cm^{-1}) and C—O (1062 cm^{-1}) groups, as a result of oxidation (Silverstein, Webster, & Kiemle, 2005). After phosphorylation (Fig. 2(B)), functional groups such as P=O (1183 cm^{-1}), C—P—O (1037 cm^{-1}) and P—O (915 cm^{-1}) emerged suggesting the presence of phosphonate functions on the pMWCNTs (Danilich, Burton, & Marchant, 1995). Furthermore, the peak at 1645 cm^{-1} is due to the C=O stretching vibrations of amides while the peak at 1509 cm^{-1} may be assigned to N—H bending vibrations of amides, suggesting the formation of an amide bond between the acylated MWCNTs and the amino-phosphonate. Additionally, the C—H bending vibration observed at 1426 cm^{-1}

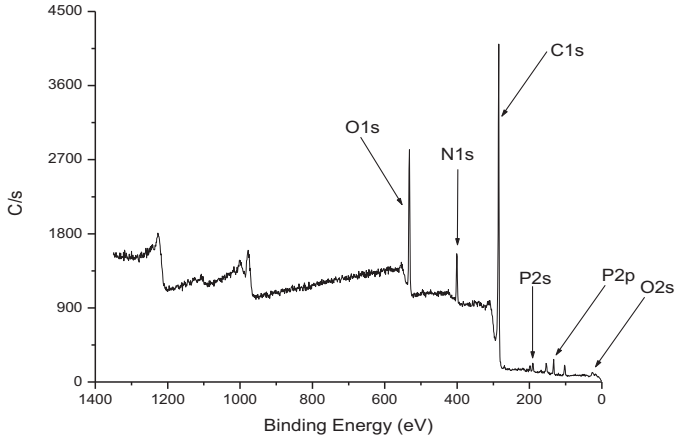


Fig. 3. XPS spectrum of pMWCNTs.

Table 1
XPS elemental analysis of pMWCNTs.

Element	Atomic concentration (%)	Binding energy (eV)	Probable compound/bonds
C	73.6	284.9 (79%)	C—C
		286.6 (16%)	C—O
		288.0 (3%)	C=O
		289.1 (2%)	O—C=O
Cl	0.4	–	–
N	7.4	400.5	N—(C,H,O)
O	15.6	532.1	O—(C,H), oxides
P	1.4	133.2	P—(C,H,O)
Si	1.7	102.7	SiO_2

suggests the presence of CH_2—O groups which could be from the amino-alcohol or the phosphonate functions.

An overview investigation of the XPS spectrum (Fig. 3) of the pMWCNTs reveals the presence of peaks due to carbon, oxygen, phosphorus and nitrogen.

Further analysis of the individual peaks by high resolution XPS showed that the C1s (Table 1) peak constituted 73.6% of the sample and the carbon atom comes from four different bonds. The main carbon peak was observed at 284.9 eV which is attributed to C—C bond from the carbon nanotube skeleton as well as the alkyl chain of the amino-alcohol. Moreover, peaks at 286.6 eV (C—O), 288.0 eV (C=O) and O—C=O (289.1 eV) were observed which can be attributed to the presence of carbonyl and carboxylic functional groups, probably from the oxidation of the MWCNTs (Datsyuk et al., 2008). A trace amount of chloride ions (0.4%) was detected by XPS which could probably originate from the chlorination of the MWCNTs *via* the OH groups which might have been introduced during oxidation of the MWCNTs. These chloride ions may not be substituted during the amidation reaction due to their poor reactivity compared to the acyl chloride.

The N1s peak is observed at 400.5 eV (7.4%), due to N—(C,H,O) and this could be from the amide functions through which phosphorylation and introduction of the amino-alcohol onto the MWCNTs, took place. A peak at 532.1 eV (15.6%) was observed and is due to O—(C,H) bonds which may have originated from carbonyl and alcoholic functions on the pMWCNTs (Datsyuk et al., 2008). The peak could also result from C—O—P groups from the phosphonate functions (Puziy, Poddubnaya, Socha, Gurgul, & Wisniewski, 2008). The peak at 133.2 eV (1.4%) may be due to phosphorus from P—(C,H,O) of the phosphonate groups on the pMWCNTs (Puziy et al., 2008). The presence of these functional groups confirms the successful incorporation of the phosphonate functions onto the MWCNTs. Silicon was also detected and it may originate from the silicon vacuum grease that was used for lubricating some of the reaction apparatus and glassware.

3.2. Characterisation of pMWCNT-CD polymer

Physically the polymer appears to be grey to pale black in colour and displayed a combination of a granular and powdery appearance. From the SEM image of the pMWCNT-CD polymer, Fig. 4(A), the polymer appears like an aggregation of numerous granular particles which have rough, irregular surfaces. At higher magnification, Fig. 4(B), the polymer displayed a woven or cotton-like structure with some spaces in between. This observation correlates well with the architecture of the MWCNT-CD polymers reported in the literature (Salipira, Krause, Mamba, et al., 2008).

FT-IR was used to monitor the progress of the reaction to ascertain its completeness. The disappearance of the isocyanate peak (Fig. 5) indicates the completeness of the reaction since it is believed that the isocyanate groups are involved during polymerisation. The FT-IR spectrum of the pMWCNT-CD polymer (Fig. 5) shows a peak at 3324 cm^{-1} which may be assigned to an N—H stretching vibration of a secondary amide peaks corresponding to amide functions, suggesting that polymerisation of the pMWCNTs and cyclodextrins did take place. This N—H may originate from the amidation of the acylated MWCNTs. The two peaks observed at 2966 cm^{-1} and 2860 cm^{-1} may be assigned to the asymmetric and symmetric C—H stretches in CH_2 which is bonded to oxygen.

The electronegativity of oxygen results in a shift of the absorption of the C—H to higher wavenumbers compared to C—H from alkane chains. These peaks indicate the presence of O—CH_2 bonds

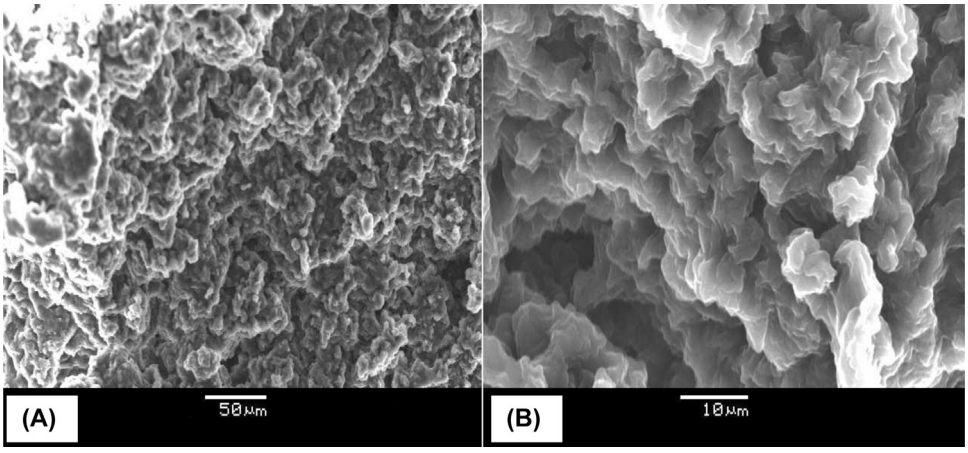


Fig. 4. SEM images of pMWCNT-CD polymer.

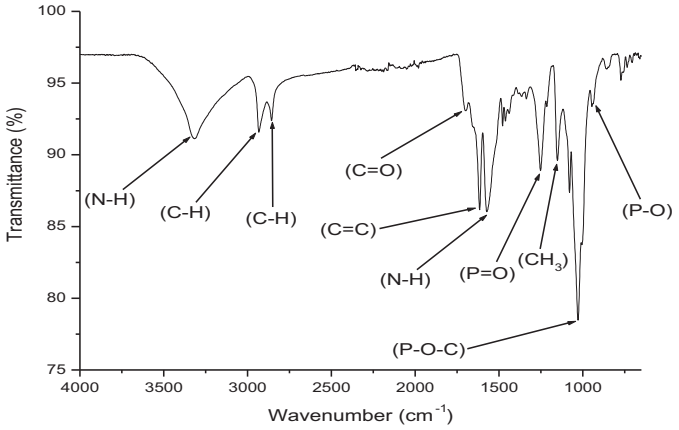


Fig. 5. FT-IR spectrum of pMWCNT-CD polymer.

in the polymer which may originate from the phosphonate groups. A carbonyl (C═O) stretch from an amide group is observed at 1705 cm^{-1}. The C═C stretch of the benzyl group is observed at 1614 cm^{-1}. The peak at 1562 cm^{-1} can be assigned to the N—H bending vibrations of secondary acyclic amides (Silverstein et al., 2005). Peaks at 1265 cm^{-1} and 1032 cm^{-1} which are assigned to P═O and P—O—C stretching vibrations, respectively, were observed and indicated the presence of phosphonate groups in the polymer. Moreover, the P—O peak is observed at 940 cm^{-1} originating from the phosphonate functions (Danilich et al., 1995).

Furthermore a peak at 1162 cm^{-1} which can be assigned to CH_3 in P—OC_2H_5, was observed further confirming the presence of the phosphonate groups in the polymer and suggesting that polymerisation of the pMWCNTs with the CDs did take place.

The surface area of the polymer from BET measurements was found to be 8.17 m^2/g with a pore volume of 0.03 cm^3/g. The polymer displayed a very small surface area compared to the pristine and functionalised MWCNTs but its surface area is comparable to that of the MWCNT-CD polymer (Mamba et al., 2010). The polymer's thermal stability was probed using TGA. Fig. 6(A) and (B) shows the TGA plot of the pMWCNT-CD polymer and its derivative, respectively.

The weight loss that occurred slightly below 100 °C may be attributed to the loss of moisture and solvents that may have been incorporated in the polymer. Temperatures in the range of 100–300 °C showed the decomposition of functional groups such as hydroxyl, carbonyl and amide groups taking place. In the range of 300–400 °C the decomposition of the CD skeleton was observed. Furthermore it has been reported that the decomposition of the organic parts of the phosphonate groups may start taking place at temperatures around 300 °C (Curic, Tusek-Bozic, & Traldi, 1998). The last decomposition step above 400 °C may be assigned to the decomposition of the carbon nanotube skeleton. From 500 °C and above a very slow rate of decomposition was observed resulting in a residual percentage weight of around 13%. This could be attributed to the formation of a stable metal phosphate (probably iron (III) phosphate, with residual iron from ferrocene used in the preparation of MWCNTs) which decomposes at higher temperatures (Chaplains, Bideau, Leclercq, & Viox, 2003).

3.3. Adsorption experiments

The amount of each of the pollutant species adsorbed was calculated using the following equation:

$$\%\ \text{pollutant adsorbed} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_0 and C_t is the initial pollutant concentration (mg/L) and the pollutant concentration after a specific time interval, respectively.

The percentage 4-CP/Co^{2+} adsorbed decreased as the initial pollutant concentration increased from 10 to 50 ppm (Fig. 7(A)). This may be attributed to saturation of the adsorption sites by the adsorbate species as the concentration increases since the amount of adsorbent used stays the same as the concentration increases. Pillay, Cukrowska, and Coville (2009) observed that the percentage of chromium ions adsorbed decreased steadily as the concentration increased from 100 to 300 ppb. Similarly, Kuleyin (2007) reported an increasing adsorption capacity of surfactant-modified natural zeolites for phenol as the initial concentration increased. However, the percentage removal of phenol decreased as the phenol concentration increased.

From Fig. 7(A), the polymer attained maximum percentage removal of 87.0% and 67.7% for 4-CP and Co^{2+}, respectively. As the concentration increased from 10 to 50 ppm the percentage removal dropped steadily with the lowest percentage removal observed at 50 ppm. A similar adsorption pattern is reported in the literature (Banat, Al-Bashir, Al-asheh, & Hayajneh, 2000; Kuleyin, 2007; Mamba et al., 2010). Adsorption of the pollutant species seem to be more effective at low concentrations probably due to the availability of free adsorption sites which quickly adsorb the small amounts of adsorbate species at low concentration. However, as the concentration increases they become saturated. Consequently, the highest percentage removal of the adsorbate species is attained at lower concentrations.

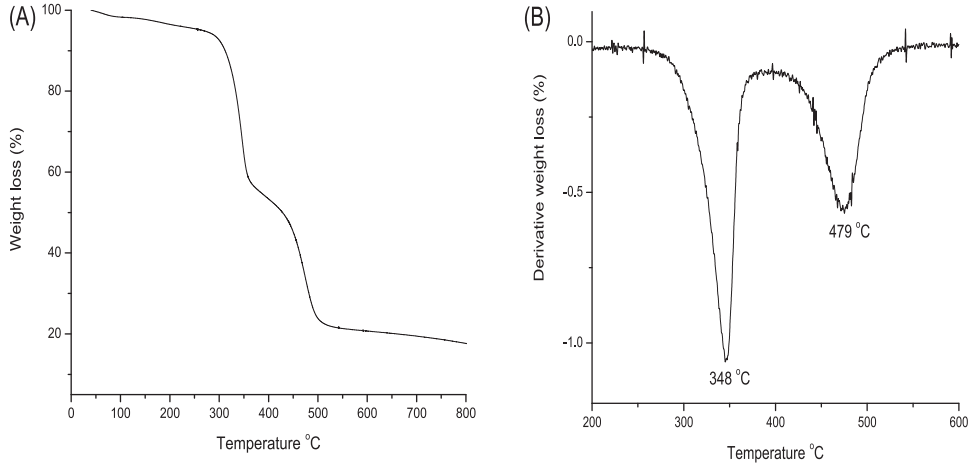


Fig. 6. TGA (A) plot and (B) derivative plot of the pMWCNT-CD polymer.

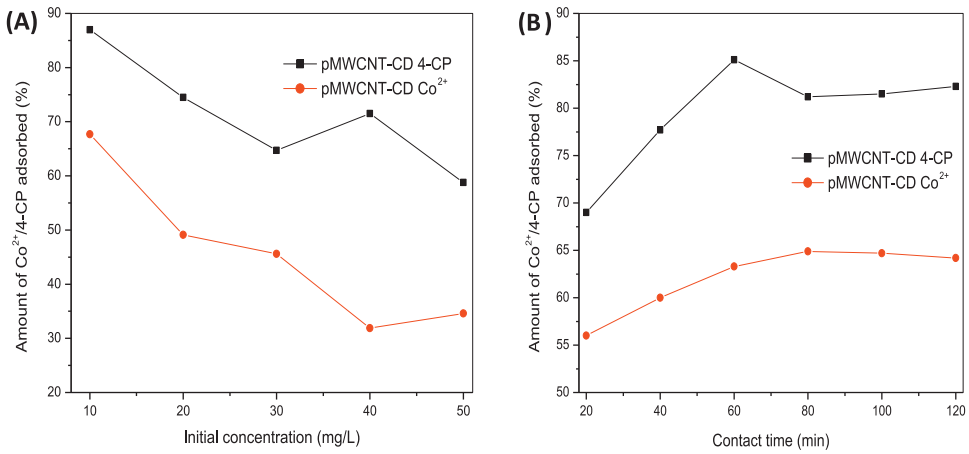


Fig. 7. Effect of initial concentration on the adsorption of 4-CP and Co^{2+} ions from single pollutant solutions.

The pMWCNT-CD polymer displayed a slightly better adsorption for Co^{2+} (67.7%) when compared to the MWCNT-CD polymer (64.8%) previously reported (Mamba et al., 2010). The improvement in the adsorption capability of the pMWCNT-CD polymer for Co^{2+} ions compared to the MWCNT-CD polymer may be attributed to the availability of more active adsorption sites in the former as a result of the phosphonate functions incorporated.

As a factor of contact time of the adsorbent and adsorbate species (Fig. 7(B)) the percentage removal of both pollutants was found to increase slightly as the time increased until it reaches maximum beyond which no further increase was recorded. This adsorption behaviour may be attributed to the fact that initially all the adsorption sites are free for adsorption but as the contact time increases, they are filled up with adsorbate species until equilibrium is reached. Beyond this point, increasing the contact time will not result to an increase in the percentage removal of the metal ions as the adsorption sites have been saturated. The polymer reached a maximum percentage removal of 85.1% after 60 min and 64.9% after 80 min for 4-CP and Co^{2+}, respectively. The time taken by the polymer to reach the maximum adsorption is considerably short which may be an indication that the polymer is an effective adsorbent for the pollutants (Li et al., 2002).

3.3.1. Isotherm models

Adsorption of the two pollutants by the polymer was studied using the Langmuir and Freundlich isotherm models to determine the model that best explains the adsorption mechanism of the pollutants by the polymer. The following linearised Langmuir (2) and Freundlich (3) equations, respectively, were used:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (2)$$

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

where C_e is the metal concentration at equilibrium (mg/L); q_m is the maximum sorption capacity (mg/g); K_L is the Langmuir sorption constant (L/mg). K_F and n are Freundlich constants related to the sorption capacity of the adsorbent and sorption energy, respectively.

The Langmuir and Freundlich parameters were calculated and presented in Table 2. As calculated from the Langmuir model the polymer was found to have a maximum sorption capacity (q_m) of 22.27 mg/g and 8.22 mg/g for 4-CP and Co^{2+} ions respectively.

From the Freundlich model the K_f value for the adsorption of 4-CP was higher than that for the adsorption of Co^{2+} implying a better adsorption capacity of the polymer for 4-CP than Co^{2+}. Moreover, the values for n were in the range of 2–10 which is an indication of good adsorption of the pollutants (Jiang, Pang, & Liao, 2009). Based on the R^2 values it was observed that the adsorption of Co^{2+} by the polymer correlates well with the Langmuir model while adsorption of 4-CP can be better explained by the Freundlich model.

Table 2
Calculated Langmuir and Freundlich parameters for the adsorption of 4-CP and Co^{2+}.

	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	r^2	n	K_f (mg/g)	r^2
pMWCNT-CD-4-CP	22.27	0.164	0.944	2.16	0.441	0.969
pMWCNT-CD-Co^{2+}	8.22	0.163	0.961	2.40	0.222	0.946

4. Conclusion

A phosphonate functionalised MWCNT-CD polymer was successfully fabricated and confirmed by the appearance of the P═O, P—O and P—C—O groups in the FT-IR spectrum. Physically the polymer was grey and displayed a combination of a granular and powdery appearance. The SEM images showed that the polymer had a spongy architecture which favours its applicability in water purification. The polymer displayed good adsorption for both 4-CP and Co^{2+} from single pollutant solutions. However, the highest amounts of pollutant species removed were recorded at lower concentrations, suggesting the applicability of the polymer in remediation of low concentration of the pollutants. Based on the R^2 values it was observed that the adsorption of Co^{2+} by the polymer correlates well with the Langmuir model while adsorption of 4-CP can be better explained by the Freundlich model.

Acknowledgements

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