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Phosphine functionalised multiwalled carbon nanotubes: A new adsorbent for the removal of nickel from aqueous solution

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Abstract

Synthesised triphenylphosphine-linked multiwalled carbon nanotubes (Tpp-MWCNTs) were used to study the adsorption of nickel in aqueous solutions and their adsorption capabilities were compared with purified MWCNTs. The adsorption capacity increased with an increase in pH for all adsorbents. The adsorption equilibrium was reached in 40 and 30 min for purified MWCNTs and Tpp-MWCNTs, respectively. Both Freundlich and Langmuir isotherms used to investigate the adsorption process fitted the experimental data well with the correlation coefficient R^2 close to 1 for all adsorbents. On the other hand, the experimental data fitted well with a pseudo second-order model. The speciation of nickel also influenced the adsorption on the purified and Tpp-MWCNTs. The adsorbents used in this study showed superior adsorption capacity when compared to other adsorbents reported in the literature.

Key words: phosphine functionalised multiwalled carbon nanotubes; adsorbent; XPS remediation; nickel

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Introduction

The presence of nickel in the environment originates from several sources. The sources include the production, the consumption; the recycling and the disposal of nickel (Ni) and Ni compounds. Nickel and nickel compounds are widely used in various industries (metallurgical, electronic, electrical, medical) as catalysts, alloys etc. (Rosenberg, 1968; Moskalyk and Alfantazi, 2002; Denkhau and Salnikow, 2002). Ni salts are often used in the metal plating industry and constitute another significant source of Ni in the environment.

This widespread and varied use has led to an increase in the release of nickel into the environment, resulting in environmental pollution (Denkhau and Salnikow, 2002). For instance, the concentrations of Ni in industrial wastewaters range from 3.40 to 900 mg/L (Özbay, 2009). This concentration is higher than the maximum limit for Ni in terms of the regulation, which is 0.15 mg/L for wastewater. The accumulation of Ni and Ni compounds in the environment causes serious hazards to the plants, animals and human health. Some of the adverse effects are skin allergies, lung fibrosis, and cancer of the respiratory tract (Denkhau and Salnikow, 2002; IARC, 1997). Several forms of nickel, including its water soluble compounds, have been found to be carcinogenic in humans (IARC, 1997). The World Health Organisation (WHO) and the European Economic Community have restricted the concentration of nickel in

drinking water to 0.02 and 0.05 mg/L respectively (Özbay, 2009; WHO, 1996, 1998).

Several methods have been developed to remove nickel from effluent solutions. These methods include chemical precipitation, solvent extraction, ion exchange, adsorption using activated carbon, and membrane processing (Fu and Wang, 2011; Ahalya et al., 2003; Crini, 2005). However, their application is sometimes restricted because of environmental, technical and/or economic constraints (Fu and Wang, 2011; Ahalya et al., 2003; Crini, 2005). It is therefore necessary to improve these removal methods. Nowadays, adsorption is the most used technique for the removal of heavy metals because of its cost-effectiveness and simplicity (Qu, 2008). Several adsorption processes and adsorbents have been applied for the removal of heavy metals such as copper, zinc, cadmium and lead from aqueous solutions including alginate immobilized kaolin (Li et al., 2011), magnetic particles modified with amino groups (Lin et al., 2011), resin (Zhu et al., 2007), chitosan (Wan Ngah and Fatinathan, 2010), micelle-template silica (Panadda et al., 2009) and tourmaline (Jiang et al., 2006). However, new and more effective adsorbents are still required.

Carbon nanotubes (CNTs) are newly developed adsorbents that prove to be efficient in the adsorption of metals such as: Ni, Cd, Zn, Mn, Co, Cu, and Cr from solutions (Lu et al., 2008; Safavi et al., 2010; Pillay et al., 2009; Lu et al., 2006). MWCNTs have demonstrated a larger potential adsorption capacity towards metals ions than the commonly

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used activated carbon (Pillay et al., 2009). CNTs offer a better surface area for adsorption, higher thermal and chemical stabilities and also the recent progress in their large-scale production make them attractive for use as ideal metal adsorbents (Lu et al., 2006). Furthermore, recent studies show that CNTs are good adsorbents for environmental pollution management (Ren et al., 2011). Although in most cases functionalisation of CNTs enhances their adsorption capacity, yet both non-functionalised and functionalised CNTs have been reported as good adsorbents of pollutants (Pillay et al., 2009). It is therefore of great interest to identify appropriate functional groups and to design methods of attaching them to the surface of CNTs. Another advantage of functionalisation is that this can enhance the selectivity of CNTs based on affinity and interaction between pollutants and functional groups.

Phosphines are phosphorus functional compounds that play an important role in the processes of metal extraction from solutions. Phosphines can function as ligands in metal complexes; these compounds also enhance the selective extraction of metals (Smith, 2008). Sánchez et al. (2001) had previously demonstrated the chelating properties of phosphorus compounds towards precious metals such as Au(III) and Pd(II). To the best of our knowledge Tpp-MWCNTs have not been tested for the uptake of Ni(II). Therefore, the aim of this study was to synthesise purified and phosphine-functionalised multiwalled carbon nanotubes and to compare their adsorption capabilities with respect to the removal of nickel from aqueous solutions. Various parameters such as the effect of pH, the contact time factor and the influence of initial concentration on the adsorption are investigated. The adsorption isotherms and kinetics are also studied.

1 Materials and methods

1.1 Chemicals

All chemicals were of analytical (AR) grade and were used as received. Nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 99%–102.0%) was purchased from Sigma-Aldrich, Germany. Sodium hydroxide (NaOH, 97%) was used as received from Merck, South Africa. Nitric acid (HNO_3 , 55%) was obtained from Associated Chemical Enterprises (ACE, South Africa). Gases (air and acetylene) were supplied by Afrox, South Africa.

1.2 Adsorbents

The adsorbents (purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2)) used in this study, were prepared by a method reported in previous manuscripts (Muleja, 2011; Muleja et al., 2012). The characterisation techniques used for the analysis of these adsorbents include transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS) as previously reported. A Micromeritics TRISTAR 3000 analyzer was used for the Brunauer-Emmett-Teller method (BET) analysis. The samples were degassed at 150°C for 4 hr under the flow of nitrogen and analysed. The

surface area and porosity for the samples were determined according to the BET method. In addition, a Malvern Zetasizer instrument was used to analyse the adsorbents. The samples were dispersed in 5 mL *n*-hexane and the pH was adjusted using 0.1 mol/L HCl or 0.1 mol/L NaCl. The point of zero charge (pH_{PZC}) was determined at the point where the plot passes through zero zeta potential.

1.3 Batch adsorption experiments

A stock solution (1000 mg/L) of Ni^{2+} was prepared by dissolving 4.48 g of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in 1000 mL deionised water. The stock solution was diluted to obtain concentrations ranging from 10, 20, 30, 40 and 100 mg/L. The investigation of parameters such as the effect of pH, the effect of contact time and the influence of initial concentration are outlined.

The pH of the solutions was adjusted to the desired values (pH 2 to pH 12) by adding solutions of 0.1 mol/L of HNO_3 and 0.1 mol/L NaOH and monitoring the pH with calibrated pH meter (HI 221, Hanna Instrument Microprocessor, Romania). The batch adsorption experiments were performed in separate conical flasks (100 mL) by mixing 10.0 mg of adsorbents with 25 mL Ni ions solution (40 mg/L) at a specific pH value. The mixtures were then agitated with a platform orbital shaker (MERX Model 261, Merck, South Africa). The contact time was kept constant (30 min) at room temperature (25°C) and the speed of 200 revolutions per minute (r/min). The selected pH values (pH 2 to pH 12) represent the pH in which the speciation of nickel can vary. Although the Ni concentration in the wastewater (environment) is higher, the initial concentration of Ni (40 mg/L) was chosen for the purpose of this study. The uptake of Ni^{2+} was determined. Besides the effect of pH on the uptake of Ni^{2+} , other parameters (contact time and initial concentration) were investigated at pH 6 to avoid the influence of precipitation at higher pH values (Kandah and Meunier, 2007).

The effect of contact time between adsorbents (10.0 mg) and Ni^{2+} solutions (25.0 mL) was performed by agitation at the speed of 200 r/min. All the flasks were mounted on the shaker. The contents were agitated for the exact time ranging from 10 to 120 min at pH 6. The suspensions (adsorbent-nickel ion solutions) were filtered over polyethersulfone (PESU) membrane (pore size 0.45 μm , diameter 47 mm). The resulting aqueous-phase solutions were analysed for Ni^{2+} content by FAAS (Flame Atomic Absorption Spectroscopy).

The effect of initial concentration on adsorption capacity was investigated with a series of conical flasks (100 mL) mounted on a shaker. The agitation of flasks containing 10.0 mg of adsorbents and 25.0 mL of Ni^{2+} solutions of different concentrations (10 to 1000 mg/L) was achieved at room temperature (25°C). The other parameters such as contact time 30 min, speed 200 r/min and pH 6 were kept constant. After 30 min of contact time, three flasks of varying adsorbents were removed from the shaker. The filtration was achieved through polyethersulfone (PESU) membrane (pore size 0.45 μm , diameter 47 mm). The filtrates were analysed to determine Ni^{2+} -ion concentration

by FAAS.

For Ni^{2+} determination, A Varian SpectrAA 220FS (Version 4.10 PRO) FAAS was used to analyse the filtrates obtained from the adsorption experiments. A combination of two gases (air/acetylene) was used to produce the flame. The instrument set-up was as follows: 1 L/min for gas flow rate, time measurement of 5 sec, at the wavelength of 232.0 nm and slit width of 0.2 nm. The instrument was calibrated using freshly prepared Ni standard solutions (10 to 100 mg/L) and later optimised.

The amount of Ni^{2+} -ion uptake was calculated by applying Eq. (1):

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

where, q_e (mg/g) is the adsorption capacity of the adsorbents, C_i (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of Ni^{2+} in solution, respectively, V (L) is the volume and m (g) is the mass of the adsorbents.

1.4 Quality control

The reliability of the analytical data was verified by conducting quality-control experiments. A blank experiment was carried out using deionised water. Aliquots of Ni^{2+} solutions (25.0 mL) without adsorbents were agitated and filtered. The filtrates were then analysed with FAAS to determine Ni^{2+} content. The final concentration was not very different from the initial concentration of the Ni^{2+} . This experiment was carried out to serve as a control. This experiment also confirmed that the changes observed between the initial Ni^{2+} concentration and the final concentrations were due to adsorption. The experiments were carried out in triplicate. Data obtained with more than 5% error were repeated. The data reported in this study are averages of replicates.

2 Results and discussion

2.1 Characterization

2.1.1 Transmission electron microscopy, FT-IR spectroscopy and X-ray photoelectron spectroscopy

As previously reported, the purified MWCNTs and functionalised MWCNTs were characterised by TEM and differences in morphology confirmed the presence of phosphine moieties.

The functional groups such as hydroxyl, carbonyl groups and characteristic peaks responsible of phenyl-groups attached directly to phosphorus were identified based on the FT-IR analysis.

The adsorbents were characterised by XPS technique and all the elements expected in the composition of the compounds were identified. The elements include carbon (C), oxygen (O) and the crucial phosphorus (P). The presence of phosphorus was critical in this study; hence its binding energy with carbon was highly expected. The atomic concentration (percentage) of the elements C, O, and P present in the samples, as well as the binding energies with their assignments are presented in Table 1.

Table 1 Deconvolution of XPS results of purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2)

Sample	Element	Atomic conc. (%)	Binding energy (eV)	Assignment
Purified MWCNTs	C	96	284.8 (92%)	C-C
			286.5 (8%)	C-O
	O	4	533.1	O-C, O-H
Tpp-MWCNTs (1)	C	89.4	284.9 (92%)	C-C
			286.6 (7%)	C-O
			289.11 (1%)	O-C=O
	O	9.7	532.17	O-C, O-H
Tpp-MWCNTs (2)	P	0.7	132.6	P-C
	C	82.8	284.8 (90%)	C-C
			286.5 (8%)	C-O
			289.0 (2%)	O-C=O
	O	14.6	532.4	O-C, O-H
	P	2.6	132.6	P-C

2.1.2 BET surface area and porosity measurements

Surface area and pore size measurements were recorded on the purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2). The BET surface area data revealed that the purified MWCNTs had a higher surface area (41.68 m^2/g) than both Tpp-MWCNTs (1) (26.53 m^2/g) and Tpp-MWCNTs (2) (0.86 m^2/g). It is noteworthy to mention that the surface areas of both Tpp-MWCNTs are lower, however the adsorption capacity of these new adsorbents is higher than that of purified MWCNTs. Thus, the surface area does not affect the adsorption capacity of the new adsorbent which is in agreement with a recent report by Yan et al. (2011). On the other hand, the pore sizes are 13.45, 11.84 and 4.36 nm for purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2), respectively. As expected, the porosity data revealed that all samples showed little microporosity. It is hence implying that the diffusion issues which occur with adsorbents that have a high microporosity are not expected in this study.

2.1.3 Zeta potential

Figure 1 shows the zeta potentials of purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2) as a function of various pH values. From Fig. 1, it can be noticed that purified MWCNTs are positively charged in acidic media up to neutral pH value of 7.6 which is the point of zero charge of purified MWCNTs. In other words, as the pH increases the surface charges of purified MWCNTs shift from being positively charged to being negatively charged. On the other hand, Fig. 1 reveals that the point of zero charge of Tpp-MWCNTs (2) is at 6.5, meaning that the Tpp-MWCNTs (2) possess negative surface charges at low pH values. The surface charges of MWCNTs become positive over the pH range of pH 6.5 to pH 10.5, meaning that Tpp-MWCNTs (2) are negatively charged over a wide range of pH values.

The negative surface charges are probably due to the high degree of functionalisation of Tpp-MWCNTs (2) which contain 2.6% of phosphorus.

For Tpp-MWCNTs (1) which contain only 0.7% of phosphorus, the surface charges were mostly positive in

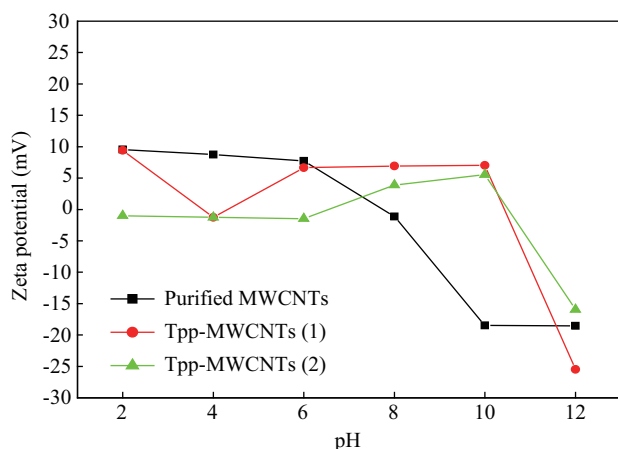


Fig. 1 Zeta potentials trends of purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2) as a function of pH.

both acidic and basic media as shown in Fig. 1. Tpp-MWCNTs (1) reveal negative surface charges at pH values ranging between pH 3.7 and pH 4.4 and above pH 10.4. In addition, the curves of the Tpp-MWCNTs (1) and Tpp-MWCNTs (2) follow a similar trend from acidic (pH 4) to basic media. This similarity could be attributed to the phosphine functional groups attached to the surface of the MWCNTs. In terms of the adsorption process, these zeta potential results indicate that both electrostatic attraction and repulsion forces could occur; it will depend on the metal species in solution.

2.2 Parameters of adsorption effects

2.2.1 Effect of pH

Figure 2 shows that pH strongly influences the adsorption of Ni. The adsorption of Ni using purified MWCNTs shows a gradual increase from pH 2 to pH 6, then the trend changes between pH 6 and pH 8 and rises sharply between pH 8 and pH 10. Upon reaching pH 10, adsorption then remains constant up to pH 12. Generally, MWCNTs are positively charged at low pH values (Lu and Chiu, 2008); this explains the electrostatic repulsions between MWCNTs and Ni^{2+} . These changes could be attributed to various factors such as: the surface charge of the MWCNTs; the degree of ionisation; and the species of Ni available in aqueous solution (Tan et al., 2008). In fact, zeta potential results in Fig. 1 show that the surface charges of purified MWCNTs shift from being positively charged in acidic media to being negatively charged in basic media. The shift is at around neutral pH of 7.6.

It has been reported that in acidic medium (up to pH ≤ 8) the predominant species of nickel is Ni^{2+} (Rao et al., 2007). At pH 2 the adsorption of nickel is low because of the high competition between H^+ ions from (HNO_3) and Ni^{2+} . The slight rise in adsorption uptake observed at pH values of between pH 4 and pH 8 is therefore due to the decrease of protons (H^+) in solution. Hence, at higher values (pH > 8) the protons are replaced by hydroxide (OH^-) forming species such as $\text{Ni}(\text{OH})^+$ and $\text{Ni}(\text{OH})_2^0$ (Tan et al., 2008; Wang et al., 2007). In addition the surface of MWCNTs is more negatively charged resulting in an electrostatic attraction of Ni^{2+} . The change in the surface charges of

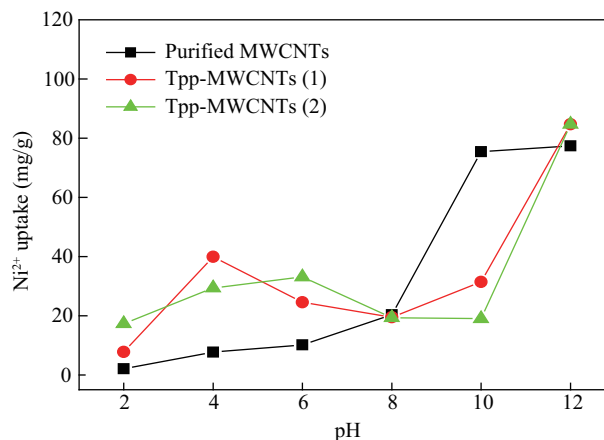
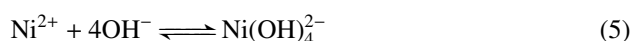
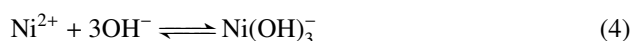
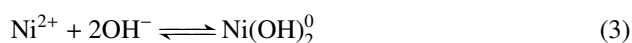
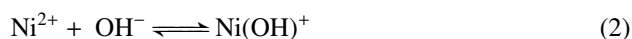


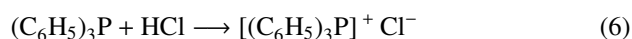
Fig. 2 Effect of pH on the uptake of Ni^{2+} . Initial concentration of 40 mg/L, contact time of 30 min, adsorbent dosage 20 mg/50 mL at room temperature.

purified MWCNTs (positive to negative) observed at pH of 7.6 and shown in Fig. 2 justifies the drastic increase in removal of Ni^{2+} . The electrostatic interactions are more likely to be the adsorption mechanism occurring at this point. The maximum nickel removal is observed over the pH range pH 10 to pH 12, which is due to the formation of hydrolysis species, i.e., $\text{Ni}(\text{OH})^+$ (Tan et al., 2008; Wang et al., 2007). Another mechanism that is likely to occur at this pH range is precipitation due to the formation of $\text{Ni}(\text{OH})_2^0$ as shown in the following hydrolysis equations sequences (Yang et al., 2009):



$\log K_a$ values of these reactions are 4.1, 8.5, 11.5 and 12 for Reactions (2), (3), (4) and (5), respectively.

A similar scenario is observed even with the phosphorylated MWCNTs. At pH values of below pH 3, the uptake was very weak due to the competition between Ni^{2+} and H^+ in the solution (Rao et al., 2007). However, Tpp-MWCNTs (2) showed higher adsorption at pH levels of pH 2 and pH 6 than Tpp-MWCNTs (1) which adsorbed more at pH 4. This is likely to be attributed to the specific functional groups attached to the MWCNTs. Zeta potential results showed that both functionalised MWCNTs are negatively charged due to the presence of phosphine moieties attached to the MWCNTs. However, triphenylphosphine forms positively charged phosphonium salt in acidic media (Honaker et al., 2007) as Reaction (6).



This effect caused a decrease in the adsorption of nickel. Figure 2 illustrates a decrease and increase in the uptake for all the adsorbents. The surface charges of the adsorbents contribute to the fluctuation observed in low and high uptake of Ni^{2+} . The oxygenated functional groups

attached to the nanotubes favour the exchange between the MWCNT surface and anions and cations in solution. The chemistry of the functional groups is responsible for the differences in the amount of nickel removed at different pH values.

Another scenario was displayed starting from pH 8 for Tpp-MWCNTs (1) and from pH 10 for Tpp-MWCNTs (2) whereby a sharp rise is observed. As mentioned before at $\text{pH} \geq 8$, nickel is hydrolysed and this hydrolysis could lead to the formation of precipitable species such as $\text{Ni}(\text{OH})_2^0$ (Yang et al., 2009). This situation is adequate for the removal of nickel ions due to precipitation and electrostatic attraction. As previously mentioned, the mechanisms by which the metal ions are sorbed onto CNTs are very complicated and appear attributable to a combination of electrostatic attraction, sorption-precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs (Yang et al., 2009). For instance, the increase in removal of Ni^{2+} noticed at pH 4 is due to the negative surface charges of Tpp-MWCNTs (1) at pH 4. This is accordance with the zeta potential results in Fig. 1. From the zeta potential, Tpp-MWCNTs (2) possess negative charged surface areas at low pH values (Fig. 1) which explains a high Ni^{2+} removal over this pH ranges. A slight decrease above pH 6 is observed because Tpp-MWCNTs (2) becomes positively charged up until pH 10. The surface charges of Tpp-MWCNTs (2) shift from being positively charged to being negatively at pH 10 which explains the sharp increase in removal of Ni^{2+} . The zeta potential results agree with the effect of pH on the adsorption of Ni^{2+} .

2.2.2 Effect of contact time

The uptake of nickel as function of contact time, ranging from 10 to 120 min, with all adsorbents was determined while all the other parameters were kept constant. From Fig. 3 it can be noticed that the removal of Ni^{2+} ions increased from 0 to 10 min, and optimal removal was practically achieved within 40 min. Results shown in Fig. 3 prove that the uptake of nickel increases with an increase in contact time. Previous studies have reported similar

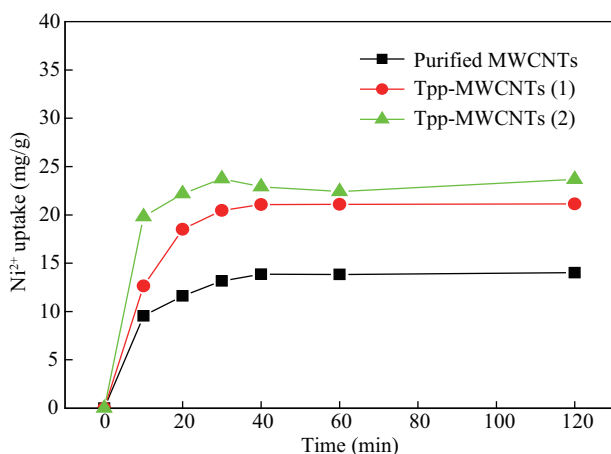


Fig. 3 Effect of contact time on the uptake of Ni^{2+} ions. Initial concentration 40 mg/L, pH 6.0, adsorbent dosage 20 mg/50 mL at room temperature.

findings, stating the short equilibrium time in the removal of nickel and indicating that CNTs have a strong potential for Ni^{2+} adsorption applications (Rao et al., 2007).

However, the difference lies on the amount of nickel adsorbed. For purified MWCNTs, for instance, the uptake of nickel increases rapidly from 0 to 30 min and reaches the equilibrium at 40 min, whereas for both functionalised MWCNTs equilibrium was attained at 30 min. This can be attributed to the chelating properties of phosphine moieties which have enhanced nickel uptake. It was determined that at equilibrium time 40 and 30 min, respectively, the amount of nickel uptake was 13.87, 20.46 and 23.73 mg/g for purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2), respectively.

2.2.3 Effect of initial concentration

The effect of initial Ni^{2+} concentration on adsorption results is shown in Fig. 4. It can be also observed in general that the uptake increases with an increase in Ni^{2+} concentration. With an initial concentration of 10 mg/L, the uptake was 1.88 mg/g for purified MWCNTs, 4.24 mg/g for Tpp-MWCNTs (1), and 4.08 mg/g for Tpp-MWCNTs (2). With an initial concentration of 100 mg/L, 15.50 mg/L, 29.88 mg/g and 32.15 mg/g of Ni^{2+} were removed by purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2), respectively. This simply suggests that the uptake is also dependent on the initial Ni^{2+} concentration. The availability of adsorption sites is still the same as that at a concentration of 10 mg/g since the adsorbent used is the same (Pillay et al., 2009; Yang et al., 2009; Kumar and Kirthika, 2009).

Generally, the effect of initial concentration on the adsorption of metals reaches a plateau at a specific concentration. The plateau is actually the equilibrium state whereby only adsorption-desorption could occur. It is very important to recall that the amount of adsorbent used for all the experiments was kept constant. In another words, the saturation of the available active sites could strongly depend on the dosage of the adsorbents rather than on the initial concentration. The equilibrium effect is known if the effect of dosage on the uptake of nickel is investigated.

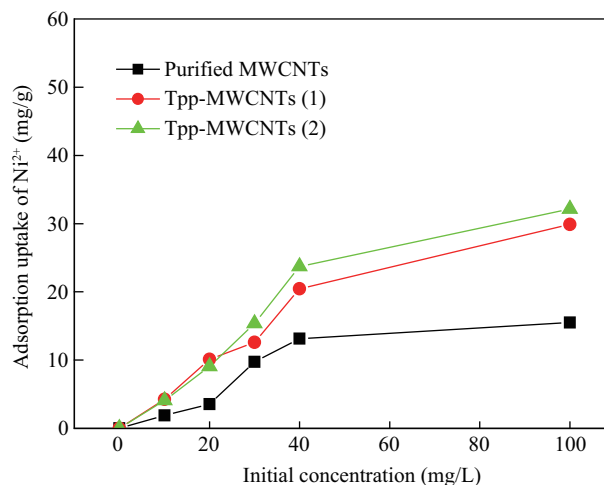


Fig. 4 Effect of initial concentration on Ni^{2+} uptake. Contact time 30 min; adsorbent dosage 10 mg/25 mL; pH 6.0 at room temperature.

2.3 Adsorption kinetics

The control of mechanism of adsorption processes such as mass transfer and chemical reaction during adsorption is often investigated by using the pseudo first- and second-order equations (Kumar and Kirthika, 2009). Pseudo first-order model can be represented by the Lagergren equation (Blanchard et al., 1984; Sui et al., 2011) as:

$$\ln \frac{(q_e - q_t)}{q_e} = -k_1 t \quad (7)$$

where, q_e (mg/g) is the amount of Ni^{2+} adsorbed at the equilibrium, q_t (mg/g) is the amount of Ni^{2+} adsorbed at time t , and k_1 (1/min) is the pseudo first-order constant. The pseudo first-order results were very poor; hence they are excluded from this report.

The pseudo second-order kinetic assumes that the adsorption process is controlled by chemisorptions (Ho and McKay, 1999). Pseudo second-order equation is often written by Eq. (8) (Ho and McKay, 1998; Sui et al., 2011):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where, q_e (mg/g) is the amount of Ni^{2+} adsorbed at the equilibrium, q_t (mg/g) is the amount of Ni^{2+} adsorbed at time t , and k_2 (g/(mg·min)) is the pseudo second-order constant. The plot t/q_t against t should be a straight line if pseudo second-order kinetics is applicable. The pseudo second-order results are displayed by Fig. 5.

The parameters q_e and k_2 were determined from the intercept and slope of the plot t/q_t versus t . A summary of the pseudo second-order results and parameters are displayed in Table 2. The results demonstrate that the adsorption data fit well the pseudo second-order with a correlation coefficient close to 1 for all the adsorbents suggesting that the adsorption mechanism of Ni^{2+} could be chemisorptions.

One should note that the amount of Ni^{2+} adsorbed at equilibrium calculated from pseudo second-order is inferior to the experimental amount of Ni^{2+} adsorbed and this is in agreement with recent studies on the adsorption of both inorganic and organic pollutants (Kumar and Kirthika, 2009; Sui et al., 2011).

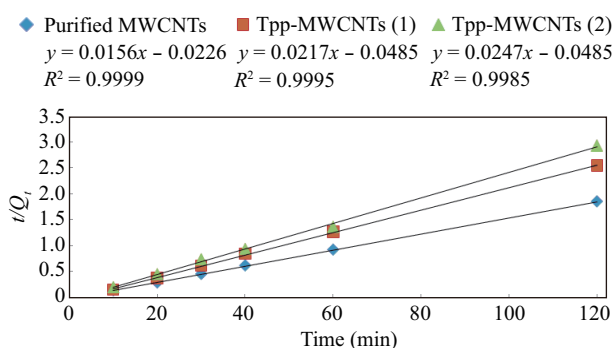


Fig. 5 Pseudo second-order reaction for Ni^{2+} adsorbed onto purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2).

2.4 Adsorption isotherms

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species (Kumar and Kirthika, 2009). Freundlich and Langmuir models are usually used as adsorption isotherms to describe the adsorption data.

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. The Freundlich adsorption isotherm is the relationship between the amounts of nickel adsorbed per unit mass of adsorbent, Q_e (mg/g), and the concentration of the nickel at equilibrium C_e , in mg/L (Kumar and Kirthika, 2009).

$$Q_e = K_f C_e^{1/n} \quad (9)$$

The linear form of the above Eq. (8) can be rewritten as:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (10)$$

where, K_f and n are the Freundlich constants, the characteristics of the system, K_f and $1/n$ are the indicators of the adsorption capacity of the adsorbent and the effect of concentration on the adsorption capacity (adsorption intensity), respectively.

The ability of Freundlich model to fit the experimental data was examined. And, the plot of $\log C_e$ against $\log q_e$ was exploited to generate the intercept value of K_f and the slope of $1/n$. Figure 6 reveals that the adsorption of Ni^{2+} using purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2) fit the Freundlich isotherm well. The correlation coefficient R^2 for each adsorbent is close to 1 (0.991, 0.998 and 0.995) for purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2), respectively. The Freundlich constants (K_f and n) for each adsorbent were determined and were found to be 1.25 and 1.21, respectively, for purified MWCNTs; 0.75 and 1.12 for Tpp-MWCNTs (1) and 0.89 and 1.21 for Tpp-MWCNTs (2).

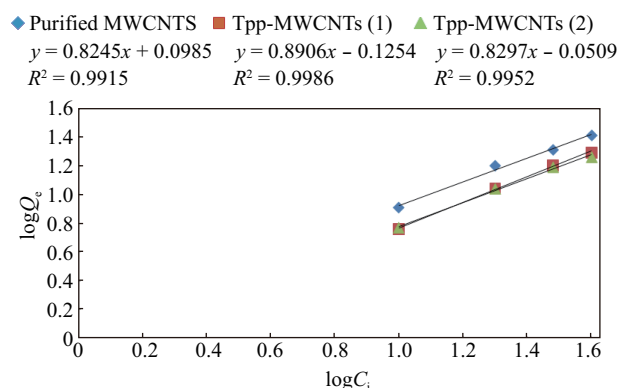


Fig. 6 Freundlich isotherm for purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2).

Table 2 Pseudo second-order kinetic parameters for Ni²⁺ adsorption

Adsorbent	C _i (mg/L)	t (min)	q _e (exp) (mg/g)	q _e (cal) (mg/g)	k ₂ (g/(mg·min))	R ²
Purified MWCNTs	40	40	65.33	64.10	0.345	0.99
Tpp-MWCNTs (1)	40	30	48.84	46.08	0.022	0.99
Tpp-MWCNTs (2)	40	30	40.67	40.49	0.012	0.99

C_i: initial concentration; t: equilibrium time; q_e (exp): the amount of Ni²⁺ adsorbed at the equilibrium (experimental data); q_e (cal): the amount of Ni²⁺ adsorbed at the equilibrium (calculated from pseudo second-order data); k₂: pseudo second-order constant; R²: correlation coefficient.

Separately, the values of $n > 1$ for each adsorbent indicating that the adsorption is highly favourable. The adsorption of Ni²⁺ using MWCNTs and other adsorbents performed by other researchers revealed similar Freundlich isotherm findings (Rao et al., 2007; Kumar and Kirthika, 2009).

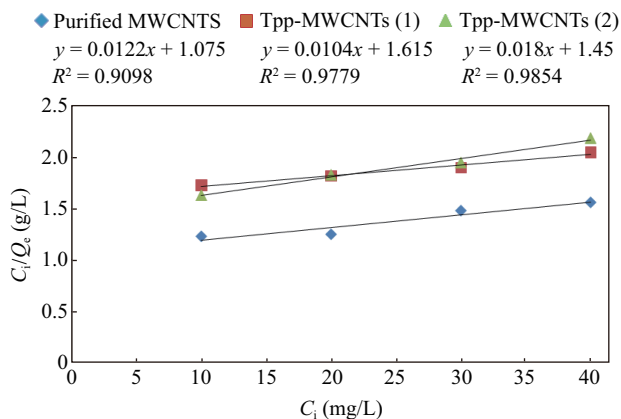
The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane (Kumar and Kirthika, 2009). The Langmuir isotherm (Pillay et al., 2009) represented by the following Eq. (11):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (11)$$

where, C_e (mg/L) is the equilibrium concentration of nickel in solution, Q_e (mg/g) is the amount of Ni²⁺ adsorbed at equilibrium, Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively.

It can be noticed from the linear plot of C_e/Q_e against C_e that the adsorption data fit the Langmuir model well (Fig. 7). This is particularly so because of the correlation coefficient R² which is 0.985, 0.909 and 0.977 for purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2), respectively.

In this study, the initial concentration (C_i) was employed to plot both Freundlich and Langmuir isotherms instead of the concentration at equilibrium (C_e). This presents the advantages of not excluding any data when complete contaminant uptake occurs and obtaining a comparable range of metal concentrations for all of the batch tests (Coles and Yong, 2006). From Fig. 7 the parameter 1/n values are found to be larger and K_f smaller, meaning that the isotherm is more linear. This is in agreement with previous reports on the application of Freundlich model using C_i rather than C_e (Coles and Yong, 2006). The isotherm experimental results suggest that the adsorption process is based on the heterogeneous surface of the adsorbents and the available active sites.

**Fig. 7** Langmuir isotherm for Purified MWCNTs, Tpp-MWCNTs (1) and Tpp-MWCNTs (2).

The correlation coefficients of all three adsorbents show that experimental data fit the Langmuir model well which means that the adsorption process occurs on a monolayer surface.

2.5 Comparison with previous results

Based on the Langmuir equation, the results obtained in this study showed superior adsorption capacity when compared to the previously reported results using different adsorbents. The findings are presented in Table 3.

The adsorbents used in this study have shown better adsorption capacity when compared to the other adsorbents including low cost activated carbon, modified chitosan, sodium polyacrylated-grafted AC, MWCNTs and oxidised MWCNTs reported in the literature. Sodium polyacrylated-grafted AC seems to have a higher adsorption capacity than purified MWCNTs, however, this could be explained by the dosage used (0.10 g/10 mL) compared to the dosage used for purified MWCNTs (0.01 g/25 mL). The phosphine functionalised MWCNTs revealed a higher adsorption capacity. This is attributed to the strong interaction between the metal ions and the Π electrons of the triphenylphosphine ligands (Elschenbroich and Salzer,

Table 3 Comparison between other adsorbents and those used in this study

Adsorbent	C _e (mg/L)	Dosage	pH	Q _e (mg/g)	Reference
Low cost activated carbon	50	0.05 g/50 mL	7	43.82	Vijayakumaran et al., 2009
Modified chitosan	50	0.10 g/100 mL	6	9.6	Justi et al., 2005
Sodium polyacrylated-grafted AC		0.10 g/10 mL		55.76	Ewecharoen et al., 2009
MWCNTs	80	0.05 g/100 mL		38.46	Lu and Liu, 2006
Oxidised MWCNTs	20	0.015 g/500 mL	6.55	9.8	Chen and Wang, 2006
Purified MWCNTs	40	0.010 g/25 mL	6	55.55	This study
Tpp-MWCNTs (1)	40	0.010 g/25 mL	6	83.33	This study
Tpp-MWCNTs (2)	40	0.010 g/25 mL	6	100	This study

1992).

3 Conclusions

Purified multiwalled carbon nanotubes and triphenylphosphine linked multiwalled carbon nanotubes (purified MWCNTs and Tpp-MWCNTs) were successfully applied in the adsorption of nickel from aqueous solution. Triphenylphosphine linked multiwalled carbon nanotubes adsorbed more Ni^{2+} from aqueous solution (at least twofold) than the purified multiwalled carbon nanotubes. The adsorption of Ni^{2+} is pH-dependent due to the changes of species in the nickel solution, and changes of charges on the surfaces of the adsorbents. The adsorption of Ni^{2+} increased with time and reached equilibrium within 30 min and 40 min for functionalised and purified MWCNTs, respectively. The adsorption of Ni^{2+} increases with an increase in initial concentration. The analytical data obtained fit the Freundlich and Langmuir isotherm models. However, they fit the Freundlich model better with the correlation coefficient ($R^2 = 0.998$) is closer to 1. The Freundlich model parameter n results were > 1 suggesting that the application of purified MWCNTs and Tpp-MWCNTs in the adsorption technique is favourable. The adsorption mechanism of Ni^{2+} onto purified MWCNTs and both Tpp-MWCNTs could be chemisorptions as proven by pseudo second-order model. Furthermore, these adsorbents showed superior adsorption when compared to the mostly used activated carbon and to the other adsorbents available in the literature.

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