



# Adsorption of Ni(II) on oxidized multi-walled carbon nanotubes: Effect of contact time, pH, foreign ions and PAA

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## ABSTRACT

The adsorption of Ni(II) on oxidized multi-walled carbon nanotubes (MWCNTs) as a function of contact time, pH and foreign ions in the absence and presence of polyacrylic acid (PAA) was studied using batch technique. The results indicated that adsorption of Ni(II) on oxidized MWCNTs increased from zero to ~99% at pH 2–9, and then maintained the high level with increasing pH. Kinetic data showed that the adsorption process achieved equilibrium within 2 h and experimental data were fitted well by the pseudo-second-order equation. A positive effect of PAA on Ni(II) adsorption was found at pH < 8, whereas a negative effect was observed at pH > 8. The effect of addition sequences of PAA/Ni(II) on the adsorption of Ni(II) to PAA–MWCNT hybrids were also studied. The results indicated that the adsorption of Ni(II) was influenced by addition sequences obviously. The adsorption of Ni(II) on oxidized MWCNTs may be mainly attributed to surface complexation and ion exchange. Oxidized MWCNTs are suitable material in the solidification and pre-concentration of Ni(II) from aqueous solutions.

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## 1. Introduction

Nickel is a non-biodegradable toxic heavy metal ion present in wastewater. The main source of nickel pollution in the water derives from industrial production processes such as galvanization, smelting, mining, batteries manufacturing and metal finishing. The presence and accumulation of nickel in industrial effluents have a toxic or carcinogenic effect on living species. Thereby, it is of great crucial to eliminate nickel ions from wastewaters. As an economical and efficient method, adsorption technique has been widely applied to remove heavy metal ions from wastewaters. Different adsorbents such as activated carbon [1], husk of *Lathyrus sativus* [2], olive stone waste [3], bagasse [4], mordenite [5] and crab shells [6] have been reported as nice adsorbents for Ni(II) removal from wastewater. However, further applications for these adsorbents are limited because of their low adsorption capacities. Therefore, researchers are still making great efforts to investigate new adsorbents with high adsorption capacities and efficiencies.

Carbon nanotubes (CNTs), a new member in carbon family, were first reported in 1991 [7]. CNTs can be regarded as cylindrical hol-

low micro-crystals of graphite [8]. CNTs include single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) depending on the amount of layers. Their unique hollow structure and remarkable electronic, mechanical, and chemical properties have attracted in interdisciplinary investigations, such as hydrogen storage, quantum nanowires, catalyst supports and chemical sensors [9–12]. With regard to the numerous possibilities of various technical applications, it is nothing unusual for the consideration of their application for environmental pollution cleaning. CNTs have aroused researchers' widespread attention as a new type of adsorbent and exhibit outstanding capability for the removal of various inorganic, organic and radioactive pollutants [13–18]. However, to the best of our knowledge, the study of MWCNTs in the simultaneous removal of metal ions and organic pollutants is still not available. Polyacrylic acid (PAA) is a non-toxic polymeric substance which contains carboxylic groups and linear CH<sub>2</sub>–CH<sub>2</sub> chains. Since it is structurally simple and has a similar property with natural organic materials (NOM), PAA is selected as the representative of NOM to study the interaction between the heavy metal ions and NOM present in wastewater.

The basic objectives of the present research are: (1) to investigate the adsorption kinetics and to analyze the experimental data with a pseudo-second-order equation; (2) to study the adsorption of Ni(II) on oxidized MWCNTs by varying experimental conditions, viz. pH, foreign ions, PAA concentrations, addition sequences, etc.; (3) to presume the adsorption mechanism of Ni(II) on oxidized MWCNTs.

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## 2. Experimental

### 2.1. Materials

#### 2.1.1. Preparation of oxidized MWCNTs

MWCNTs were prepared by using chemical vapor deposition (CVD) of acetylene in hydrogen flow at 760 °C using Ni-Fe nanoparticles as catalysts.  $\text{Fe}(\text{NO}_3)_2$  and  $\text{Ni}(\text{NO}_3)_2$  were treated by sol-gel process and calcinations to get FeO and NiO and then deoxidized by  $\text{H}_2$  to get Fe and Ni [19]. The as-grown MWCNTs (named as untreated MWCNTs) were added into the solution of 3 mol/L  $\text{HNO}_3$  to remove the hemispherical caps of the nanotubes. The mixture of 3 g MWCNTs and 400 mL 3 mol/L  $\text{HNO}_3$  was ultrasonically stirred for 24 h. The suspension was filtrated, and rinsed with deionized water until the pH of the suspension reached about 6, and then was dried at 80 °C. Thus prepared MWCNTs (named as oxidized MWCNTs) were calcined at 450 °C for 24 h to remove the amorphous carbon. The  $\text{N}_2$ -BET surface area of the oxidized MWCNTs was 197  $\text{m}^2/\text{g}$ . The oxidized MWCNTs were used in the experiments.

#### 2.1.2. Preparation of Ni(II) stock solution

Ni(II) stock solution (1000 mg/L) was prepared as follows: 0.10 g nickel metal powder (purity >99.9%) was dissolved in 10 mL 3 mol/L  $\text{HNO}_3$  and then shifted to a 100 mL volumetric flask. The stock solution was diluted with deionized water to obtain standard solutions with concentrations ranging from 2 to 24 mg/L.

All chemicals used in the experiments were purchased in analytical purity and used without any purification. All solutions were prepared with deionized water.

### 2.2. Procedures

The adsorption experiments were performed in the polyethylene test tubes under ambient conditions by using batch technique. The stock suspension of oxidized MWCNTs and  $\text{NaClO}_4$  solution were first contacted for 24 h to achieve the equilibration between oxidized MWCNTs and  $\text{NaClO}_4$ . Then, nickel stock solution and PAA stock solution were added to achieve the desired concentrations of different components. Negligible amount of 0.1 or 0.01 mol/L  $\text{HClO}_4$  or  $\text{NaOH}$  was added to achieve the desired pH of the aqueous solutions. The samples were gently shaken for 24 h to achieve sorption equilibration and centrifuged at 9000 rpm for 30 min. Then the supernatant was filtered using 0.45  $\mu\text{m}$  membrane filters to separate the solid from liquid phases. It was necessary to note that the adsorption of Ni(II) on the tube wall was negligible according to the test of Ni(II) adsorption in the absence of oxidized MWCNTs.

The concentration of Ni(II) was analyzed by spectrophotometer at wavelength 530 nm through the formation of Ni butanedione dioxime complex. Two milliliters supernatant and 8 mL deionized water were added in 25 mL volumetric flask, then 2 mL 500 g/L  $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$ , 1 mL 0.05 mol/L  $\text{I}_2$  solution and 7 mL deionized water were added to flask sequentially. After the bottle was shaken well, 2 mL 5 g/L  $(\text{CH}_3)_2\text{C}_2(\text{NOH})_2$ , 2 mL 50 g/L EDTA and 1 mL deionized water were added to the solution sequentially. Then the Ni Butanedione dioxime complex was formed. The amount of Ni(II) adsorbed on oxidized MWCNTs was calculated from the difference between the initial concentration and the equilibrium one.

The adsorption of PAA on oxidized MWCNTs as a function of pH was investigated and expressed by the measurement of the total carbon (TC) of each filtrate sample using a total organic carbon analyzer. Prior to the TC analysis,  $\text{CO}_2$  was eliminated from each sample by purging with nitrogen gas for about 15 min.

In addition, the effect of addition sequences on Ni(II) adsorption was investigated. The sequences of additions were: (1) oxidized MWCNTs,  $\text{NaClO}_4$  and nickel solution were pre-equilibrated for 24 h before the addition of PAA (called batch 1); (2) oxidized MWCNTs,

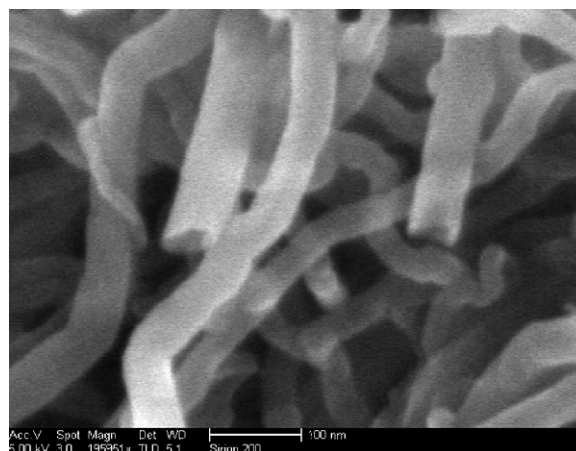


Fig. 1. SEM image of oxidized MWCNTs.

$\text{NaClO}_4$  and PAA were pre-equilibrated for 24 h before the addition of nickel solution (called batch 2); and (3) oxidized MWCNTs,  $\text{NaClO}_4$ , nickel solution and PAA were added into the test tube at the same time and the mixtures were equilibrated for 24 h (called batch 3).

All the experimental data were the averages of duplicate or triplicate determinations. The average uncertainties were about 5%.

## 3. Results and discussion

### 3.1. Characterization of oxidized MWCNTs

Fig. 1 displays the scan electron microscope (SEM) image of oxidized MWCNTs. As can be observed, the oxidized MWCNTs have very smooth surfaces and cylindrical shapes with an external diameter of 10–30 nm. Due to the inter-molecular force, the MWCNTs of different sizes and directions form an aggregated structure.

Fig. 2 shows the Fourier transform infrared spectrum (FTIR) of oxidized MWCNTs in pressed KBr pellets. The FTIR spectrum indicates that the acid treatment process introduces many functional groups onto the surface of oxidized MWCNTs: hydroxyl groups ( $3500\text{ cm}^{-1}$ ), carboxyl groups ( $1650\text{ cm}^{-1}$ ), and carbonyl groups ( $1400\text{ cm}^{-1}$ ) [20], which can provide a large number of chemical adsorption sites and thereby can increase the adsorption capacity of

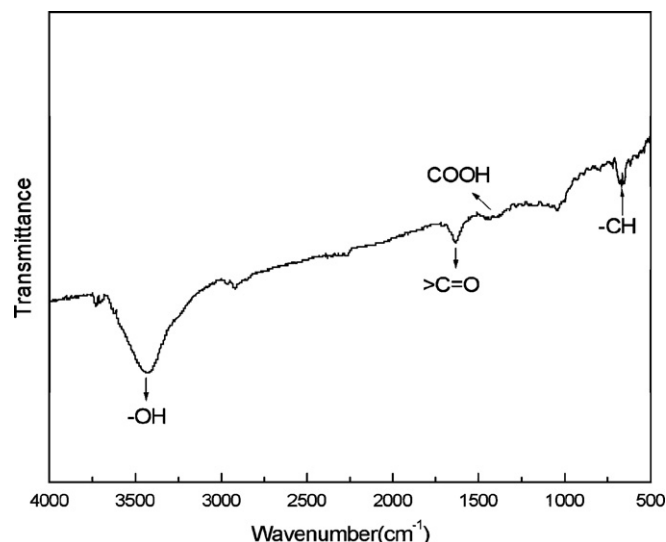
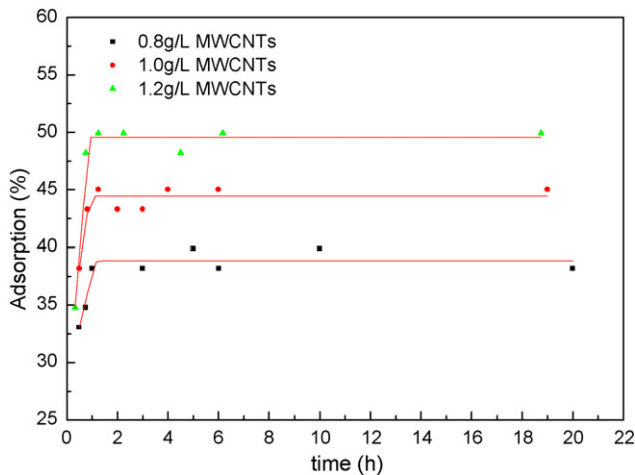


Fig. 2. FTIR spectrum of oxidized MWCNTs.



**Fig. 3.** Adsorption of Ni(II) on oxidized MWCNTs as a function of contact time.  $T=20 \pm 2^\circ\text{C}$ ,  $\text{pH}=6.4 \pm 0.1$ ,  $C_{(\text{Ni})\text{initial}}=1.02 \times 10^{-4} \text{ mol/L}$  and  $I=0.01 \text{ mol/L NaClO}_4$ .

oxidized MWCNTs. Meanwhile, the hydrophilic properties of these functional groups improve the dispersivity of oxidized MWCNTs in aqueous solution.

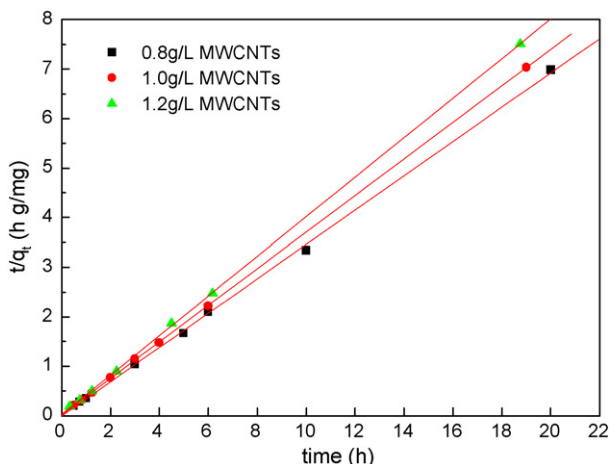
### 3.2. Adsorption kinetics

The effect of contact time on Ni(II) adsorption to oxidized MWCNTs is shown in Fig. 3. One can see that 2 h is enough to achieve the adsorption equilibrium for all oxidized MWCNT contents under our experimental conditions, which indicates that chemical adsorption rather than physical adsorption contributes mainly to the adsorption of Ni(II) [21]. In the following experiments, 24 h is selected to achieve the adsorption equilibrium.

The pseudo-second-order rate equation is used to simulate the kinetic adsorption process [22]:

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

Linear plot of  $t/q_t$  vs.  $t$  is achieved according to Eq. (1) (Fig. 4). The  $k$  and  $q_e$  values calculated from the slope and intercept are summarized in Table 1. The correlation coefficients of the pseudo-second-order equation for the linear plots are very close to 1, which indicates that the experimental data can be described by the pseudo-second-order model very well.



**Fig. 4.** Pseudo-second-order rate equation fit of the adsorption kinetics.

**Table 1**

Kinetic parameters of Ni(II) adsorption on oxidized MWCNTs at various MWCNT contents.

m/V (g MWCNTs)/L	Pseudo-second-order parameters		
	$q_e$ (mg/g)	$k$ (g/(mg h))	$R^2$
0.8	2.9036	3.1214	0.9994
1.0	2.7099	3.3295	0.9999
1.2	2.5048	3.1414	0.9999

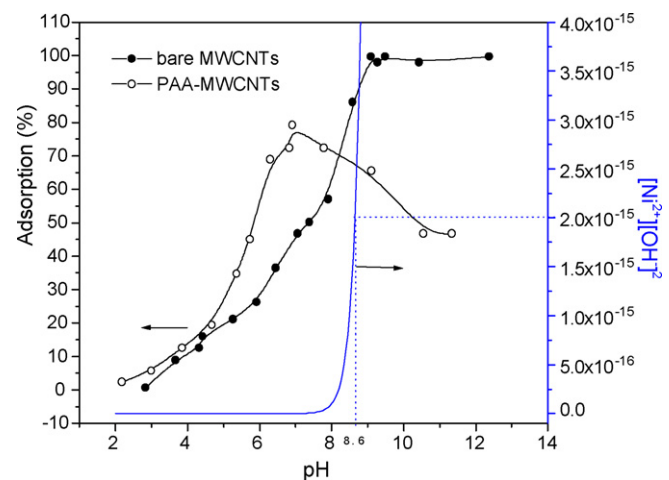
**Table 2**

Equilibrium constants [ $\log K_a$ ] for Ni(II) hydrolysis reactions [42].

Hydrolysis reactions	$\log K_a$
$\text{Ni}^{2+} + \text{OH}^- = \text{Ni}(\text{OH})^+$	4.1
$\text{Ni}^{2+} + 2\text{OH}^- = \text{Ni}(\text{OH})_2^0$	8.5
$\text{Ni}^{2+} + 3\text{OH}^- = \text{Ni}(\text{OH})_3^-$	11.5
$\text{Ni}^{2+} + 4\text{OH}^- = \text{Ni}(\text{OH})_4^{2-}$	12

### 3.3. Effect of pH on Ni(II) adsorption in the absence/presence of PAA

Fig. 5 shows the pH dependence of Ni(II) adsorption on oxidized MWCNTs in the presence and absence of PAA. It is clear that the pH of solution plays an important role on the adsorption of Ni(II) to oxidized MWCNTs. In the absence of PAA, the removal of Ni(II) increases gradually from about zero to ~99% at pH 2–9, and then maintains high level with increasing pH values. The results are consistent with the adsorption of Ni(II) on Na-rectorite [21] and the adsorption of Cu(II) on MWCNTs [23]. The increase of Ni(II) adsorption on oxidized MWCNTs with increasing pH is probably attributed to the hydrolysis of Ni(II) and the surface properties of oxidized MWCNTs. Fig. 6 shows the relative proportion of nickel species calculated from the hydrolysis constants of Ni(II) listed in Table 2. It is clear that nickel presents in the species of  $\text{Ni}^{2+}$ ,  $\text{Ni}(\text{OH})^+$ ,  $\text{Ni}(\text{OH})_2^0$ ,  $\text{Ni}(\text{OH})_3^-$  and  $\text{Ni}(\text{OH})_4^{2-}$  at different pH values. At  $\text{pH} < 9$ , the predominant species is  $\text{Ni}^{2+}$ . Therefore, the low  $\text{Ni}^{2+}$  adsorption at low pH is attributed partly to the competition between  $\text{H}^+/\text{Na}^+$  and  $\text{Ni}^{2+}$  on the surface sites [24,25]. Furthermore, the zeta potential of MWCNTs becomes negative with the increase of pH due to the deprotonation reaction (i.e.  $\text{MWCNT}-\text{OH} \rightarrow \text{MWCNT}-\text{O}^- + \text{H}^+$ ), which results in the electrostatic attraction of  $\text{Ni}^{2+}$  to the deprotonated surface of MWCNTs [26,27]. The point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of oxidized MWCNTs was measured to be at  $\text{pH} \approx 5.0$  by potentiometric titration method



**Fig. 5.** Effect of pH on adsorption of Ni(II) on bare and PAA bound MWCNTs.  $T=20 \pm 2^\circ\text{C}$ ,  $C_{(\text{Ni})\text{initial}}=1.02 \times 10^{-4} \text{ mol/L}$ ,  $C_{[\text{PAA}]}=10 \text{ mg/L}$ ,  $m/V=0.8 \text{ g/L}$  and  $I=0.01 \text{ mol/L NaClO}_4$ .

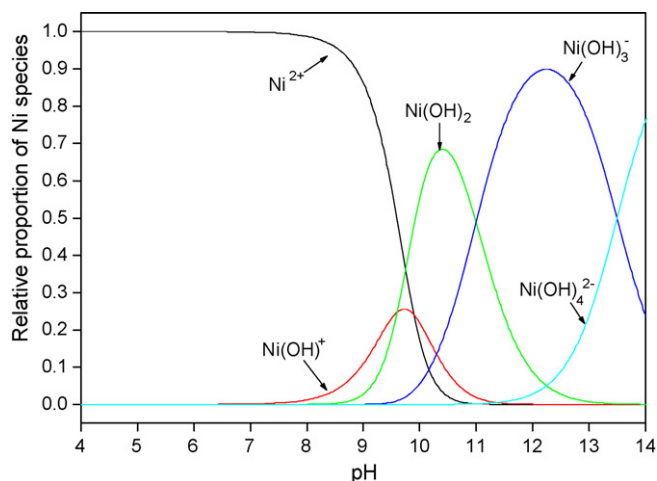


Fig. 6. Relative proportion of Ni(II) species as a function of pH.

using a computer controlled PC-titration system (DL50 Automatic Titrator, Mettler Toledo) [18,23]. At  $\text{pH} < \text{pH}_{\text{pzc}}$ , the surface charge of oxidized MWCNTs is positive. The ion exchange between  $\text{Ni}^{2+}$  and  $\text{H}^+/\text{Na}^+$  on oxidized MWCNT surface can lead to the adsorption of  $\text{Ni}^{2+}$ . At  $\text{pH} > \text{pH}_{\text{pzc}}$ , it is easily for the positively charged  $\text{Ni}^{2+}$  to be adsorbed on the negatively charged oxidized MWCNTs. The adsorption of  $\text{Ni}^{2+}$  on oxidized MWCNTs is not attributed to the precipitation of  $\text{Ni}(\text{OH})_2$  (s) because of the low precipitation constant ( $2.0 \times 10^{-15}$ ). The precipitation curve of nickel at the concentration of  $1.02 \times 10^{-4}$  mol/L is also shown in Fig. 5. It is clear that Ni(II) begins to form precipitation at  $\text{pH} \sim 8.6$  if no Ni(II) is adsorbed on oxidized MWCNTs. However, more than 90% Ni(II) is adsorbed on oxidized MWCNTs at  $\text{pH} 8.6$ . It is also necessary to note that the adsorption edges spread over three pH units are often relevant of the presence of many surface complexes [28,29]. The adsorption of Ni(II) on oxidized MWCNTs is complicated and cannot be described clearly by one or two mechanisms.

In the presence of PAA, the pH dependent adsorption curve shifts to left at  $\text{pH} < 8$ . The negatively charged PAA is easily adsorbed on oxidized MWCNTs at  $\text{pH} < 8$ . After the adsorption of negatively charged PAA on oxidized MWCNTs, the surface charge of oxidized MWCNTs becomes more negative as compared to the bare oxidized MWCNTs, which results in a more favorable electrostatic attraction for  $\text{Ni}^{2+}$  and thereby enhances the formation of Ni–PAA–MWCNTs ternary surface complexes [30]. The high complexation ability of PAA with Ni(II) also contributes the adsorption of Ni(II) because the adsorbed PAA forms strong complexes with Ni(II) on oxidized MWCNT surfaces. The result indicates that the complexation between PAA and Ni(II) is stronger than that between oxidized MWCNTs and Ni(II). A negative effect of PAA on Ni(II) adsorption at  $\text{pH} > 8$  is also found in Fig. 5. At  $\text{pH} > 8$ , the surface charge of oxidized MWCNTs is negative, thus the negatively charged PAA is difficult to be adsorbed on oxidized MWCNTs due to electrostatic repulsion. The soluble PAA forms strong PAA–Ni complexes in solution, and thereby results in the decrease of Ni(II) adsorption on PAA–MWCNT hybrids at high pH values.

The adsorption of Ni(II) on PAA–MWCNT hybrids is dependent on the adsorption of PAA on oxidized MWCNTs. As shown in Fig. 5, the effect of PAA on Ni(II) adsorption was dependent on pH values, which should be related to the adsorption of PAA on oxidized MWCNTs. The adsorption of PAA on oxidized MWCNTs as a function of pH is shown in Fig. 7. PAA is strongly adsorbed over the entire pH range studied. The strong adsorption affinity of PAA on oxidized MWCNTs is due to  $\pi$ – $\pi$  interactions between PAA and the grapheme sheets of oxidized MWCNTs. Gotovac et al. [31] proposed  $\pi$ – $\pi$  interac-

tions between the surface of purified SWCNTs and phenanthrene molecules. Long and Yang [32] attributes the strong adsorption of dioxin to MWCNTs to the strong interaction between the benzene rings of dioxin and the grapheme sheets composing the surface of MWCNTs. From Fig. 7, adsorption of PAA decreased a little with increasing pH. It is well known that PAA adsorbed on oxidized MWCNTs experiences not only an electrostatic attraction to the surface but also an electrostatic repulsion within the polymer itself. The latter case takes place at high pH when ionization of carboxylic groups increases the repulsion. At high pH values, more soluble PAA forms PAA–Ni complexes in solution and thereby reduces Ni(II) adsorption on oxidized MWCNTs.

### 3.4. Effect of foreign ions

In order to investigate the influence of background electrolyte ions on Ni(II) adsorption, the adsorption of Ni(II) on oxidized MWCNTs was studied as a function of pH values in 0.01 mol/L  $\text{NaClO}_4$ , NaCl,  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and  $\text{LiNO}_3$ , respectively. Fig. 8A shows that the adsorption of Ni(II) is the highest in 0.01 mol/L  $\text{KNO}_3$  solution and is the lowest in 0.01 mol/L  $\text{LiNO}_3$  solution at  $\text{pH} < 9$ , indicating that cations can alter the surface property of oxidized MWCNTs and thus can influence the adsorption of Ni(II) on oxidized MWCNTs. Fan et al. [29] investigated the effect of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  on Ni(II) adsorption to attapulgite and also found a similar result. The adsorption of Ni(II) on oxidized MWCNTs can be considered as a competition of Ni(II) with foreign cations ( $\text{Li}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$ ) at oxidized MWCNT surfaces. The radius of  $\text{Li}^+$  is smaller than those of  $\text{Na}^+$  and  $\text{K}^+$ , therefore  $\text{Li}^+$  has the highest affinity to the surface of oxidized MWCNTs and the highest tendency for counter-ion exchange with the surface groups of oxidized MWCNTs, which reduces ion interaction sites on the surface of oxidized MWCNTs with Ni(II). However, the adsorption of Pb(II) to oxidized MWCNTs is weakly influenced by the background foreign ions [20]. The influence sequence of foreign alkali metal ions on adsorption of Pb(II) to bentonite at low pH is in the range of  $\text{Li}^+ \approx \text{Na}^+ > \text{K}^+$  [33], which is similar to the results of this work. The results indicate that the influence of foreign ions on metal ions' adsorption is dominated by the properties of metal ions, the properties of adsorbent and other parameters such as pH, ionic strength, etc.

From Fig. 8B, one can see that the adsorption of Ni(II) on oxidized MWCNTs is the lowest in 0.01 mol/L NaCl solution and is the highest in 0.01 mol/L  $\text{NaClO}_4$  solution at  $\text{pH} < 8$ . This phenomenon

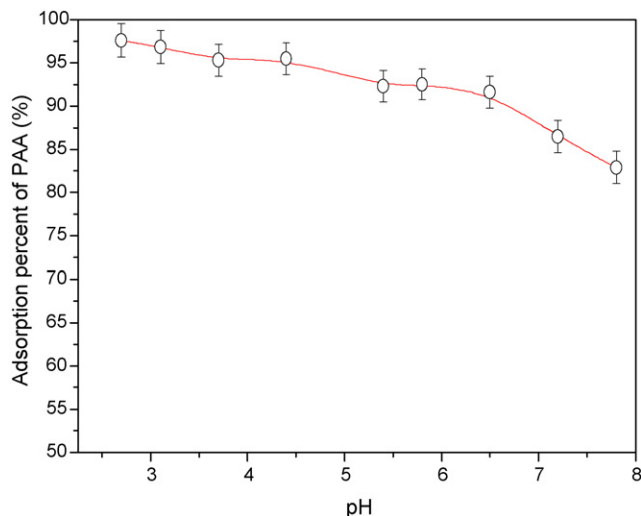


Fig. 7. Adsorption of PAA on oxidized MWCNTs as a function pH.  $T = 20 \pm 2^\circ \text{C}$ ,  $C_{\text{PAA}} = 10$  mg/L,  $m/V = 0.8$  g/L and  $I = 0.01$  mol/L  $\text{NaClO}_4$ .

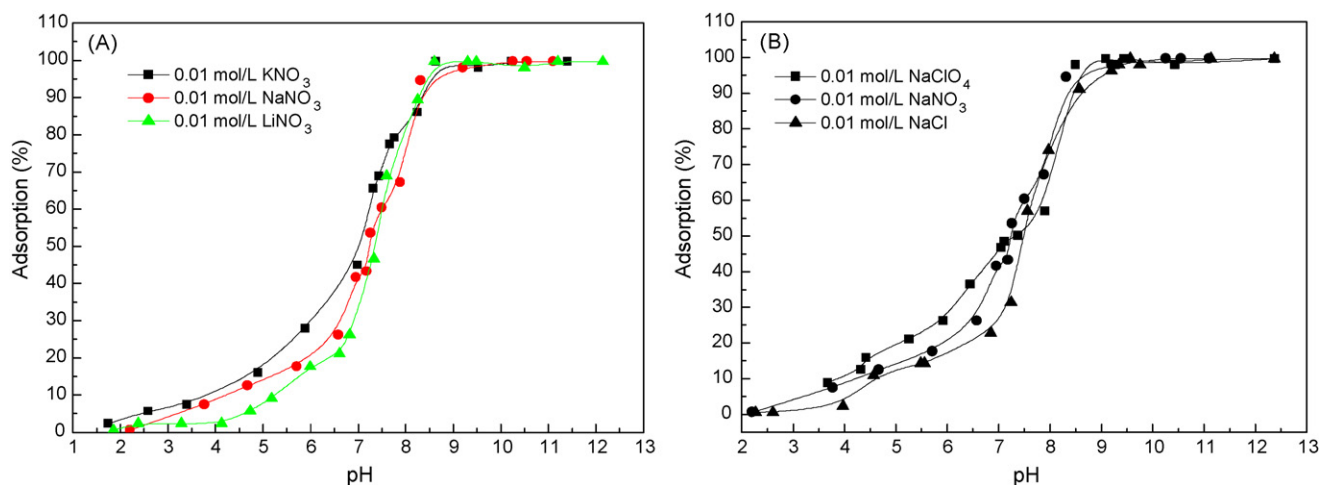


Fig. 8. Influence of foreign ions and pH on the adsorption of Ni(II) on oxidized MWCNTs.  $T = 20 \pm 2^\circ\text{C}$ ,  $C_{(\text{Ni})\text{initial}} = 1.02 \times 10^{-4}$  mol/L and  $m/V = 0.8$  g/L.

may be attributed to: (1)  $\text{Cl}^-$  and  $\text{NO}_3^-$  can form soluble complexes with Ni(II) (e.g.  $\text{NiCl}^+$  and  $\text{NiNO}_3^+$ ), whereas  $\text{ClO}_4^-$  does not form complexes with Ni(II). Ni(II) has higher affinity with  $\text{Cl}^-$  than  $\text{NO}_3^-$  and  $\text{ClO}_4^-$ ; (2) compared with  $\text{NO}_3^-$  and  $\text{ClO}_4^-$ ,  $\text{Cl}^-$  is easier to form idiocratic adsorption on the solid surface, which changes the surface state of oxidized MWCNTs and decreases the availability of binding sites; (3) the inorganic acid radical radius order is  $\text{Cl}^- < \text{NO}_3^- < \text{ClO}_4^-$ , the smaller radius inorganic acid radicals takes up more ionic exchange sites and leads to the decrease of Ni(II) adsorption on oxidized MWCNTs [29,34].

### 3.5. Effect of PAA concentration on Ni(II) adsorption

The adsorption of Ni(II) to PAA–MWCNT hybrids as a function of initial PAA concentration at  $\text{pH} = 5.4 \pm 0.1$  and in 0.01 mol/L  $\text{NaClO}_4$  solution is shown in Fig. 9. One can see that the adsorption of Ni(II) increases with increasing PAA initial concentration. The distribution coefficient ( $K_d$ ) values show a similar change tendency with the adsorption percentage. The  $K_d$  value is calculated as [35]:

$$K_d = \frac{C_0 - C_{\text{eq}}}{C_{\text{eq}}} \frac{V}{m} \quad (2)$$

At higher concentration of PAA, more PAA molecules are adsorbed on oxidized MWCNTs and thereby provides more functional groups

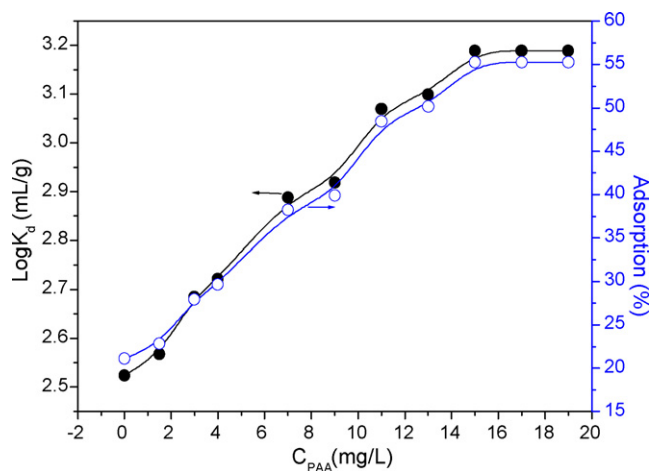


Fig. 9. Effect of PAA initial concentrations on the adsorption of Ni(II) on oxidized MWCNTs.  $\text{pH} = 5.4 \pm 0.1$ ,  $T = 20 \pm 2^\circ\text{C}$ ,  $C_{(\text{Ni})\text{initial}} = 1.02 \times 10^{-4}$  mol/L,  $m/V = 0.8$  g/L and  $I = 0.01$  mol/L  $\text{NaClO}_4$ .

to form strong complexes with Ni(II) at oxidized MWCNT surfaces. The adsorbed PAA molecules screen the high-energy sites and produce new energetic peaks on the surfaces of oxidized MWCNTs [36]. Such surface energetic heterogeneity changes make oxidized MWCNTs more stable in water, which is more advantageous to the adsorption of heavy metal ions.

### 3.6. Adsorption isotherms of Ni(II) on bare and PAA bound MWCNTs

Fig. 10 shows the adsorption isotherms of Ni(II) on oxidized MWCNTs in the absence and presence of PAA. One can see that the adsorption isotherm of Ni(II) on PAA–MWCNT hybrids is higher than that of Ni(II) on bare oxidized MWCNTs. The positive effect of PAA on Ni(II) adsorption can be explained by metal ion complexation with the surface adsorbed PAA, and suggests a surface-binding of Ni(II) via PAA “bridge” between the solid surface and metal ion. In order to optimize the adsorption process and to forecast adsorption behavior, Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models are conducted, respectively, to simulate the adsorption isotherms of Ni(II) on bare and PAA bound oxidized MWCNTs.

As an equilibrium model describing the quantification relations between the heavy metal ion adsorptive capacities and metallic ion equilibrium concentration in solution, the Langmuir adsorp-

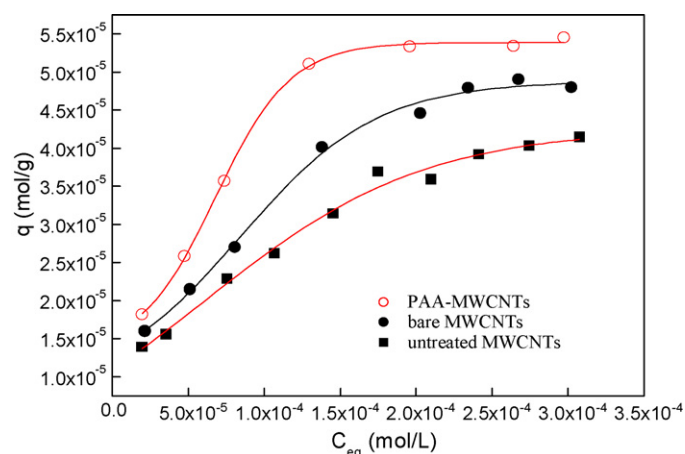


Fig. 10. Adsorption isotherms of Ni(II) on bare and PAA bound MWCNTs.  $C_{[\text{PAA}]} = 10$  mg/L,  $m/V = 0.8$  g/L,  $\text{pH} = 5.4 \pm 0.1$ ,  $I = 0.01$  mol/L  $\text{NaClO}_4$  and  $T = 20 \pm 2^\circ\text{C}$ .

tion isotherm has been used successfully to characterize monolayer adsorption process. It can be represented by the following equation [5,24]:

$$q = \frac{bq_{\max}C_{\text{eq}}}{1 + bC_{\text{eq}}} \quad (3)$$

Eq. (3) can be expressed in linear form:

$$\frac{C_{\text{eq}}}{q} = \frac{1}{bq_{\max}} + \frac{C_{\text{eq}}}{q_{\max}} \quad (4)$$

The Freundlich isotherm model is a semi-empirical equation based on the adsorption phenomenon occurred on heterogeneous surface. It has the following form [37]:

$$q = k_F C_{\text{eq}}^n \quad (5)$$

Eq. (5) can be expressed in linear form:

$$\log q = \log k_F + n \log C_{\text{eq}} \quad (6)$$

The D–R isotherm model is valid at low concentration ranges and can be used to describe adsorption on both homogeneous and heterogeneous surfaces. The D–R equation has the general expression [33,37]:

$$q = q_{\max} \exp(-\beta\varepsilon^2) \quad (7)$$

or in the linear form:

$$\ln q = \ln q_{\max} - \beta\varepsilon^2 \quad (8)$$

The Polanyi potential ( $\varepsilon$ ) is equal to:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_{\text{eq}}} \right) \quad (9)$$

$E$  is defined as the free energy change ( $\text{kJ mol}^{-1}$ ), which requires to transfer 1 mol of ions from solution to the solid surfaces. The relation is as the following:

$$E = \frac{1}{\sqrt{2\beta}} \quad (10)$$

The relative parameters calculated from the three models are listed in Table 3. It can be concluded from the correlation coefficients that Langmuir model fits the experimental data better than Freundlich and D–R models. The values of  $q_{\max}$  obtained from Langmuir model for Ni(II) adsorption on PAA bound oxidized MWCNTs is higher than that on bare oxidized MWCNTs, which indicates that the adsorbed PAA on oxidized MWCNTs enhances the adsorption of Ni(II) on PAA–MWCNT hybrids. The value of  $k_F$  calculated from the Freundlich model is large, which indicates that oxidized MWCNTs has a high adsorption affinity towards Ni(II). The deviation of  $n$  from unity indicates a non-linear adsorption that takes place on the heterogeneous surfaces. The magnitude of  $E$  is useful for estimating the mechanism of the adsorption reaction. Adsorption is dominated by chemical ion-exchange if  $E$  is in the range of 8–16  $\text{kJ mol}^{-1}$ , whereas physical forces may affect the adsorption in the case of  $E < 8 \text{ kJ mol}^{-1}$  [38,39]. The  $E$  values obtained from Eq. (10) are 10.99 for bare MWCNTs and 11.39  $\text{kJ mol}^{-1}$  for PAA–MWCNT hybrids, which are in the adsorption energy range of chemical ion-exchange reaction. This suggests that Ni(II) adsorption onto oxidized MWCNTs is attributed to chemical adsorption rather than physical adsorption.

The adsorption of Ni(II) on the untreated MWCNTs is also shown in Fig. 10 as a comparison. After the oxidation process, the functional groups at surfaces of oxidized MWCNTs increase and thereby enhance the adsorption of Ni(II) obviously. From Fig. 10, the adsorption isotherm of Ni(II) on the untreated MWCNTs is lower than that of Ni(II) on the oxidized MWCNTs, which is also the evidence of the presence of oxygen-containing functional groups on

**Table 3**

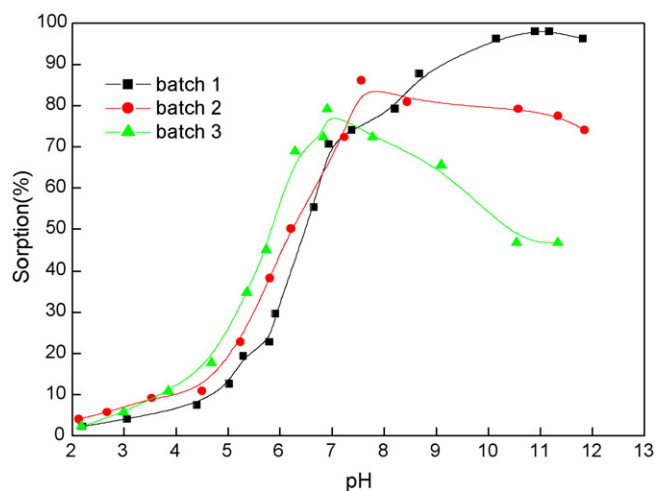
The parameters for Langmuir, Freundlich and D–R isotherm models of Ni(II) adsorption on bare and PAA bound oxidized MWCNTs.

Models	Parameters			
	$q_{\max}$ (mol/g)	$b$ (L/mol)	$R^2$	
Langmuir				
Bare MWCNTs	$6.346 \times 10^{-5}$	11593.094	0.9901	
PAA–MWCNTs	$6.615 \times 10^{-5}$	17503.867	0.9938	
Models	Parameters			
	$k_F$ ( $\text{mol}^{1-n} \text{L}^n/\text{g}$ )	$n$	$R^2$	
Freundlich				
Bare MWCNTs	$2.118 \times 10^{-3}$	0.4575	0.9896	
PAA–MWCNTs	$1.931 \times 10^{-3}$	0.4262	0.9716	
Models	Parameters			
	$q_{\max}$ (mol/g)	$\beta$ ( $\text{mol}^2/\text{kJ}^2$ )	$E$ (kJ/mol)	$R^2$
D–R				
Bare MWCNTs	$2.531 \times 10^{-4}$	$4.137 \times 10^{-3}$	10.99	0.9888
PAA–MWCNTs	$2.672 \times 10^{-4}$	$3.857 \times 10^{-3}$	11.39	0.9772

the surfaces of oxidized MWCNTs. These functional groups are active to form complexes with Ni(II) on the surfaces of oxidized MWCNTs.

### 3.7. Influence of addition sequences in the ternary Ni–PAA–MWCNT systems

In order to check for the reversibility of the adsorption process, the adsorption of Ni(II) in the ternary Ni–PAA–MWCNT systems for three different addition sequences are investigated and the results are shown in Fig. 11. At  $\text{pH} < 7$ , the adsorption percentage of Ni(II) is the highest for batch 3 and is the lowest in batch 1. However, the adsorption percentage of Ni(II) is the highest for batch 1 and is the lowest in batch 3 at  $\text{pH} > 7$ . Bryce et al. [40] found that the fraction of nickel adsorbed to the hydrous ferric oxide depended on the component addition sequence. However, Tan et al. [27] found that different addition sequences of Ni(II)/SDBS/MWCNTs have no obvious influences on the adsorption of Ni(II) on oxidized MWCNTs. Many literatures gave the interpretation that the fraction of organic matter adsorbed on solid surfaces was different to the fraction of organic matter remained in solution, and thereby the adsorption



**Fig. 11.** The addition sequences of Ni(II) and PAA on Ni(II) adsorption to PAA bound MWCNTs.  $T = 20 \pm 2^\circ\text{C}$ ,  $C_{\text{Ni(II)initial}} = 1.02 \times 10^{-4} \text{ mol/L}$ ,  $C_{\text{PAA}} = 10 \text{ mg/L}$ ,  $m/V = 0.8 \text{ g/L}$  and  $I = 0.01 \text{ mol/L NaClO}_4$ .

of metal ions was affected by the addition sequences [30,41]. The adsorption of Ni(II) is dominated by the interaction of Ni(II) with surface sites of MWCNTs, by the interaction of Ni(II) with surface adsorbed PAA on MWCNT surface and by the interaction of Ni(II) with solution soluble PAA in solution. In batch 1, Ni(II) was first adsorbed to MWCNTs and then PAA was added to Ni–MWCNTs. At low pH values, the adsorption of Ni(II) on bare MWCNTs is lower than that of Ni(II) on PAA–MWCNT hybrids, whereas the adsorption of Ni(II) on bare MWCNTs is higher than that of Ni(II) on PAA–MWCNT hybrids at high pH values. In batch 1, Ni(II) first formed adsorption equilibration with bare MWCNTs before the addition of PAA. This is the plausible interpretation to the results.

The species of heavy metal ions adsorbed on organic material bound solid surfaces are dependent on both the solid surface properties and the organic material. Without a doubt, the effect of organic material on the adsorption of metal ions on solid surfaces is important. The influence of addition sequences of organic material/metal ion on metal ion adsorption to solid surface is significant to evaluate the physicochemical behavior of metal ion in the natural environment.

#### 4. Conclusions

From the results of Ni(II) adsorption on oxidized MWCNTs under our experimental conditions, the following conclusions can be obtained:

- (1) The adsorption of Ni(II) on oxidized MWCNTs achieves equilibration rapidly. The kinetic adsorption of Ni(II) on oxidized MWCNTs can be described by a pseudo-second-order model well.
- (2) The adsorption of Ni(II) on oxidized MWCNTs increases with increasing pH.
- (3) The adsorption of Ni(II) on oxidized MWCNTs is dependent on foreign ions at low pH values, and independent of foreign ions at high pH values.
- (4) The adsorption of Ni(II) is influenced by PAA significantly, and the effect of PAA on Ni(II) adsorption is dependent on pH values. In the presence of PAA, the adsorption is enhanced at low pH values and is reduced at high pH values.
- (5) The adsorption of Ni(II) on oxidized MWCNTs in the presence of PAA is dependent on the addition sequences of PAA, Ni(II) and MWCNTs. The relative strength between the complexes of Ni(II) with PAA adsorbed on oxidized MWCNTs or soluble PAA in solution is higher than the complexation of Ni(II) with surface sites of oxidized MWCNTs.
- (6) Ion exchange or outer-sphere surface complexation is the main mechanism for the adsorption of Ni(II) at low pH values, whereas inner-sphere surface complexation is the main mechanism for the adsorption of Ni(II) at high pH values. The adsorption of Ni(II) on oxidized MWCNTs is complicated and cannot be described by one or two mechanisms simply.
- (7) Oxidized MWCNTs is a promising material for pre-concentration and solidification of Ni(II) ion from large volume of solutions. The presence of organic material can promote the removal of metal ions from solution to oxidized MWCNTs.

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#### Appendix A. Notation

Parameter	Description	
$k$ ( $\text{g mg}^{-1} \text{h}^{-1}$ )	pseudo-second-order rate constant of adsorption	pseudo-second-order model parameters
$q_t$ ( $\text{mg g}^{-1}$ of dry mass)	amount of Ni(II) adsorbed on oxidized MWCNTs at time $t$ (h)	
$q_e$ ( $\text{mg g}^{-1}$ of dry mass)	equilibrium adsorption capacity	
$t$ (h)	contact time	
$K_d$ (mL/g)	distribution coefficient	distribution coefficient parameters
$C_0$ (mol/L)	the initial concentration of Ni(II)	
$C_{eq}$ (mol/L)	the equilibrium concentration of Ni(II) in supernatant	
$V$ (L)	the volume of the suspension	
$m$ (g)	the mass of oxidized MWCNTs	
$q$ (mol/g)	amount adsorbed on oxidized MWCNTs after equilibrium	Langmuir model parameters
$q_{max}$ (mol/g)	maximum adsorption capacity at complete monolayer coverage	
$b$ (L/mol)	a constant that relates to the heat of adsorption	
$k_f$ ( $\text{mol}^{1-n} \text{L}^n/\text{g}$ )	represents the adsorption capacity when metal ion equilibrium concentration equals to 1	Freundlich model parameters
$n$	the degree of dependence of adsorption with equilibrium concentration	
$\beta$ ( $\text{mol}^2/\text{kJ}^2$ )	the activity coefficient related to mean adsorption energy	D–R model parameters
$R$ (8.3145 J/(mol K))	the ideal gas constant	
$T$ (K)	the absolute temperature in Kelvin	
$E$ (kJ/mol)	the free energy change	
$\varepsilon$	the Polanyi potential	

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