

Available online at www.sciencedirect.com



*Journal of* Hazardous Materials

Journal of Hazardous Materials 151 (2008) 239-246

www.elsevier.com/locate/jhazmat

# Comparisons of sorbent cost for the removal of Ni<sup>2+</sup> from aqueous solution by carbon nanotubes and granular activated carbon

Chungsying Lu\*, Chunti Liu, Gadupudi Purnachadra Rao

Department of Environmental Engineering, National ChungHsing University, 250 Kuo Kuang Road, Taichung 402, Taiwan

Received 28 August 2006; received in revised form 3 May 2007; accepted 28 May 2007

Available online 2 June 2007

#### Abstract

The reversibility of Ni<sup>2+</sup> sorption by NaOCl oxidized single-walled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs) and granular activated carbon (GAC) was investigated to evaluate their repeated availability performance in water treatment. Under the same conditions, the SWCNTs and MWCNTs possess more Ni<sup>2+</sup> sorption capacities and show better reversibility of Ni<sup>2+</sup> sorption and less weight loss after being repeated sorption/desorption processes than the GAC, suggesting that they are effective Ni<sup>2+</sup> sorbents and can be reused through many cycles of water treatment and regeneration. A statistical analysis on the replacement cost of these sorbents revealed that SWCNTs and MWCNTs can be possibly cost-effective Ni<sup>2+</sup> sorbents in water treatment regardless of their high unit cost at the present time.

Keywords: Carbon nanotubes; Granular activated carbon; Sorption; Desorption; Nickel

# 1. Introduction

Removal of heavy metals from wastewaters and industrial wastes has become a very important environmental issue. Nickel salts are commonly used in silver refineries, electroplating, zinc base casting, storage battery industries, printing, and in the production of some alloys [1] and discharge significant amount of nickel in various forms to the environment. At higher concentrations, Ni<sup>2+</sup> causes lungs, nose and bone cancer, headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [2]. Hence, it is essential to remove Ni<sup>2+</sup> from industrial wastewaters before discharge into natural water sources. Several treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly ion exchange, solvent extraction, evaporation, electrochemical reduction, chemical precipitation, reverse osmosis, and adsorption. Among all the above methods adsorption is effective and simple. Different kinds of adsorbents have been employed for nickel ion removal including activated carbon [3], kaolinite [4], sugar beet pulp [5], activated carbon cloths [6], peanut hulls [7],

0304-3894/\$ – see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2007.05.078

modified chitosan [8] granular biomass [9] and crab shell [10]. However, these adsorbents suffer from low adsorption capacities or removal efficiencies. Therefore, researchers carried out investigation for new promising adsorbents.

Carbon nanotubes (CNTs) are unique and one-dimensional macromolecules that possess outstanding thermal and chemical stability [11]. These nanomaterials have been proven to be effective sorbents for removing many kinds of heavy metals such as lead [12], cadmium [13], copper [14] and zinc [15] from an aqueous environment. The sorption mechanisms of heavy metal by CNTs are very complicated and appear mainly attributable to the chemical interactions between the metal ions and the negatively charged surface functional groups of the CNTs [15]. Although the CNTs possess large sorption capacity of heavy metal, the very high unit cost when compared to the other commercially available adsorbents such as activated carbons currently restricts their potential use for environmental protection applications. Thus, developing a new method of CNT production to reduce their unit cost or testing the reversibility of heavy metal ion sorption with CNTs to diminish their replacement cost is needed before practical use of CNTs in water treatment can be realized.

The paper tested the reversibility of Ni<sup>2+</sup> sorption in an aqueous solution, which is discharged from many kinds of industrial activities [16], by single-walled CNTs (SWCNTs), multiwalled

<sup>\*</sup> Corresponding author. Tel.: +886 4 22852483; fax: +886 4 22862587. *E-mail addresses:* clu@nchu.edu.tw, clu@dragon.nchu.edu.tw (C. Lu).

CNTs (MWCNTs) and granular activated carbon (GAC) to evaluate their repeated availability performance in water treatment. A statistical analysis on the replacement cost of these sorbents was also given.

# 2. Materials and methods

# 2.1. Sorbents

Commercially available MWCNTs with outer diameter (dp) < 10 nm, SWCNTs with dp < 2 nm (L-type, Nanotech Port Co., Shenzhen, China) and GAC with particle diameter range 0.55–0.75 mm (Filtrasorb 400, Calgon Carbon Co., Tianjia, China) were selected as sorbents in this study. The length of CNTs was in the range 5–15  $\mu$ m and the amorphous carbon content in the CNTs was <5 wt%. These data were provided by the manufacturer.

Raw sorbents (1 g) were heated at 350 °C using an oven for 20 min to remove amorphous carbon. After this thermal treatment, the sorbents were dispersed into a flask containing 40 ml of 40% NaOCl (24 ml of H<sub>2</sub>O + 16 ml of NaOCl). The mixture was then shaken in an ultrasonic cleaning bath (Model D400H, Delta Instruments Co., USA) for 20 min and was refluxed at 100 °C for 40 min to remove metal catalysts (Ni nanoparticles). After cooling to room temperature, the mixture was filtered through a 0.45  $\mu$ m Nylon fiber filter and the solid was washed with deionized water until the pH of the filtrate was 7. The filtered solid was then dried at 70 °C for 2 h. The weight loss of sorbents after purification process was <4 wt%.

# 2.2. Sorbates

Analytical grade nickel sulphate (Merck Ltd., Taipei, Taiwan, 97% purity) was employed to prepare a stock solution containing  $1 \text{ g l}^{-1}$  of Ni<sup>2+</sup>. The stock solution was further diluted with deionized water to the desired Ni<sup>2+</sup> concentrations. The use of deionized water was to prevent the effect of ionic strength on Ni<sup>2+</sup> sorption.

#### 2.3. Batch sorption experiments

Batch sorption experiments were conducted using 150 ml glass bottles with addition of 50 mg of sorbents and 100 ml of Ni<sup>2+</sup> solution of initial concentrations ( $C_0$ ) from 10 to 80 mg l<sup>-1</sup>. The concentration ranges were chosen to be representative of Ni<sup>2+</sup> concentration in raw water and wastewater. The glass bottles were sealed with 20 mm rubber stopper and then were mounted on a shaker, which was placed in a temperaturecontrolled box (Model CH-502, Chin Hsin, Taipei, Taiwan) and operated at 25 °C and 180 rpm for 12 h. The choice of agitation speed of 180 rpm was to provide a high degree of mixing while the selection of contact time of 12 h was to assure the attainment of sorption equilibrium. All the experiments were triplicated and only the mean values were reported. The maximum deviation is <5%. Blank test was conducted without addition of sorbents, and the results indicated that only very little Ni<sup>2+</sup> uptake was occurring which had no influence on the sorption experiments.

The initial pH of the solution was adjusted at neutrality using  $0.1 \text{ M HNO}_3$  or 0.1 M NaOH, in which the predominant nickel species is always Ni<sup>2+</sup> [17].

The amount of sorbed  $Ni^{2+}$  was calculated as follows:

$$q = (C_0 - C_t) \times \frac{V}{m} \tag{1}$$

where q is the amount of Ni<sup>2+</sup> sorbed onto sorbents (mg g<sup>-1</sup>);  $C_0$  is the initial Ni<sup>2+</sup> concentration (mg l<sup>-1</sup>);  $C_t$  is the Ni<sup>2+</sup> concentration after a certain period of time (mg l<sup>-1</sup>); V is the initial solution volume (l); and m is the sorbent mass (g).

## 2.4. Batch sorption/desorption experiments

To evaluate the reversibility of Ni<sup>2+</sup> sorption, 50 mg of sorbents were added into 100 ml of solution with a  $C_0$  of 60 mg l<sup>-1</sup>. As the sorption reached equilibrium, the amount of Ni<sup>2+</sup> sorbed onto sorbents ( $q_e$ ) was measured and then the solution was filtered using a 0.45  $\mu$ m Nylon fiber filter to recover sorbents. These sorbents were added into 45 ml of HNO<sub>3</sub> solution whose strength was adjusted using 70% HNO<sub>3</sub> solution (JT Baker Chemicals BV, Deventer Holland, USA). Desorption experiments were also conducted at 25 °C and 180 rpm. The strength of regeneration solution and regeneration time to reach effective Ni<sup>2+</sup> desorption must be determined by laboratory testing. The sorbent weight after regeneration was measured to evaluate their chemical stability. The sorption/desorption process was repeated for 10 cycles.

# 2.5. Analytical methods

The Ni<sup>2+</sup> concentration was determined by a flame atomic absorption spectrometer (FAAS, model 100, Perkin-Elmer, USA). The physical properties of sorbents were determined by nitrogen adsorption at 77 K using ASAP 2020 surface area analyzer (Micromertics Inc., Norcross, GA, USA). N<sub>2</sub> adsorption isotherms were measured at a relative pressure range of 0.0001–0.99. The adsorption data were then employed to determine surface area using the Brunauer, Emmett, and Teller (BET) equation and pore size distribution (including average pore diameter and pore volume) using the Barrett, Johner, and Halenda (BJH) equation.

The surface functional groups of sorbents were detected by a Fourier transform infrared (FTIR) spectroscometer (model FT/IR-200, JAS Co., Tokyo, Japan). The acidic and basic site concentrations of sorbents were determined by Boehm titration method [18]. One hundred millligrams of sorbents were placed in 100 ml flask containing 50 ml of the following 0.1 M solutions: Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, NaOH and HCl. The flask was sealed and shaken for 48 h. The solution was then filtered through a 0.45  $\mu$ m Nylon fiber filter and 10 ml of each filtrate was pipetted. The excess of base was titrated with 0.1 M HCl while the excess of acid was titrated with 0.1 M NaOH. The acidic site concentrations of various types were determined from the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na<sub>2</sub>CO<sub>3</sub> only neutralizes carboxylic groups. The

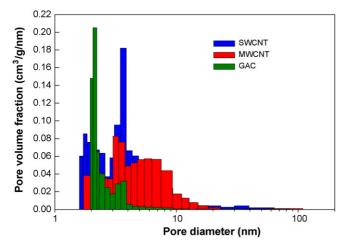


Fig. 1. Pore size distributions of sorbents.

basic site concentrations were determined from the amount of HCl reacted with the sorbents.

## 3. Results and discussion

#### 3.1. Characterization of sorbents

Fig. 1 exhibits the pore size distributions of CNTs and GAC. Pore size distributions of SWCNTs and MWCNTs are similar and can be characterized as a bimodal distribution including a fine fraction and a coarse fraction. The pores in the coarse fraction are likely to be contributed by aggregated pores which are formed within the confined space among the isolated CNTs. The pores in the fine fraction are the CNT inner cavities, close to the inner CNT diameter. The fine and coarse fractions, respectively, are concentrated in the 1-2 and 3-5 nm width range for the SWCNTs and in the 2-4 and 5-7 nm width range for the MWCNTs. The GAC has also a bimodal pore size distribution but contains finer pore volume fractions than the CNTs, which could be attributed to the formation of aggregated pores among the isolated CNTs. The fine and coarse fractions of GAC are concentrated near  $\sim 2$  and 3–4 nm width range, respectively.

Fig. 2 presents the adsorption–desorption isotherms of  $N_2$  onto CNTs and GAC. It is apparent that the adsorption and desorption curves of CNTs follow the type IV adsorption isotherms, with a rounded knee at low relative pressures representing a micropore volume in the CNTs, a rise in  $N_2$  adsorption capacity

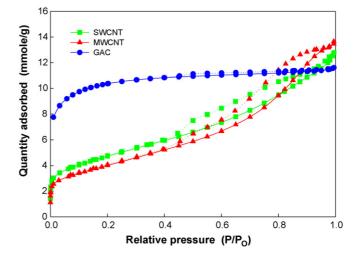


Fig. 2.  $N_2$  adsorption (solid line) and desorption (dash line) isotherms of oxidized CNTs and GAC.

with relative pressure. The adsorption and desorption curves of GAC display a plateau with relative pressure and nearly coincide with each other, indicating the absence of adsorption hysteresis.

The physical properties of CNTs and GAC are given in Table 1. The BET surface area, average pore diameter, and pore volume of CNTs were decreased after treated with NaOCl solution. This could be evident that the pore entrance blockage by the formation of oxygen-containing functional groups that are direct products of oxidation [19]. As can be observed, the GAC possesses more BET surface areas but smaller average pore diameter and pore volume than the CNTs. Most pore volume fractions of SWCNTs and GAC are in the 2–5 nm width range.

Fig. 3 shows the Fourier transform infrared spectra of oxidized CNTs and GAC. The IR spectra of these sorbents display very similar peak distributions. The peak at  $\sim$ 3324 cm<sup>-1</sup> can be assigned to –OH stretch from carboxylic groups (–COOH and –COH) while the peak at  $\sim$ 2354 cm<sup>-1</sup> can be related to –OH stretch from strong H-bonded-COOH [20]. The peak at  $\sim$ 1700 and 1540 cm<sup>-1</sup> is associated with the carboxylic acid and carboxylate anion stretch mode, the adsorption band at 1392 cm<sup>-1</sup> ( $\sim$ 1410 cm<sup>-1</sup>) assigned to lactones [21]. The peak between  $\sim$ 1000 and 1300 cm<sup>-1</sup> can be attributed to C–O stretching and –OH bending modes of alcoholic, phenolic, and carboxylic groups. The peaks at  $\sim$ 1175, 1130, and 1000 cm<sup>-1</sup> associated with phenolic –OH group, carboxylic –OH group

Table 1
Physical properties of CNTs and GAC

Sorbents	BET SA	APD	PV	% of total PV in stated pore size (nm) range		
				<2	2-50	>50
Raw-SWCNT	514	7.98	1.15	1.12	91.54	7.34
SWCNT	380	4.62	0.46	5.84	89.54	4.62
Raw-MWCNT	482	8.27	1.15	0.83	91.75	7.42
MWCNT	323	5.21	0.49	3.48	92.68	3.84
GAC	800	2.99	0.11	11.83	83.98	4.18

*Note*: SA, surface area (m<sup>2</sup> g<sup>-1</sup>); APD, average pore diameter (nm), PV, pore volume (cm<sup>3</sup> g<sup>-1</sup>).

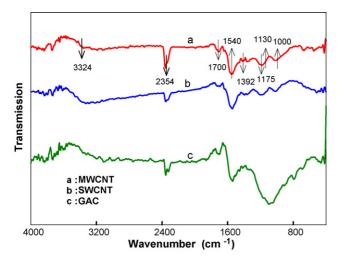
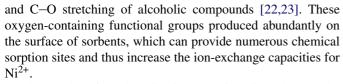


Fig. 3. Fourier transform infrared spectra of sorbents.



The results of Boehm titration are given in Table 2. The amounts of lactonic groups on the SWCNTs are the greatest, followed by the phenolic groups, and then the carboxylic groups. The quantities of phenolic groups on the MWCNTs are the most, followed by the lactonic groups, and then the carboxylic groups. The numbers of carboxylic groups on the GAC are the greatest, followed by the phenolic groups, and then the lactonic groups. These sorbents have more surface total acidities than surface total basicities, reflecting that the surface of these sorbents maintained acidic characteristics. The surface total acidities and basicities which are responsible for the sorption of cations and anions from aqueous solution [24], respectively, are the most for the SWCNTs, followed by the MWCNTs and then the GAC. The mechanism for sorption of Ni<sup>2+</sup> onto CNTs is graphically presented in Fig. 4.

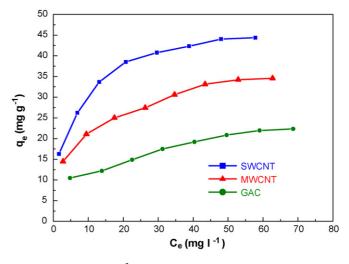


Fig. 5. Ni<sup>2+</sup> sorption isotherms of sorbents.

# 3.2. Sorption isotherm

Fig. 5 presents the Ni<sup>2+</sup> sorption isotherms of CNTs and GAC. The  $q_e$  of SWCNTs, MWCNTs and GAC, respectively, are 16.22, 14.76 and 10.61 mg g<sup>-1</sup> with a  $C_0$  of 10 mg l<sup>-1</sup> and 42.35, 33.12 and 20.82 mg g<sup>-1</sup> with a  $C_0$  of 60 mg l<sup>-1</sup>. It is apparent that the SWCNTs and MWCNTs have better performance of Ni<sup>2+</sup> sorption than the GAC, suggesting that they are efficient Ni<sup>2+</sup> sorbents in water treatment.

The  $q_e$  are correlated with isotherm models of Langmuir [25] and Freundlich [26],

$$q_{\rm e} = \frac{abC_{\rm e}}{1+bC_{\rm e}} \tag{2}$$

$$q_{\rm e} = K_{\rm f} C_{\rm e}^{1/n} \tag{3}$$

where  $C_e$  is the equilibrium Ni<sup>2+</sup> concentration (mg l<sup>-1</sup>); *a* is the maximum Ni<sup>2+</sup> sorption capacity (mg g<sup>-1</sup>); *b* is the Langmuir sorption constant (l mg<sup>-1</sup>); and  $K_f$  and *n* are the Freundlich constants. The constants of the isotherm model were obtained from

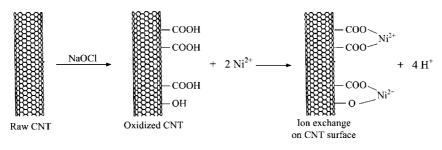


Fig. 4. Schematic diagram of the major mechanism for sorption of Ni<sup>2+</sup> onto sorbents.

Table 2
Results of Boehm titration

Sorbents	Carboxyls (mmol $g^{-1}$ )	Lactones (mmol $g^{-1}$ )	Phenols (mmol $g^{-1}$ )	Total acidity $(mmol g^{-1})$	Total basicity $(mmol g^{-1})$
SWCNT	0.8404	1.9905	1.5924	4.4234	0.3519
MWCNT	0.4583	1.2222	1.3750	3.0556	0.3109
GAC	1.2778	0.3310	0.4467	2.0555	0.2428

Sorbents	Concentration of Ni <sup>2+</sup> (mg l <sup>-1</sup> )	Langmuir	Langmuir			Freundlich		
		a	b	$R^2$	$\overline{K_{\mathrm{f}}}$	1/n	$R^2$	
SWCNT	10-80	47.85	0.207	0.9982	15.05	0.286	0.9747	
MWCNT	10-80	38.46	0.115	0.9939	10.75	0.293	0.9926	
GAC	10-80	26.39	0.073	0.9794	5.95	0.313	0.9603	

Table 3 Constants of Langmuir and Freundlich isotherm models

Unit:  $a = \operatorname{mg} g^{-1}$ ;  $b = 1 \operatorname{mg}^{-1}$ ;  $K_{f} = (\operatorname{mg} g^{-1}) (1 \operatorname{mg}^{-1})^{1/n}$ ; n, R = dimensionless.

fitting the isotherm model to the  $q_e$  and are given in Table 3. As can be seen, the  $q_e$  are better correlated with the Langmuir model than with the Freundlich model. The *a* and  $K_f$ , which represent the Ni<sup>2+</sup> sorption capacity, are the most for the SWCNTs, followed by the MWCNTs and then the GAC. The *b* which denotes the free energy of sorption presents the same trend as the *a* and  $K_f$ .

The *a* of SWCNTs, MWCNTs and GAC are 47.85, 38.46 and 26.39 mg g<sup>-1</sup>, respectively. The CNTs contain larger *a* than the GAC even though the surface area of GAC is more than that of CNTs, which could be explained by the fact that the CNTs possess greater surface total acidities than the GAC as shown in Table 2. This reflects that Ni<sup>2+</sup> sorption onto these sorbents is dependent on the concentration of specific active sites on the sorbent surface rather than the total surface area available. Similar findings have been reported in the literature for sorption of Zn<sup>2+</sup> onto activated carbons [27].

# 3.3. Comparisons with literature results

Maximum  $Ni^{2+}$  sorption capacities of CNTs and other adsorbents are given in Table 4. The sorption capacity of NaOCl oxidized CNTs is much higher compared to oxidized MWCNTs by HNO<sub>3</sub>, activated carbons (activated cloths, Almond husk), sugar beet pulp, and granular biomass. This indicates that NaOCl oxidized CNTs are promising sorbents for the removal of Ni<sup>2+</sup> from aqueous solutions.

# 3.4. Sorption/desorption study

Although both CNTs show more Ni<sup>2+</sup> sorption capacities than the GAC, the very high unit cost currently restricts their potential use in water treatment [4]. Thus, testing the reversibil-

Table 4 Maximum sorption capacities of Ni<sup>2+</sup> onto CNTs and other sorbents

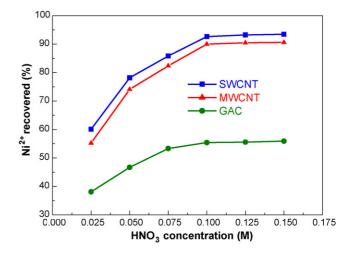


Fig. 6. Ni<sup>2+</sup> recoveries of sorbents under various strengths of HNO<sub>3</sub> solution.

ity of  $Ni^{2+}$  sorption with these sorbents is required in order to reduce their replacement cost. For this purpose, the optimum conditions to reach effective  $Ni^{2+}$  desorption, such as the strength of regeneration solution and the regeneration time, must be determined.

Fig. 6 shows the Ni<sup>2+</sup> recoveries of CNTs and GAC under various strengths of HNO<sub>3</sub> solution. Desorption experiments were conducted for 12 h to assure the achievement of desorption equilibrium. The Ni<sup>2+</sup> recovery is defined as the percentage ratio of the  $q_e$  of the regenerated sorbents to that of the virgin sorbents. As the HNO<sub>3</sub> strength increased from 0.025 to 0.1 M, the Ni<sup>2+</sup> recoveries of SWCNTs, MWCNTs and GAC increased from 60.2, 55.5 and 37.5% to 92.5, 90.2 and 55.3%, respectively. This could be explained by the fact that the surface charge of sorbent becomes more positive with a rise in HNO<sub>3</sub> strength, probably

Sorbents	а	Conditions	Reference
SWCNTs (NaOCl)	47.85	pH 7.0, T: 25, S/L: 0.05/100, C <sub>0</sub> = 10–80	This study
MWCNTs (NaOCl)	38.46	-	
GAC (NaOCl)	26.39		
MWCNTs (HNO <sub>3</sub> )	9.80	pH 6.55, <i>T</i> : 60, S/L: 0.15/200, <i>C</i> <sub>0</sub> = 6–20	[29]
AC cloths: CS 1501	5.80	pH 5.0, <i>T</i> : 20, S/L: 0.5/250, <i>C</i> <sub>0</sub> = 40	[6]
RS 1301	5.10	-	
Almond husk	37.18	pH 5.0, <i>T</i> : 20, S/L: 0.5/100, <i>C</i> <sub>0</sub> = 25	[3]
Sugar beet pulp	11.86	pH 4.7, T: 20, $C_0 = 2.5 \times 10^{-3}$ M	[5]
Granular biomass	26.00	pH 4.0–5.5, T: 21, S/L: 0.5/50, $C_0 = 10$	[9]

*Note*:  $a = \text{maximum sorption capacity (mg g^{-1})}; T = \text{temperature (°C)}; S/L = \text{solid/liquid (g ml^{-1})}, C_0 = \text{initial Ni}^{2+} \text{ concentration (mg l^{-1})}.$ 

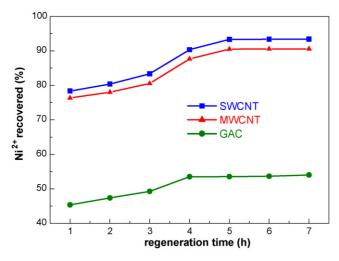


Fig. 7. Ni<sup>2+</sup> recoveries of sorbents under various regeneration times.

because of the deposition of more H<sup>+</sup> ions, which causes more electrostatic repulsions between the Ni<sup>2+</sup> and the sorbent surface. The Ni<sup>2+</sup> recoveries of these sorbents reached maximum for HNO<sub>3</sub> concentrations  $\geq 0.1$  M. Therefore, a 0.1 M HNO<sub>3</sub> solution was chosen in the following studies.

Fig. 7 exhibits the Ni<sup>2+</sup> recoveries of CNTs and GAC under various regeneration times. The Ni<sup>2+</sup> recoveries increased with regeneration time and achieved maximum after 5 h of regeneration, in which 93.4, 90.6 and 52.5% Ni<sup>2+</sup> recoveries were obtained for the SWCNTs, MWCNTs and GAC, respectively. Therefore, a regeneration time of 5 h was selected in the following studies.

It should be noted that the strength of HNO<sub>3</sub> solution and the regeneration time used in the desorption experiment depend on the  $C_0$ . A greater  $q_e$  was obtained with a higher  $C_0$  as shown in Fig. 5, which makes desorption of Ni<sup>2+</sup> ions more difficult. Thus, a higher HNO<sub>3</sub> strength or a longer regeneration time is needed to reach effective Ni<sup>2+</sup> desorption.

The  $q_e$  and the Ni<sup>2+</sup> recoveries of CNTs and GAC under various cycles of water treatment and regeneration (*n*) are presented in Figs. 8 and 9, respectively. As the *n* increased, the  $q_e$  and

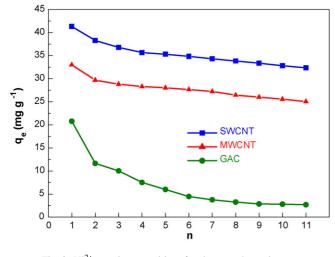


Fig. 8. Ni<sup>2+</sup> sorption capacities of sorbents under various n.

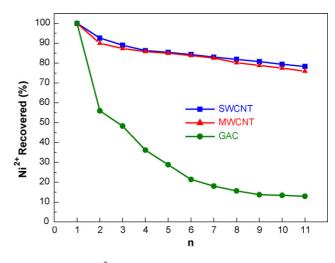


Fig. 9. Ni<sup>2+</sup> recoveries of sorbents under various n.

the Ni<sup>2+</sup> recovery of CNTs slightly decreased but those of GAC sharply decreased. This could be explained by the fact that the GAC has a porous structure in which Ni<sup>2+</sup> ions have to move from the inner surface to the exterior surface of the pores and thus make desorption of Ni<sup>2+</sup> more difficult.

The  $q_e$  under *n* of 1, 2, 6 and 11 are 41.32, 38.27, 34.84 and 32.35 mg g<sup>-1</sup> for the SWCNTs; 32.98, 29.68, 27.65 and 25.03 mg g<sup>-1</sup> for the MWCNTs; and 20.77, 11.63, 4.45 and 2.69 mg g<sup>-1</sup> for the GAC. The Ni<sup>2+</sup> recoveries under *n* of 2, 6 and 11 are 92.63, 84.32 and 78.29% for the SWCNTs; 89.98, 83.83 and 75.89% for the MWCNTs; and 55.98, 21.42 and 12.94% for the GAC. It is apparent that the Ni<sup>2+</sup> ions could be easily removed from the CNT surface by a 0.1 M HNO<sub>3</sub> solution and the  $q_e$  was maintained after 10 cycles of water treatment and regeneration.

#### 3.5. Stability of sorbents

Fig. 10 shows the percentage ratios of CNTs and GAC weight loss under various n. As can be observed, considerable sorbent weight losses occurred under n of 1 and 2, in which 11.1 and

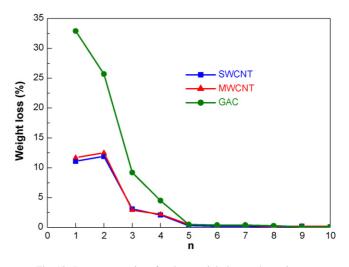


Fig. 10. Percentage ratios of sorbent weight loss under various n.

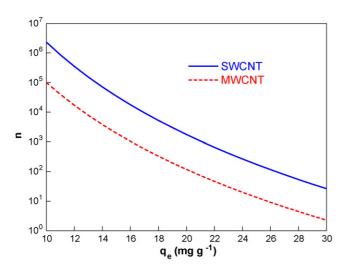


Fig. 11. Predicted n of sorbents under various  $q_e$ .

11.9% weight loss for the SWCNTs, 11.7 and 12.5% weight loss for the MWCNTs, and 32.9 and 25.7% weight loss for the GAC were found. The average percentage ratio of weight loss was the most for the GAC (6.74%), followed by the MWCNTs (2.84%), and then the SWCNTs (2.66%). Both CNTs appear rather stable after being repeated sorption/desorption processes. This could be due to high degree of graphitization of CNTs. However, the weight losses of these sorbents become insignificant after five cycles of water treatment and regeneration.

#### 3.6. Cost-effective analysis

The typical cost per gram of employed SWCNTs, MWCNTs and GAC is US\$ 90, US\$ 12 and US\$  $1 \times 10^{-3}$ , respectively. The unit cost of CNTs is much higher than that of GAC. Therefore, if the regeneration of CNTs is not carried out, the practical use of CNTs in water treatment is not possible. If the regeneration of CNTs is performed, the CNTs should be reused through over thousands of water treatment and regeneration cycles and then can possibly be cost-effective sorbents.

To evaluate the replacement cost of SWCNTs, MWCNTs and GAC in water treatment, a statistical analysis based on the best-fit regression of  $q_e$  versus *n* of Fig. 8 was conducted, and the results are expressed as Eqs. (4)–(6), respectively,

$$q_{\rm e} = 41.11 \times n^{-0.0964} \tag{4}$$

$$q_{\rm e} = 32.63 \times n^{-0.1026} \tag{5}$$

$$a_{\rm e} = 23.10 \times n^{-0.9069} \tag{6}$$

The  $R^2$  of above equations are all >0.99.

Fig. 11 shows the predicted *n* of SWCNTs and MWCNTs with a  $q_e$  range of 10–30 mg g<sup>-1</sup>. As can be observed, the predicted *n* of SWCNTs and MWCNTs decreased with a rise in  $q_e$ . The predicted *n* are  $3.5 \times 10^4$  and 1950 with a  $q_e$  of 15 mg g<sup>-1</sup> (estimated by substituting  $q_e = 15$  mg g<sup>-1</sup> into Eqs. (4) and (5), and calculating *n*) and are 175 and 13 with a  $q_e$  of 25 mg g<sup>-1</sup>. The predicted *n* of GAC is only 1 with a  $q_e$  of 15 mg g<sup>-1</sup> and non-achievable with a  $q_e$  of 25 mg g<sup>-1</sup>.

It is apparent that both CNTs can be reused for the removal of  $Ni^{2+}$  through a large number of water treatment and regeneration cycles. This is the key factor for whether a novel but expensive sorbent can be accepted by the field or not. It is expected that the unit cost of both CNTs can be further reduced in the future [28] so that the SWCNTs and MWCNTs appear possibly cost-effective  $Ni^{2+}$  sorbents in water treatment.

It should be noted that the predicted n was estimated based on the  $q_e$  of only 10 cycles of water treatment and regeneration since it is quite time-consuming for over thousands of tests. Furthermore, the sorbent weight loss was neglected in the estimation of n. Thus, the departures of predicted results from real conditions may possibly occur and a prolonged test on the sorption performance of regenerated CNTs is required.

#### 4. Conclusions

The reversibility of Ni<sup>2+</sup> sorption by NaOCl oxidized SWC-NTs, MWCNTs and GAC was tested to evaluate their repeated availability performance in water treatment. Under the same conditions, the SWCNTs and MWCNTs possess better performance of Ni<sup>2+</sup> sorption than the GAC and their performance was maintained after 10 cycles of sorption/desorption process. This suggests that SWCNTs and MWCNTs are efficient Ni<sup>2+</sup> sorbents and can be reused through many cycles of water treatment and regeneration. A statistical analysis on the replacement cost of these adsorbents revealed that the SWCNTs and MWCNTs can be possibly cost-effective Ni<sup>2+</sup> sorbents in water treatment regardless of their high unit cost at the present time.

# Acknowledgement

Support from the National Science Council, Taiwan, under a contract no. NSC 94-2211-E-005-038 is gratefully acknowledged.

# References

- W.W. Eckenfelder Jr., Industrial Water Pollution Control, 2nd ed., McGraw-Hill International Editions, Singapore, 1989.
- [2] P. Parker, Encyclopedia of Environmental Sciences, 2nd ed., McGraw Hill, New York, 1980.
- [3] H. Hasar, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk, J. Hazard. Mater. 97 (2003) 49–57.
- [4] Ö. Yavuz, Y. Altunkaynak, F. Güzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, Water Res. 37 (2003) 948–952.
- [5] Z. Reddad, C. Gerente, Y. Andresp, P.L. Ecloirec, Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.
- [6] K. Kadirvelu, C.F. Brasquet, P.L. Cloirec, Removal of Cu(II), Pb(II), and Ni(II) by adsorption onto activated carbon cloths, Langmuir 16 (2000) 8404–8409.
- [7] P. Brown, I.A. Jefcoat, D. Parrish, S. Gill, S. Graham, Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution, Adv. Environ. Res. 4 (2000) 9–29.
- [8] K.C. Justi, V.T. Fávere, M.C.M. Laranjeira, A. Neves, R.A. Peralta, Kinetics and equilibrium adsorption of Cu(II), Cd(II), and Ni(II) ions by chitosan functionalized with 2[-bis-(pyridylmethyl)aminomethyl]-4methyl-6-formyl-phenol, J. Colloid Interf. Sci. 291 (2005) 369–374.

- [9] A.H. Hawari, C.N. Mulligan, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass, Bioresour. Technol. 97 (2006) 692–700.
- [10] H.K. An, B.Y. Park, D.S. Kim, Crab shell for the removal of heavy metals from aqueous solution, Water Res. 35 (2001) 3356–3451.
- [11] S.K. Smart, A.I. Cassady, G.Q. Lu, D.J. Martin, The biocompatibility of carbon nanotubes, Carbon 44 (2006) 1034–1047.
- [12] Y.H. Li, S. Wang, J. Wei, X. Zhang, C. Xu, Z. Luan, D. Wu, B. Wei, Lead adsorption on carbon nanotubes, Chem. Phys. Lett. 357 (2002) 263–266.
- [13] Y.H. Li, S. Wang, Z. Luan, J. Ding, C. Xu, D. Wu, Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes, Carbon 41 (2003) 1057–1062.
- [14] Y.H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu, B. Wei, Competitive adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> ions from aqueous solutions by multiwalled carbon nanotubes, Carbon 41 (2003) 2787–2792.
- [15] C. Lu, H. Chiu, Adsorption of zinc(II) from water with purified carbon nanotubes, Chem. Eng. Sci. 61 (2006) 1138–1145.
- [16] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith, Sep. Purif. Technol. 24 (2001) 497–505.
- [17] R.M. Smith, A.E. Martell, Inorganic Complexes, vol. 4, Plenum Press, New York, 1976.
- [18] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, Carbon 32 (1994) 759–769.
- [19] P. Chingombe, B. Saha, R.J. Wakeman, Surface modification and characterisation of a coal-based activated carbon, Carbon 43 (2005) 3132–3143.

- [20] W.M. David, C.L. Erickson, C.T. Johnston, J.J. Delfino, J.E. Porter, Quantitative Fourier transform infrared spectroscopic investigation of humic substance functional group composition, Chemosphere 38 (1999) 2913–2928.
- [21] J.W. Shim, S.J. Park, S.K. Ryu, Effect of modification with HNO<sub>3</sub> and NaOH on metal adsorption by pitch-based activated carbon fibers, Carbon 39 (2001) 1635–1642.
- [22] B.K. Pradhan, N.K. Sandle, Effect of different oxidizing agents on the surface properties of activated carbons, Carbon 37 (1999) 1323–1332.
- [23] G. Ovejero, J.L. Sotelo, M.D. Romero, A. Rodríguez, M.A. Ocaña, G. Rodríguez, J. García, Multiwalled carbon nanotubes for liquid-phase oxidation. Functionalization, characterization, and catalytic activity, Ind. Eng. Chem. Res. 45 (2006) 2206–2212.
- [24] M.F.R. Pereira, S.F. Soares, J.M. Órfão, J.L. Figueiredo, Adsorption of dyes on activated carbons: influence of surface chemical groups, Carbon 41 (2003) 811–821.
- [25] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.
- [26] H.M.F. Freundlich, Über die adsorption in Iösungen, J. Phys. Chem. 57 (1906) 385–470.
- [27] R.R. Leyva, J.L.A. Bernal, B.J. Mendoza, R.L. Fuentes, C.R.M. Guerrero, Adsorption of zinc(II) from an aqueous solution onto activated carbon, J. Hazard. Mater. B 90 (2002) 27–38.
- [28] J. Yu, J. Lucas, V. Strezov, T. Wall, Coal and carbon nanotubes production, Fuel 82 (2003) 2025–2032.
- [29] C. Chen, X. Wang, Adsorption of Ni(II) from aqueous solution using oxidized multiwall carbon nanotubes, Ind. Eng. Chem. 45 (2006) 9144–9149.