Adsorption of aqueous cadmium (II) onto modified multi-walled carbon nanotubes following microwave/chemical treatment

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1. Introduction

Removing toxic heavy metals from industrial wastewater is an urgent environmental issue. Heavy metals are non-degradable and can accumulate in animals and plants, so they must be removed from wastewater. Heavy metal ions such as cadmium (II) ions are the main contaminants of surface water, groundwater, and soils; the main sources are the metal plating industry [1,2]. Due to their non-biodegradability and persistence, they can accumulate in the environment elements such as food chain, and thus may pose a significant danger to human health [2–5]. Exposure to cadmium (II) can result in osteoporosis, anaemia and renal damage [6,7]. However, the use of cadmium in paint pigments, electroplating, batteries, is increasing.

Carbon nanotubes (CNTs) are new adsorbents of trace pollutants from water, because they have a large specific surface area, and small, hollow and layered structures. Considerable attention has been paid to adsorption by CNTs of such ions as Cd2+. Earlier works have suggested hollow and layered structures. Considerable attention has been paid to from water, because they have a large specific surface area, and small, hollow and layered structures. Considerable attention has been paid to adsorption by CNTs of such ions as Cd2+. Earlier works have suggested hollow and layered structures. Considerable attention has been paid to adsorption by CNTs of such ions as Cd2+.

This study evaluates the aqueous cadmium (II) adsorption efficiency of as-grown carbon nanotubes (CNTs) and of those modified by microwave (MW)/H2SO4 and MW/H2SO4/KMnO4 processes. The surface area, pHpzc, and FTIR spectra of CNTs were, before and after modification, compared. Aromatic groups, carbonyl groups and hydroxyl groups were herein detected on the surfaces of MW/H2SO4 and MW/H2SO4/KMnO4-modified CNTs. At a particular pH, the adsorption capacity of Cd2+ of the MW/H2SO4/KMnO4-modified CNTs exceeded that of MW/H2SO4-modified CNTs and as-grown CNTs. The kinetic analyses of adsorption were performed and a pseudo second-order model accurately captured the adsorption kinetics. This study suggests that MW/H2SO4 and MW/H2SO4/KMnO4 modification not only increased the area of active adsorption sites of CNTs but also reduced the modification period by microwave heating.

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A R T I C L E  I N F O
Article history:
Accepted 11 November 2008
Available online 4 October 2009

Keywords:
Microwave
Carbon nanotubes
Adsorption

A B S T R A C T
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2. Materials and methods

The as-grown CNTs herein were multi-wall CNTs (CBT, MWNTs-2040, length: 5–15 μm, purity of carbon: above 90%). They were formed by the pyrolysis of methane gas on particles of Ni by chemical vapor deposition. The Cd2+ stock solution was prepared from Cd(NO3)2·3H2O and Milli-Q deionized water. The zeta potentials of the
as-grown and oxidized CNTs were measured using a Zeta-Meter 3.0 (Zeta-Meter Inc., U.S.A.). The acidity or basicity of the CNTs surface and the isoelectric point of \( \text{pH}_{\text{IEP}} \) were determined by measuring the zeta potential as a function of pH of the CNT solution from 2.0 to 9.0 at 300 K.

The functional groups of CNTs were identified by Fourier Transform Infrared Spectroscopy (FTIR) analysis and an autoimage system (Perkin Elmer, USA) using the KBr pressed disc method. Scanning electron microscopic/energy dispersive X-ray spectroscopic (SEM/EDS) analyses (JEOL, JSM-T330A) yielded the number of oxygen and nickel atoms in as-grown and modified CNTs. The specific surface area of CNTs was measured using the BET method, using a Model ASAP 2010 surface area analyzer (Micromeritics, USA). The size and morphology of the CNTs were elucidated by transmission electron microscopy (TEM) using a Model JEM-2010 (JEOL, Japan).

The configuration of microwave is in a closed microwave oven system and the volumetric capacity of Teflon flasks of microwave oven is 100 ml. As-grown CNTs (1 g) were immersed in Teflon flasks with 20 ml of 1 M \( \text{H}_2\text{SO}_4 \) and 20 ml of 1 M \( \text{H}_2\text{SO}_4 \) adding 1 g of \( \text{KMnO}_4 \) then rotated in a microwave system (400 W) for 10 min in the modification of MW/\( \text{H}_2\text{SO}_4 \) and MW/\( \text{H}_2\text{SO}_4/\text{KMnO}_4 \). 10 min and the potency (400 W) were chosen in the modification of MW/\( \text{H}_2\text{SO}_4/\text{KMnO}_4 \) oxidation significantly increased this peak. Lu et al. [12] found that the chemical oxidation of CNTs introduces various acidic functional groups on their surfaces, improving their hydrophilicity. The MW/\( \text{H}_2\text{SO}_4 \)-modified CNTs yielded a peak at about 3200–3400 cm\(^{-1} \), which was assigned to the hydroxyl –OH groups [24–26] and hydroxyl groups at 3200 cm\(^{-1} \), respectively and the external surface area was 78, 98 and 112 (m\(^2\)/g) in as-grown, MW/\( \text{H}_2\text{SO}_4 \)-modified CNTs, respectively and the external diameters of the nano-materials [21]. The surface area was 78, 98 and 112 (m\(^2\)/g) in as-grown, MW/\( \text{H}_2\text{SO}_4 \)-modified and MW/\( \text{H}_2\text{SO}_4/\text{KMnO}_4 \)-modified CNTs, respectively. The results indicate that carboxyl and hydroxyl groups [24,26] and hydroxyl groups at 3200 cm\(^{-1} \) were formed on the surface of these-modified CNTs as the number of oxygen atoms increased.

The chemical modification of MWCNT with oxidant acids lead to increase of external diameters of the nano-matters [21]. The surface area was 78, 98 and 112 (m\(^2\)/g) in as-grown, MW/\( \text{H}_2\text{SO}_4 \)-modified and MW/\( \text{H}_2\text{SO}_4/\text{KMnO}_4 \)-modified CNTs, respectively and the external diameters were not increased due to the short microwave heating. The number of oxygen atoms on modified CNTs exceeded that on as-grown CNTs, revealing that the modification processes promoted the formation of the oxygenic functional groups on the modified surfaces of the CNTs. This observation was consistent with those of Li et al. [10], Kuo [15] and Montioux et al. [23]. Accordingly, the experimental results indicate that oxidation treatments may have not only removed Ni particles and amorphous carbons but also produced some structural defects.

Fig. 1 displays the FTIR spectra of as-grown and modified CNTs. The as-grown CNTs yielded three peaks. A peak at near 1450–1600 cm\(^{-1} \), which was assigned to the aromatic –C–C groups [24], a peak at approximately 1700–1740 cm\(^{-1} \), which was assigned to the carbonyl –C=O groups [25] and a peak at about 3200–3400 cm\(^{-1} \), which was assigned to the hydroxyl –OH groups [24–26]. MW/\( \text{H}_2\text{SO}_4 \) and MW/\( \text{H}_2\text{SO}_4/\text{KMnO}_4 \) oxidation significantly increased this peak. Lu et al. [12] found that the chemical oxidation of CNTs introduces various acidic functional groups on their surfaces, improving their hydrophilicity. The MW/\( \text{H}_2\text{SO}_4 \)-modified CNTs yielded a peak at about 3200–3400 cm\(^{-1} \), which was assigned to the aromatic –OH groups. MW/\( \text{H}_2\text{SO}_4/\text{KMnO}_4 \)-modified CNTs yielded four major peaks, which were associated with aromatic groups at 1450–1600 cm\(^{-1} \), carbonyl groups at 1700–1740 cm\(^{-1} \), carboxylic acids at 2400 cm\(^{-1} \), –CH groups at 2800–3100 cm\(^{-1} \) [24,26] and hydroxyl groups at 3200–3400 cm\(^{-1} \), the latter two from carboxylic acids or alcoholic groups. Evidently, several functional groups were formed on the surface of modified CNTs, providing various adsorption sites, and increasing the adsorption capacity. Modification by MW/\( \text{H}_2\text{SO}_4/\text{KMnO}_4 \) increased the discretization of CNTs, enlarging the external surface area of the CNTs. The TEM images revealed that the as-grown and modified CNTs were cylindrical and that the main external diameters of as-grown, MW/\( \text{H}_2\text{SO}_4 \) and MW/\( \text{H}_2\text{SO}_4/\text{KMnO}_4 \)-modified CNTs were 20–30 nm (Fig. 2(a–c)).

### 3.2. pH effects

The adsorption capacity of Cd\(^{2+} \) onto the surface of CNTs increased with both the pH of the system from acidic to alkaline and the temperature (Fig. 3(a–c)). pH is one of the most important factors that affect the sites of dissociation of CNTs and the hydrolysis, complexation and precipitation of Cd\(^{2+} \). At acidic pH, the surface is expected to have a net positive charge, and to adsorb few Cd\(^{2+} \) ions. Above pH\(_{\text{IEP}} \), a net

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**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Purity C (%)</th>
<th>Element O/Ni (atoms %)</th>
<th>pH(_{\text{IEP}} )</th>
<th>Surface area (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown</td>
<td>&gt;90</td>
<td>5.4/1.0</td>
<td>4.9</td>
<td>78</td>
</tr>
<tr>
<td>MW/( \text{H}_2\text{SO}_4 ) process</td>
<td>&gt;90</td>
<td>7.8/0.5</td>
<td>3.8</td>
<td>98</td>
</tr>
<tr>
<td>MW/( \text{H}_2\text{SO}_4/\text{KMnO}_4 ) process</td>
<td>&gt;85</td>
<td>12.2/0.5</td>
<td>–</td>
<td>112</td>
</tr>
</tbody>
</table>

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![Fig. 1. FTIR spectra of CNTs.](image-url)
negative charge is present on the surface of the CNTs, promoting the adsorption of Cd$^{2+}$, because of the electrostatic force of attraction between Cd$^{2+}$ and the surface of the CNTs. The Cd$^{2+}$ adsorption capacity rapidly increased with pH above 8.5, which in fact can be explained by the precipitation of Cd$^{2+}$ from solution [14,27]. Therefore, the experiments were performed to determine the adsorption isotherms at a fixed pH of 6. At pH values of over pH$_{iep}$, a net negative charge is present on the surface of the CNTs, promoting the adsorption of Cd$^{2+}$, because of the electrostatic force of attraction between Cd$^{2+}$ and the surface of the CNTs. The MW/H$_2$SO$_4$/KMnO$_4$-modified CNTs had the highest adsorption capacity of the three CNTs of interest. The dependence of adsorption on pH is associated with the dependence of the surface charge on CNTs on pH. For a given pH, the zeta potentials followed the order as-grown CNTs > MW/H$_2$SO$_4$-modified CNTs > MW/H$_2$SO$_4$/KMnO$_4$-modified CNTs. Therefore, the adsorption capacity of Cd$^{2+}$ followed the order MW/H$_2$SO$_4$/KMnO$_4$-modified CNTs > MW/H$_2$SO$_4$-modified CNTs > as-grown CNTs. This study suggests that modifying the surface of CNTs not only can make it more negatively charged and hydrophilic but can also form various functional groups, substantially promoting the adsorption of Cd$^{2+}$ onto modified CNTs. The previous report [21] also indicated that the functional groups by acid/oxidation improved the ion-exchange capabilities of the CNTs and increased Cd (II) adsorption capacities correspondingly.

3.3. Kinetic analyses

Fig. 4 presents the kinetic analysis of the adsorption of Cd$^{2+}$ onto as-grown and modified CNTs. Pseudo first- and second-order models and intraparticle diffusion and Bangham’s models were tested against the experimental data to explicate the kinetics of the adsorption process. The pseudo first-order and pseudo second-order models are

$$\ln(q_e - q) = \ln(q_e) - k_1t$$

Fig. 2. TEM images of CNTs (a) as-grown CNTs, (b) MW/H$_2$SO$_4$ process modified CNTs and (c) MW/H$_2$SO$_4$/KMnO$_4$ process modified CNTs.

Fig. 3. Effects of pH (a) 290 K, (b) 300 K, and (c) 310 K, (initial Cd$^{2+}$ = 40 mg/l, ionic strength = 0.01 M, CNTs = 0.25 g/l, and contact time = 24 h).

Fig. 4.
was not perfectly linear (Fig. 5). Since neither the pseudo first-order nor the second-order model yields the diffusion of Cd^{2+} into pores of CNTs was not the only rate-controlling step [34].

4. Conclusion

This study examines the equilibrium adsorption of Cd^{2+} onto as-grown and modified CNTs at various pH values and temperatures. The MW/H_2SO_4 and MW/H_2SO_4/KMnO_4 modifications reduced the pH_{eqp} by

\[ \frac{t}{q} = \frac{1}{k_1q_e} + \frac{t}{q} \]

where \( q_e \) and \( q \) are the amounts of Cd^{2+} adsorbed on CNTs at equilibrium and at various times \( t \) (mg/g); \( k_1 \) is the rate constant of the pseudo first-order model of adsorption (1/h) [28] and \( k_2 \) is the rate constant of the pseudo second-order model of adsorption (g/mg h) [29]. The adsorption was rapid during 0.5 h of contact time, and then slowed, because numerous vacant surface sites were available for adsorption during the initial stage, and then, the remaining vacant surface sites could not be easily occupied because of the repulsive forces between the Cd^{2+} molecules on the CNTs and the bulk phase.

The initial adsorption rate \( h \) (mg/g h) can be given by \( h=k_2q_e^2 \).

\[ \log \left( \frac{C_0}{C_q-qm} \right) = \log \left( \frac{k_m}{2.303V} \right) + \alpha \log t \]

where \( q \) and \( t \) are defined as in the pseudo first-order model; \( C_0 \) represents the initial concentration of Cd^{2+} in solution (mg/l); \( V \) is the volume of solution (ml); \( m \) is the mass of CNTs per liter of solution (g/l) and \( k_0 \) and \( \alpha \) are constants.

Table 2 provides the kinetic parameters given which the \( R^2 \) value of the pseudo first-order model are 0.54–0.87 and second-order model exceeded 0.989; moreover, the \( q \) value (\( q_{exp} \)) calculated from the pseudo second-order model was consistent with the experimental \( q \) values (\( q_{cal} \)). Accordingly, this study suggests that the pseudo second-order model best represented the adsorption kinetics (Fig. 5).

Various mechanisms determine the adsorption kinetics; the most limiting mechanisms are the diffusion mechanisms, including external diffusion, boundary layer diffusion and intraparticle diffusion [32]. If the plot of \( q \) as a function of \( t^{1/2} \) is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step [29,33]. Therefore, the intraparticle diffusion model was applied to determine the rate-limiting step of the adsorption process. In Table 2, the \( R^2 \) value of regression was 0.54–0.87 and the plot did not pass through the origin, revealing that adsorption involved intraparticle diffusion hardly, and was not the only rate-controlling step. The double logarithmic plot based on Bangham’s model was not perfectly linear (\( R^2 = 0.522–0.863 \))

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the formation of some functional groups. The adsorption capacity of aqueous cadmium (II) onto as-grown and modified CNTs increased with the pH and temperature. The negatively charged surfaces of modified CNTs electrostatically favored the adsorption of Cd²⁺ in MW/H₂SO₄/KMnO₄-modified CNTs more than in MW/H₂SO₄-modified CNTs. At a particular pH, the adsorption capacity of Cd²⁺ of the MW/H₂SO₄/KMnO₄-modified CNTs exceeded that of MW/H₂SO₄-modified CNTs and as-grown CNTs. The kinetic analyses of adsorption were performed using pseudo first- and second-order models and the regression results indicated that a pseudo second-order model more accurately captured the adsorption kinetics.

Acknowledgements

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financially supporting this research under Contract No. NSC 97-2622-E-224-001-CC3. Additionally, Mr. Tan is appreciated for assistance in conducting some of the experiments.

References