

Removal of nickel ions from water by multi-walled carbon nanotubes

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Abstract

Multi-walled carbon nanotubes (MWCNTs) were produced by chemical vapor decomposition using acetylene gas in the presence of Ferrocene catalyst at 800 °C, and then oxidized with concentrated nitric acid at 150 °C. Both (as-produced and oxidized) CNTs were characterized by TEM, Boehm titration, N₂-BET and cation exchange capacity techniques. The adsorption capacity for nickel ions from aqueous solutions increased significantly onto the surface of the oxidized CNTs compared to that on the as-produced CNTs. The effects of adsorption time, solution pH and initial nickel ions concentrations on the adsorption uptake of Ni²⁺ for both the as-produced and oxidized CNTs were investigated at room temperature. Both Langmuir and Freundlich isotherm models match the experimental data very well. According to the Langmuir model the maximum nickel ions adsorption uptake onto the as-produced and oxidized CNTs were determined as 18.083 and 49.261 mg/g, respectively. Our results showed that CNTs can be used as an effective Ni²⁺ adsorbent due to the high adsorption capacity as well as the short adsorption time needed to achieve equilibrium.

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1. Introduction

The removal of toxic heavy metals such as cadmium, copper, lead, nickel, mercury, and zinc from aqueous environment has received considerable attention in recent years due to their toxicity and carcinogenicity which may cause damage to various systems of the human body. They also can be readily adsorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers [1]. Nickel ions are non-biodegradable toxic heavy metals and may cause dermatitis and allergic sensitization [2,3]. According to the World Health Organization guidelines, the maximum permissible concentration of nickel in effluents in the US from the electroplating process wastewater is 4.1 mg/l, while that in drinking water should be less than 0.1 mg/l [4]. The major sources of nickel contamination to water comes from industrial process such as electroplating, batteries manufacturing, mine, metal finishing and forging. Different methods were investigated and applied

to remove nickel ions from water such as adsorption, chemical precipitation, ion exchange, filtration, membrane separation, and reverse osmosis. Adsorption is widely used because it is cost-effective and simple. Different adsorbents such as seaweeds [5], crab shell [6], dried aerobic activated sludge [7], loofa sponge-immobilized biomass of *Chlorella sorokiniana* [8], activated carbon prepared from almond husk [9], spent animal bones [10], and waste factory tea [11] have been used to remove nickel ions from aqueous water, but low adsorption capacities or efficiencies limit their applications. Therefore, investigating new adsorbents with higher adsorption capacities and efficiencies has been the aims of many researchers.

Carbon nanotubes (CNTs) are new adsorbents that have been discovered in 1991 by Iijima [12] and recently found more efficient than activated carbon for the removal of dioxin [13], hydrogen [14], ammonia [15], ozone [16], nitrogen, and methane [17] from air. CNTs have also been used as adsorbents to remove cadmium(II) (by Li et al. [18]), lead(II) [19], zinc(II) [20], fluoride [21], 1,2-dichlorobenzene [22] and trihalomethanes [23] from water. However, the studies on the adsorption of heavy metals with CNTs are still very limited in the literature. According to our knowledge, nickel removal by CNTs has not been investigated yet. The objectives of

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the present study are to produce and oxidize CNTs, then to investigate their capabilities to adsorb nickel ions from aqueous solutions. The effects of adsorption time, initial pH and initial nickel ions concentrations on the adsorption uptake for the as-produced and oxidized CNTs were investigated. Langmuir and Freundlich models were applied to fit the experimental data.

2. Experimental procedure

2.1 Production and oxidation of CNTs

Multi-walled carbon nanotubes (MWCNTs) used in this work were produced by catalytic decomposition of acetylene gas (as a hydrocarbon source) in the presence of Ferrocene (as a catalyst) and nitrogen gas at 800 °C. The catalyst was placed on the bottom of a ceramic boat, which was placed inside a horizontal tubular reactor (50 mm inner diameter and 122 cm length). Nitrogen gas was introduced into the reactor at a flow rate of 43 cm³/min; then the whole system was heated gradually to 800 °C within 30 min. When the boat reached the desired temperature, it was kept at this temperature for 30 min. For CNTs formation, acetylene was supplied into the reactor at a flow rate of 570 cm³/min for 20 min, while nitrogen gas was still flowing at the 43 cm³/min. After that, the acetylene supply was stopped and the reactor was cooled to room temperature in about 2 h under nitrogen environment; then the powder collected on the boat was called the as-produced CNTs and immediately observed by transmission electron microscopy (TEM).

The as-produced CNTs were immersed in 4 M nitric acid for 2 h to remove the amorphous carbon and iron catalyst at room temperature and then washed by de-ionized water several times until the washing water showing no pH changes, then dried at 110 °C for 24 h. The clean CNTs were then oxidized by concentrated nitric acid, refluxed at 150 °C for 2 h, washed with de-ionized water many times until no pH changes in the washing water was detected, dried at 110 °C for 24 h and observed by TEM. Both the as-produced and the oxidized CNTs were used as adsorbents for nickel removal from water.

2.2 Adsorption procedure

Batch adsorption experiments were carried out using diluted 1000 mg/l stock solutions prepared from analytical reagent grade of Ni(NO₃)₂·6H₂O in deionized water. The solution was further diluted to the required concentrations (from 10 to 200 mg/l) before used. Initial pH was adjusted by diluted hydrochloric acid and diluted sodium hydroxide. All the experiments were performed by agitating 50 ml of the nickel solution at the desired concentration and 20 mg CNTs in 100 ml bottles. Agitation was performed for a predetermined time at room temperature in a reciprocating shaker. The suspension was filtered through 0.45 μm filters and the nickel was determined in the liquid phase using atomic absorption spectrophotometer. The amount of nickel adsorbed was obtained using the following equation

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (1)$$

where q_e is the equilibrium uptake (mg/g), C_0 is the initial nickel ion concentration (mg/l), C_e is the equilibrium nickel ion concentration (mg/l), V is the volume of the solution (l) and w is the mass of the adsorbent (g).

2.3 Cation exchange capacity

Sample of 1 g of the as-produced and oxidized CNTs were mixed with 33 ml of 1 M sodium acetate solutions, resulting in an exchange between the added sodium ions and the matrix cations. Subsequently, the samples were washed with 33 ml of isopropyl alcohol. A volume of 33 ml ammonium acetate solution (1 M) was then added, which replaces the adsorbed sodium with ammonium. The concentration of displaced sodium was then determined by atomic absorption spectrophotometer.

2.4 Specific surface area

The specific surface areas for both the as-produced and oxidized CNTs were determined by N₂-BET method.

3. Results and discussions

3.1 TEM observations

Fig. 1a and b show the TEM images of the as-produced and oxidized MWCNTs, respectively, while Fig. 1c is a higher magnification of Fig. 1b. Fig. 1c shows clearly a MWCNT with the hollow inner tube diameter of about 8.8 nm and outer diameter of about 23.5 nm. It could be noticed from Fig. 1b that MWCNTs have different diameters ranging from 5.5 to 14 nm inner diameters and from 8.3 to 34 nm outer diameters, while the lengths are larger than 1 μm.

3.2 Functional groups determination

The surface functional groups formed on the as-produced and oxidized CNTs surfaces due to nitric acid oxidation were quantified by Boehm method [24] and presented in Table 1. This method is based on sodium hydrogen carbonate neutralizing only carboxyl groups, sodium bicarbonate neutralizing carboxyl groups and lactones, and sodium hydroxide neutralizing carboxyl groups, lactones, and phenols. By subtracting of any base from the next more exclusive base, it is possible to estimate surface charge residing in a variety of functional groups as mmol H⁺ equivalent/g CNTs. So the different kinds of functional groups can be calculated through the known volume of used acid and bases. Table 1 shows that different functional groups such

Table 1
The amount of functional groups on the surfaces of the as-produced and oxidized CNTs determined by Boehm's method

CNTs type	Carboxyl (mmol/g)	Lactones (mmol/g)	Phenols (mmol/g)
As-produced	0.2	0.93	0.47
Oxidized	0.97	2.34	1.95

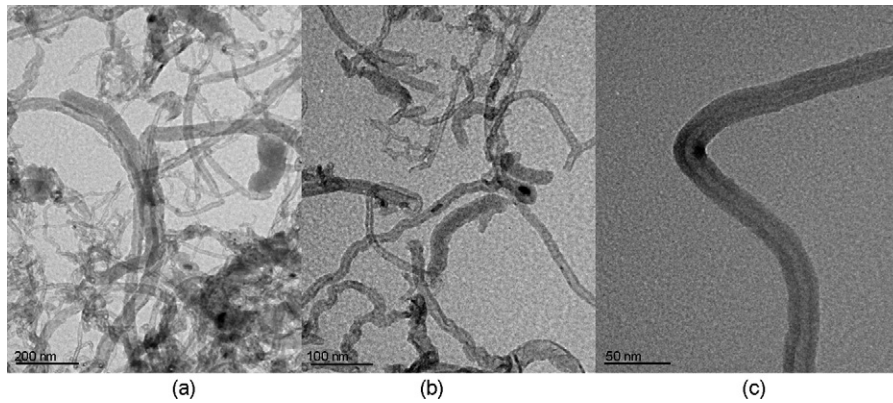


Fig. 1. TEM image for (a) as-produced CNTs, (b) oxidized CNTs and (c) CNTs at higher magnification.

as carboxylic, lactones and phenols were formed by nitric acid oxidation. These acidic nature functional groups can dissociate at different pH values and are expected to enhance the attractive forces between Ni^{2+} and OH^- which increases the adsorption capacity. It is known that the surface oxides provide hydrophilic sites on a hydrophobic surface and the adsorption properties of the oxidized carbons are greatly affected [25].

3.3 Effect of equilibrium concentration on adsorption uptake

The oxidation treatment for CNTs has improved the adsorption uptake of nickel ions significantly as shown in Fig. 2. The maximum adsorption uptake for the oxidized CNTs reaches 38 mg/g at equilibrium Ni^{2+} concentration of 74 mg/l, compared to 12.5 mg/g for the as-produced CNTs at equilibrium Ni^{2+} concentration of 175 mg/l. This significant adsorption improvement is expected due to the presence of the different functional groups formed on the CNTs surface during the oxidation, which also improved their hydrophilic and cation exchange properties. This is in agreement with Li et al. [26] who found that adsorption of activated carbon strongly affected by the presence of different

functional groups on its surface, and Li et al. [27] showed that oxidation of CNTs with oxidized acid can introduce different functional groups on the surface of CNTs.

In addition to the presence of the functional groups, the increase in the oxidized CNTs specific surface area (Table 2) supports the higher adsorption capability and the increase in the active adsorption sites. The larger specific surface area may be due to the removed amorphous carbon particles and metal catalyst in addition to the fracture caused by oxidation on their surface. This is also clear from the cation exchange capacity differences between the as-produced and oxidized CNTs, which was found as 110 meq./100-g CNTs and 253 meq./100-g CNTs, respectively. This is in agreement with Dabrowski [28] who found that the oxidation treatment by nitric acid can cause an increase in the cation exchange capacity and a decrease in the anion exchange capacity of carbon.

3.4 Effect of pH

The effect of pH on the adsorption uptake of nickel ions was investigated for both the as-produced and oxidized CNTs. The solution pH affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbates. Fig. 3 shows that as the pH increases, the adsorption uptake increases for both CNTs due to the increase in the electrostatic attractive forces between OH^- and Ni^{2+} . This experimental work was performed at pH 6 in order to avoid any precipitation effect at higher pH values except when pH effect was needed to be investigated. At pH 6, the adsorption uptake reaches the maximum due to the effect of the functional groups formed on the CNTs surface during oxidation. At pH values below 3, the adsorption uptake was very weak due to the competition between Ni^{2+} and H^+ in the solution.

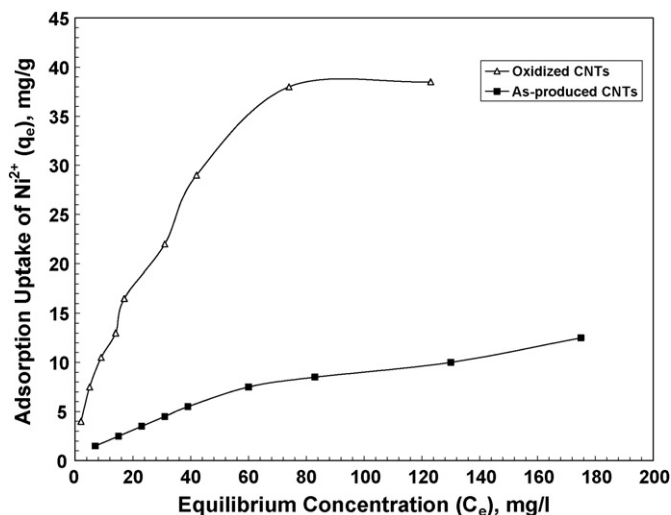


Fig. 2. Effect of equilibrium concentration on the adsorption uptake of nickel ions for both the as-produced and the oxidized CNTs.

Table 2
Characterization of the as-produced and oxidized CNTs

	Surface area (m^2/g)	Cation exchange capacity (meq./100-g CNTs)
As-produced CNTs	134	110
Oxidized CNTs	145	253

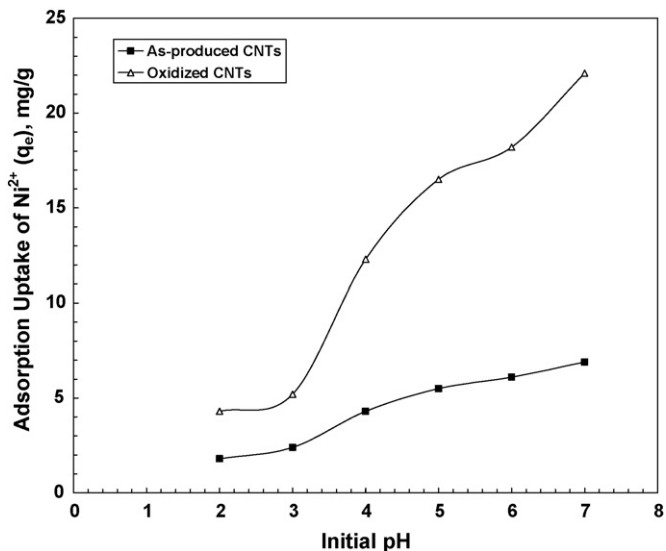


Fig. 3. Effect of initial solution pH on the adsorption uptake of nickel ions for both the as-produced and the oxidized CNTs.

3.5 Effect of adsorption time and ions concentrations

Figs. 4 and 5 show the adsorption behavior of nickel ions onto both the as-produced and oxidized CNTs with adsorption time at initial nickel ions concentrations between 10 and 200 mg/l and pH 6. The nickel ions uptake for the as-produced CNTs increased slowly and reached the maximum uptake of 12.3 mg/g after 50 min for initial nickel ions concentration of 200 mg/l, while that for the oxidized CNTs was 37 mg/g, which was achieved within the first 20 min. This short equilibrium time indicates that CNTs have a strong potential for nickel ion adsorption applications. It is clear that the increase in the initial nickel ions concentrations did not affect the equilibrium time, but increased significantly the nickel ions uptake per unit weight of CNTs.

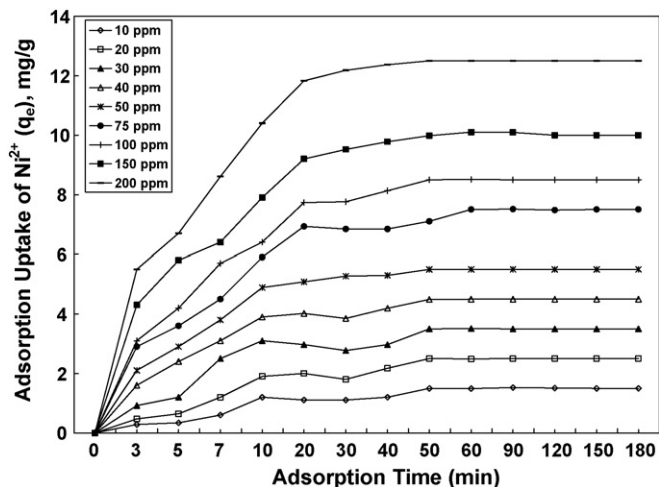


Fig. 4. Effect of adsorption time and initial nickel ions concentrations on the adsorption uptake of nickel ions for the as-produced CNTs.

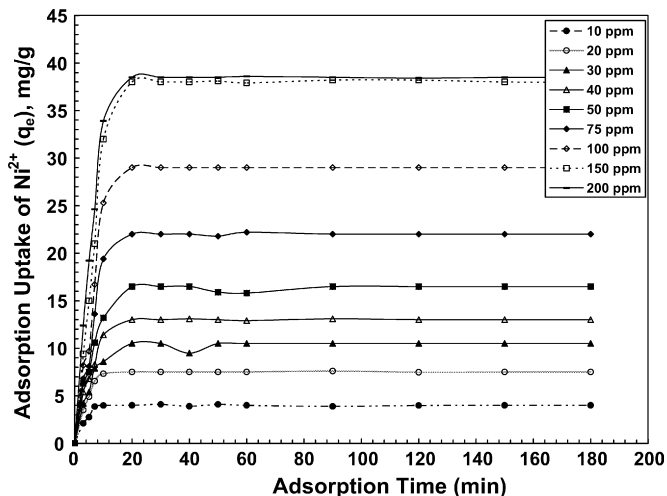


Fig. 5. Effect of adsorption time and initial nickel ions concentrations on the adsorption uptake of nickel ions for the oxidized CNTs.

3.6 Adsorption isotherms

The experimental data for nickel ions adsorption could be approximated by the Langmuir and Freundlich isothermal models for both the as-produced and oxidized CNTs. The Langmuir isotherm, which is valid for monolayer sorption onto a surface with a finite number of identical sites and uniform adsorption energies, is given by the equation

$$q_e = \frac{q_{mon} K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_{mon} is the amount of adsorption corresponding to monolayer coverage, K_L is the Langmuir constant which is related to the energy of adsorption, and C_e is the equilibrium liquid-phase concentration. Equation (2) can be linearized to determine the Langmuir parameters; q_{mon} and K_L , by plotting C_e/q_e versus C_e . The adsorption data of nickel on both the as-produced and oxidized CNTs at pH 6, shown in Fig. 6, were fitted to the

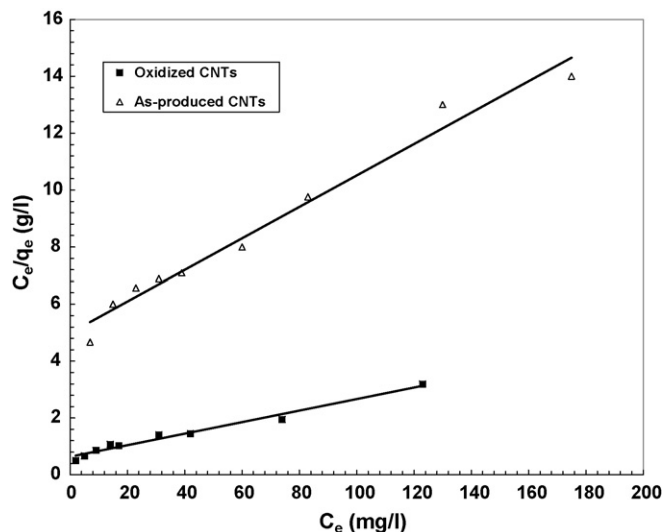


Fig. 6. Langmuir isotherms for the as-produced and oxidized CNTs.

Table 3
Langmuir and Freundlich constants

Model	Langmuir				Freundlich	
	q_{mon} (mg/g)	K_L (l/mg)	R^2	n	K_F (mg/g)	R^2
As-produced CNTs	18.083	0.011	0.9765	1.51	2.267	0.9865
Oxidized CNTs	49.261	0.032	0.9764	1.725	2.921	0.9821

Langmuir equation and the results are listed in Table 3. The correlation coefficients of the linear regressions (R^2) for both the as-produced and oxidized CNTs were found to be 0.9765 and 0.9764, respectively.

The Freundlich equation, given by

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F and n are the Freundlich constants which are indicators of adsorption capacity and adsorption intensity, respectively, is based on sorption on heterogeneous surfaces and does not provide any information on the monolayer adsorption capacity. Eq. (3) can be linearized to determine the Freundlich parameters; K_f and n , by plotting $\ln q_e$ versus $\ln C_e$ (Fig. 7). The correlation with the Freundlich equation of the adsorption of nickel on both CNTs samples are very good, the correlation coefficients of the linear regressions being 0.9865 for the as-produced CNTs and 0.9821 for the oxidized CNTs. The values of the Freundlich parameters are listed in Table 3. As can be noticed, the value of n was greater than 1, which indicates favorable adsorption of nickel on CNTs.

Table 4 shows a comparison for the adsorption capacity between a commercial activated carbon called MINOTAUR produced by Calgon Carbon Corporation and used in drinking water purification [29], activated carbon made from peanut shells [29], as-produced CNTs, and oxidized CNTs. The more efficient one was the oxidized CNTs where its amount of adsorption according to Langmuir parameters was 49.26 mg/g compared to 39.79 mg/g for MINOTAUR, 26.35 mg/g for peanut shell, and

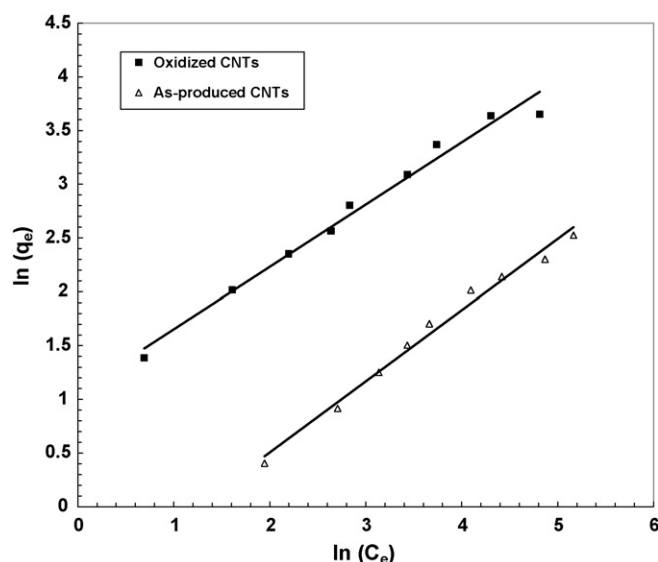


Fig. 7. Freundlich isotherms for the as-produced and oxidized CNTs.

Table 4
Comparison between oxidized CNTs and three different carbons

Carbon type	q_{mon} (mg-Ni ²⁺ /g-carbon)
Oxidized CNTs	9.26
MINOTAUR	39.79
Peanut shells	26.35
As-produced CNTs	18.08

18.01 mg/g for the as-produced CNTs. These results indicate that oxidized CNTs can replace the commercial activated carbon for the removal of nickel ions from water.

4. Conclusions

MWCNTs have been produced by decomposing acetylene gas in the presence of Ferrocene as a catalyst. The collected powder was used to remove nickel ions from water and proved to be very effective. The oxidation of the as-produced MWCNTs improved their hydrophilic properties and increased their cation exchange capacity from 110 to 253 meq./100-g CNTs due to the formation of different functional groups on the CNTs surface. Langmuir parameters showed that the oxidized CNTs have greater adsorption capacity for nickel ion removal from water than that for the MINOTAUR, peanut shells or as-produced CNTs.

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