Acid Activated Bamboo-Type Carbon Nanotubes and Cup-Stacked-Type Carbon Nanostructures as Adsorbent Materials: Cadmium Removal from Water

G. Andrade-Espinosa, J.R. Rangel-Mendez, E. Muñoz-Sandoval, H. Terrones, M. Terrones*
Institute for Scientific and Technological Research in San Luis Potosí (IPICyT), Mexico. Lomas 4a. sección, C.P. 78216.

ABSTRACT

Considerable amounts of heavy metals have been discharged to the environment since the beginning of the industrialization. Consequently, the concentration of toxic metals in rivers, lakes and oceans has increased notably. Cadmium, arsenic, copper, zinc, lead and other metals have been listed by the USEPA as the most common contaminants in wastewaters. Cadmium, in particular, has been identified as one of the most toxic contaminants that causes severs health problems to human beings, and harms flora and fauna. A wide variety of adsorbents materials, such as activated carbons, clays, zeolites, etc., have been utilized to remove heavy metals from aqueous solutions, although in recent years nanostructured materials have taken special attention due to their excellent physicochemical characteristics such as high surface area and strength, and have already had an ample application in electronic devices and composite materials. The applications of carbon nanostructures as adsorbent materials of contaminants present in solution have just begun to be explored; and recent reported results appear very promising despite the fact that these materials are not yet produced in large amounts. In this investigation bamboo-type carbon nanotubes and cup-stacked-type carbon nanostructures were modified with nitric acid at boiling point (about 84 ^{o}C) for one to three hours. The carbon nanostructures were characterized before and after oxidation by SEM, EDX, FTIR, and acid/base titration. Plus cadmium adsorption experiments were carried out at an initial concentration of 60 mg/L, 25 ^{o}C and pH 6 in batch reactors. Preliminary results have shown that the three hours oxidized carbon nanostructures have less Fe (catalyst) and the oxygen content increased about 2%, which was also reflected in a high amount of acid sites (about 2 mmol/g). These last findings were also supported by FTIR; treated materials showed more accentuated energy absorption peaks at wavelengths between 1750 and 1700 cm^{-1}, which is attributed to higher concentration of carboxylic acids (COOH). Untreated and oxidized carbon nanostructures adsorbed about 2 and 14 mg of cadmium per g of material, respectively, which demonstrates that the introduction of oxygen-containing surface groups in the nanostructures enhanced the adsorption capacity. These preliminary findings indicate that the modified nanostructure materials studied herein have a potential application in the removal of contaminants and/or recovery of precious metals present in aqueous phase.

INTRODUCTION

The presence of heavy metals (Cu, CD, Pb, Ace, Hg, etc.) in aqueous solutions is a high-priority problem world-wide, due to the enormous damage that these cause to human beings, to flora and fauna. The cadmium is a very toxic element that seriously affects to plants and animals, and causes certain diseases; emphysema, obstructive bronchitis, pulmonary fibrosis, damages in the kidney (Galvao and Corey, 1987), etc. The cadmium is introduced to the body through the ingestion of foods and water and also through the particle inhalation suspended in air. The contamination of cadmium occurs by natural and human sources. The main sources of cadmium are the industrial activities that process cadmium and in the second place the industrial activities that make products with this. There are several physical and chemical processes that can be used to remove cadmium dissolved in aqueous solution, for example adsorption, ionic exchange resins, membranes, chemical precipitation, electrochemical deposition, etc. One of the most used processes is adsorption, due to its low cost and high efficiency. The main element in this process is the adsorbent material, which at the moment presents a limited adsorption capacity. An ample variety of materials has been used to remove cadmium from aqueous solutions, such as activated charcoals, clays, zeolites, activated alumina, biosorbents, ion exchange resins, etc. In recent years the nanostructures materials have obtained a special attention thanks to their physical and chemical properties, and they have already had an ample application in electronic devices and composite materials. The materials that were used in this work are bamboo-type carbon nanotubes (CNx) of multiple layers doped with nitrogen (M. Terrones 1999, R. Czerw 2001) and cup-stacked-type carbon nanofibers (CST), a new type of carbon nanofiber that exhibits conical morphology; the conical layers are truncated and they have a central hollow base (M Endo 2003). The objective of the present study is functionalize carbon nanostructures (CNx and CST) by means of an acid treatment to obtain an adsorbent that will be able to adsorb cations, such as cadmium, present in solution.

EXPERIMENTAL METHODOLOGY

Functionalization of Carbon nanostructures

The functionalization of carbon nanostructures was carried out by means of the following procedure: a certain amount of material was placed in concentrated nitric acid solution (min. 68% - max. 71%) in a 3 mouths distillation flask which was connected to a condenser. The flask, that contained the solution and the material, was submerged in a water bath at 84 °C, The experiments were conducted for one, two and three hours. After this period of time, the flask was retired from the water bath and cooled down to room temperature. Then the excess of acid was retired and the material was repeatedly washed with deionized water until it reached approximately neutral pH. Finally, the material was dried in a stove at 105 ºC.

Carbon nanostructures characterization

The synthesized and oxidized for three hours Carbon nanostructures were characterized by Scanning Electron Microscopy (SEM). The Micrographs obtained helped to observe the morphology of the nanostructures. The chemical composition of these nanostructures was determined by Energy Dispersive X-Ray (EDX). Plus the carbon nanostructures were analyzed by Fourier Transform Infrared (FTIR). This technique was used to determine the presence of functional groups on the carbon nanostructures. These last analyses utilized the potassium bromide technique.

Determination of total acid sites

The acid-base titration method was implemented to determine the total concentration of oxygen-containing groups of the carbon nanostructures. The acid active sites were neutralized with a solution of sodium hydroxide (0.01 N). The determination of the active sites was carried out as follows: a determined amount of material was placed in 10 milliliters of alkaline solution. This mixture was agitated during 24 h and later it was centrifuged by approximately one hour. A sample of 4 milliliters was taken and three drops of methyl red were added to this sample, then the titration was made with hydrochloric acid (0,01 N).

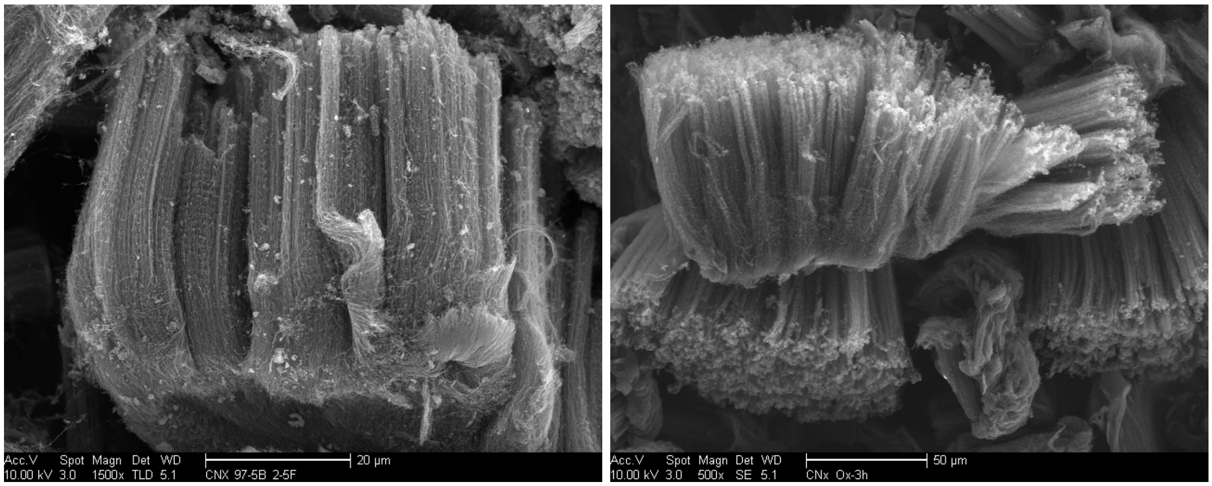
Cadmium adsorption by carbon nanostructures

The adsorption capacity of the carbon nanostructures was determined in batch reactors. A cadmium solution of 60 mg/L of initial concentration was placed in a conical flask and then certain amount of carbon nanostructures was added. The reactors were partially submerged in a water bath maintained at constant temperature (25°C). The adsorbent and the adsorbate were left in contact until the equilibrium was reached. Later the final concentration was measure by Atomic Absorption Spectroscopy. The mass of adsorbate removed was calculated by a mass balance.

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM).

Figure 1 presents the morphology of the modified CNx for 3 h. Aggregates of hundreds of carbon nanotubes can be observed with approximately 50 microns in length and 20 nanometers of diameter.



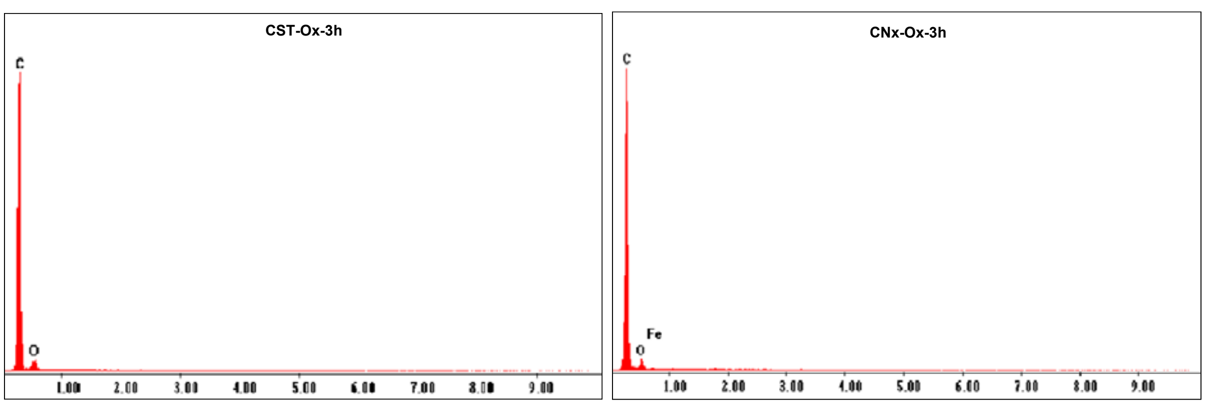
(A) (B)

Figure 1. (A) Micrograph of CNx synthesized; (B) Micrograph of CNx modified for 3 h

These micrographs also show that the synthesized nanostructures are aligned between each other; however, when these materials were oxidized the agglomerates of carbon nanotubes were dispersed. Plus some shany points were observed in both materials, which correspond to the catalyst (ferrocene)

Energy Dispersive X-Ray (EDX)

The spectrograms obtained by (EDX) revealed that the synthesized CNx posses 91.87 % of carbon, 4.05% of oxygen and 4.08 % of Fe. On the other hand, the modified CNx reported a change in the percentage of these elements: 90.93, 5.81, and 3.26% of carbon, oxygen and Fe, respectively (Figure 2(B)).



(A) (B)

Figure 2. (A) Quantitative analysis of the CST modified for 3 h; (B) Quantitative analysis of the CNx modified for 3 h

Conversely CST without functionalization showed about 95% of carbon and 4.4% of oxygen, whereas for modified CST by 3 h this technique reported 93.5% and 6.49% of carbon and oxygen, respectively (Figure 2(A)). These previous findings indicated that the acid activation managed to dissolve a part of the catalyst of CNx and also increase the oxygen concentration as it was expected.

Fourier Transform Infrared (FTIR)

The spectrums for carbon nanostructures, before and after its functionalization with nitric acid for 3 h, indicated the more predominant wavelengths. The tension bands are located at 1758 and 1610 cm^{-1} for the CNx and 1751 and 1644 cm^{-1} for the CST correspond to COOH groups. The increase of absorbance in these wavelengths, corresponding to the modified carbon nanostructures; indicates a greater concentration of oxygenated groups. (Figure 3)

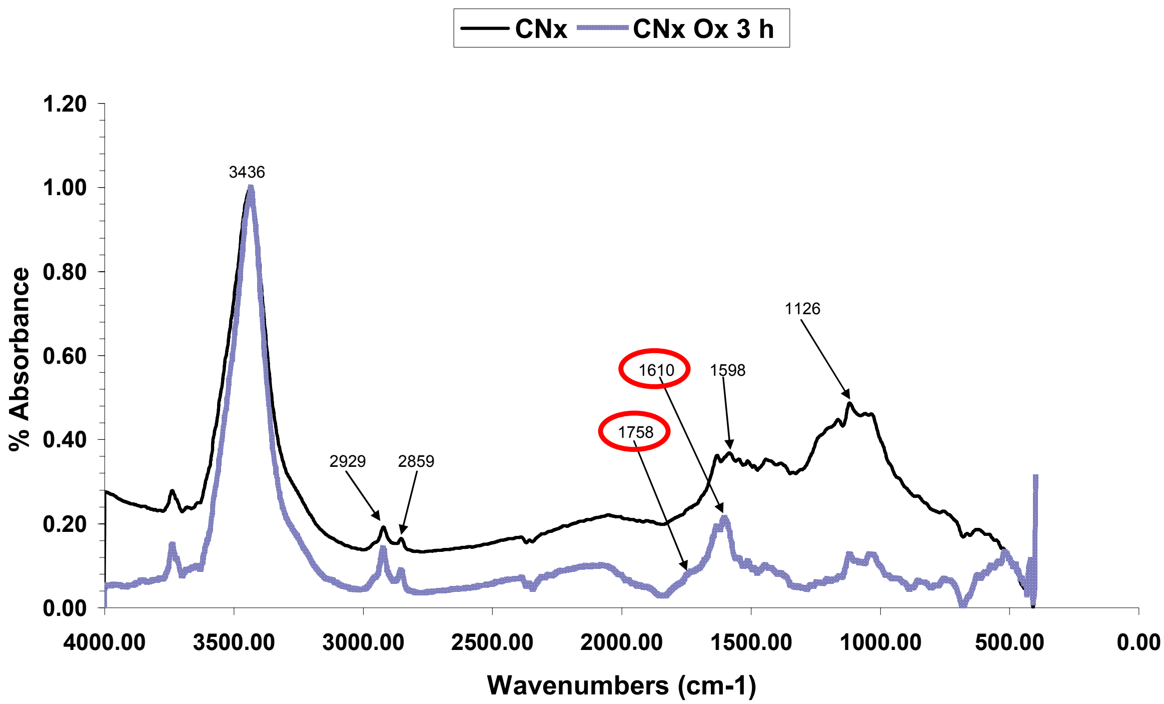


Figure 3. Infrared spectrum for CNx before and after its functionalization with HNO_3

Determination of total acid sites

The acid-base titration method was used to determine the total active sites of the carbon nanostructures (Table 1).

Table 1. Concentration of acid sites in CNx synthesized and modified by 3 hours

Material	Total acid sites (mmol/g)
CNx	0.94
CNx-Ox-3h	2.9

These results indicated that the total concentration of acid groups increased three times when the carbon nanostructures were functionalized, which is a result of the increase of the oxygen concentration in the modified materials.

Cadmium adsorption

The following bar chart (Figure 4) shows the difference in cadmium adsorption capacity of the synthesized and the modified nanostructures. It is observe that one hour oxidation is not enough to improve the cadmium sorption capacity. However, when the oxidation time increased to two and three hours the sorption capacity improved. The highest cadmium uptake was 14 mg/L for modified CNx for 3 h.

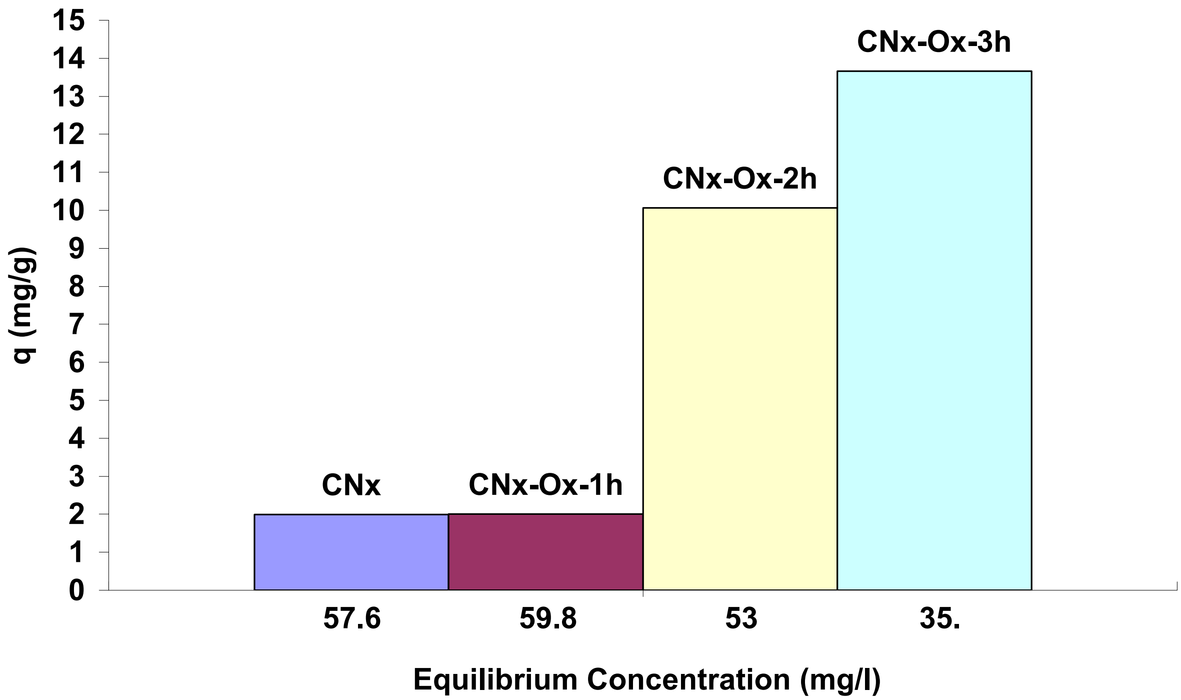


Figure 4. Cadmium adsorption capacity of CNx. Initial concentration of 60 mg/L, pH 6, and 25° C.

CONCLUSIONS

An increase in oxygen concentration and a decrease in Fe concentration, which correspond to dissolution of catalyst, occur in modified carbon nanostructures. The spectrums for carbon nanostructures oxidized for 3 h indicate more accentuated energy absorption peaks that correspond to COOH groups. Also the functionalized carbon nanostructures show an increase in the total concentration of acid groups, which is a result of a higher oxygen concentration in the modified materials. On the other hand, the cadmium adsorption capacity improves when the oxidation time increases; oxidized CNx for 3 h removed 14 mg/L at pH 6 and 25° C. These preliminary results suggest that modified carbon nanostructures have potential to removed toxic cations from water. Plus these materials could be applied to remove or recover precious metals or substances from aqueous solutions.

REFERENCES

Galvao, A.C. y Corey, G., 1987, “Serie Vigilancia 4(Cadmio)”, Organización Mundial de la Saluds, México.

M. Terrones, et al, Applied Physics Letters 75, 3932-3934 (1999)

R. Czerw, et al. Nanoletters 1, 457-460 (2001)

Endo, M.; Appl. Phys. Lett 2002, 80,1267

ACKNOWLEDGEMENTS

The autors appreciate the economical support from Fondos Mixtos CONACyT-Estado de Puebla (Clave: PUE-2004-C02-5) and Fondos CONACyT-Investigación Básica (Clave: SEP-2004-C01-45764).