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Chemically Modified Carbon Nanotubes (CNTs) with Oxygen and Sulfur Containing Functional Groups for Adsorption of Mercury

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Abstract. Surface functionalization of multi-walled carbon nanotubes (MWCNTs) was carried out using a gas phase treatment in a Universal Temperature Program (UTP) reactor by flowing SO_3 gas onto the CNTs while being heated to different temperatures. The functionalized nanotubes were characterized using X-ray Fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FT-IR), and Raman Spectroscopy. The amount of oxygen and sulfur containing groups was determined by acid-base titration and thermogravimetric analysis (TG-MS). The titration results were in good agreement with TG-MS data and elemental analysis using XRF. FTIR analysis shows the formation of oxygen and sulfur containing groups, S=O, C-S, C=O and -COOH. Raman spectroscopy confirmed that oxygen and sulfur containing acidic groups covalently attached to the sidewall of the MWCNTs.

Keywords: Carbon nanotubes, Functionalization, characterization, sulphur-based surface.

1. Introduction

In recent years, a great deal of attention has been focused onto the application of carbon nanotubes as adsorbents to remove toxic and harmful substances from wastewater and air. The large specific surface areas, as well as the high chemical and thermal stabilities, make carbon nanotubes an attractive adsorbent for heavy metals. However, due to its low dispersibility in aqueous systems caused by high Van der Waals forces among tubes, CNTs tend to agglomerate and form bundles in composites instead of individual tubes [1, 2]. Therefore, chemical modifications of CNTs surfaces have been a key research area due to their hydrophobicity properties in aqueous systems. Surface functionalization can effectively improve the dispersibility and reactivity of the CNTs for application in aqueous systems. It is also important to develop adsorbent material that can perform the function via two mechanisms simultaneously which are chemisorptions and physisorption. Physisorption is the interaction when an atom or molecule is bound to the surface of a solid by Van der Waals forces. On the other hand, chemisorption involves stronger forces and forms chemical bonds that involve the transfer or sharing of electrons. It is an interaction that occurs when an atom or molecule is bound to a surface through overlapping of one or more of its electron orbitals [3]. In this study, we investigate the optimum conditions needed to functionalize CNTs with high amounts of acidic sides while achieving a porous material with high surface area. The aim of modification is to introduce oxygen and sulphur containing functional groups as well as to increase the dispersibility in aqueous environment.

2. Material and Methods

In this study, functionalization process was carried out by gas phase treatment in a UTP reactor by flowing SO_3 gas onto the MWCNTs while being heated to different end temperature, see Table 1. The gas phase reaction was carried out in a horizontal quartz tube reactor heated by a UTP reactor. A weighed sample

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of MWCNTs (~3g) was placed in the horizontal quartz tube reactor fitted with gas inlet and the outlet was connected to H_2SO_4 bubbler trap. A multi-neck flask containing 20% SO_3 in concentrated H_2SO_4 fitted with gas inlet/outlet tubes was connected to reactor tubes. Argon stream was used to carry SO_3 vapor into the quartz tubes.

Table 1. Parameters for functionalization process

Samples	Parameters		Treatment
	Temperatures (^oC)	Time (h)	
B6	100	2	Pretreatment in conc.HNO_3
B7	200	2	and Gas Sulfonation
B8	300	2	[SO_3/H_2SO_4]

3. Result and Discussion

Carbon surfaces were modified by reaction with nitric acid and SO_3 vapor treatments to introduce sulfur and oxygen containing functional groups. These treatments were done at different duration and various temperature conditions which results in the formation of acidic carboxylic groups. Using acid-base titration, the number of surface acidic functional groups was determined as assumed that base neutralizes acidic functional groups. The results presented in Table 2 show the titration profile of the functionalized samples.

Table 2: Total number of surface acidic functional groups and pKa values for functionalized samples.

Treatment	pKa values		Total number of surface acidic functional groups ($molg^{-1}$)	Functional group present
	pKa_1	pKa_2		
B6	3.50	5.98	4.36×10^{-4}	Carboxyl and lactone
B7	3.34	7.10	6.05×10^{-4}	Carboxyl and phenol
B8	4.02	7.00	2.70×10^{-4}	Carboxyl and lactone

The B7 sample consumed more volume of NaOH thus the amount of acidic sites were significantly higher than other treated samples of 6.05×10^{-4} $molg^{-1}$. The amount of acidic sites for B6 samples was 4.36×10^{-4} $molg^{-1}$, which is lower than B7 due to the low treatment temperature which results in less number of functional groups created on the surfaces. Sample treated at higher temperature of 300 ^oC (B8) exhibits the lowest number of acidic site created on the carbon surface.

Thermal behaviors of the functionalized samples were measured by thermogravimetric analysis. Figure 1 shows, the TGA curves of the functionalized samples in the range of 30 – 1000 ^oC. The diagram of functionalized samples of B6 and B7 decomposes in three distinct steps which is at 30 – 200 ^oC, 200 – 300 ^oC and 300 – 1000 ^oC . The samples of B6 and B7 exhibit almost the same TGA curve whereby the first, second and third weight losses detected were about 0.5, 2.0 % and 4.0 % respectively. In contrast, B8 exhibits two region of decomposition at onset temperature of 30 – 400 ^oC and 400 – 1000 ^oC with weight loss of 0.5 % and 3.0% respectively. This result indicates the highly thermal stability of the samples. The TGA results were in good agreement with the amount of acid determined from acid base titration finding.

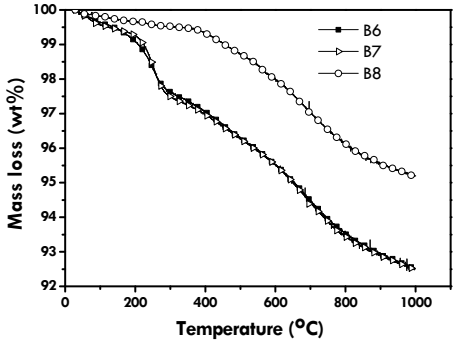

Fig. 1: Thermalgravimetric curve for functionalized samples

ATR-IR spectroscopy was carried out to identify the functional groups present on the sidewall of the functionalized MWCNTs samples. The IR transmittance band of all functionalized samples are shown in Fig. 2.

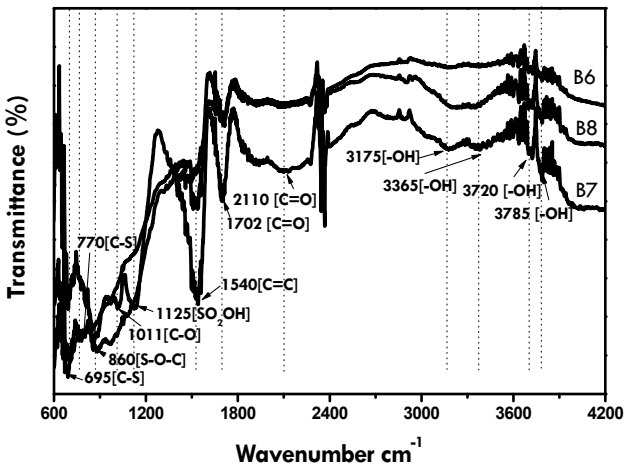

Fig. 2: IR spectra for functionalized samples

Raman spectroscopy has been successfully applied for studying the order of carbon atoms. The degree of functionalization was quantified using the D to G band intensity ratio (I_D/I_G) ratio which is the intensity of the disorder mode at 1360 cm^{-1} divided by the intensity of graphite mode at 1600 cm^{-1}. In this study, the I_D/I_G ratio shown in Table 3 gave values of 1.51, 1.59 and 1.53 for samples B6, B7 and B8 respectively. The B7 sample showed the highest number of I_D/I_G ratio values of 1.59 as compared to B6 and B8 samples. Raman spectra of the functionalized samples and the quantitative results are summarized in Table 3 and Fig 3.

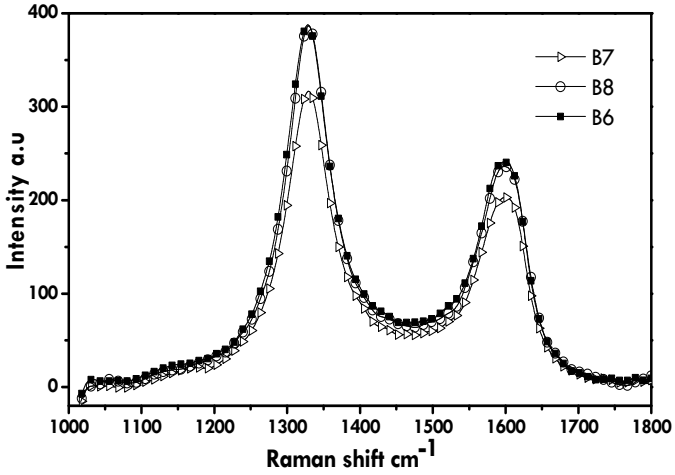

Fig. 3: Raman scattering spectra of functionalized sample

Table 3: The Raman shift (cm^{-1}) and the I_D/I_G ratio for functionalized MWCNTs samples.

Treatment	Raman shift (cm^{-1})		I_D/I_G
	D	G	
B6	1327.94	1598.05	1.51
B7	1328.74	1601.81	1.59
B8	1327.15	1601.06	1.53

The functionalized samples were quantified by XRF analysis to determine carbon and sulfur content. The number of molecules for carbon and sulfur was calculated to compare the changes of sulfur loading. Compositional data in terms of changes in sulfur loading obtained using XRF are presented in Table 4. Bulk composition analysis using XRF shows that, B7 sample exhibit the highest sulfur loading followed by B6 and B8.This results confirm the optimum temperature for introducing sulphur functional groups is 200 ^{o}C.

Table 4: Number of carbon and sulphur molecules of functionalized samples

Samples	Elements	Number of Molecules (moles)
B6	C	0.1124
	S	6.841 x 10-5
B7	C	0.1580
	S	16.45 x 10-5
B8	C	0.145
	S	2.618 x 10-5

The BJH data from N_2 adsorption-desorption method employed for all functionalized samples shows the continuous size distribution with two different pore modes. The width between 2 and 5 nm in diameter (see Figure 4) indicates properties of the small pores. While pores of width of 6 to 130 nm in diameter indicate large pore surface properties. The pore size distribution shows the characteristic of mesoporous surface with the size between 2 to 50 nm (20 -500 Å).

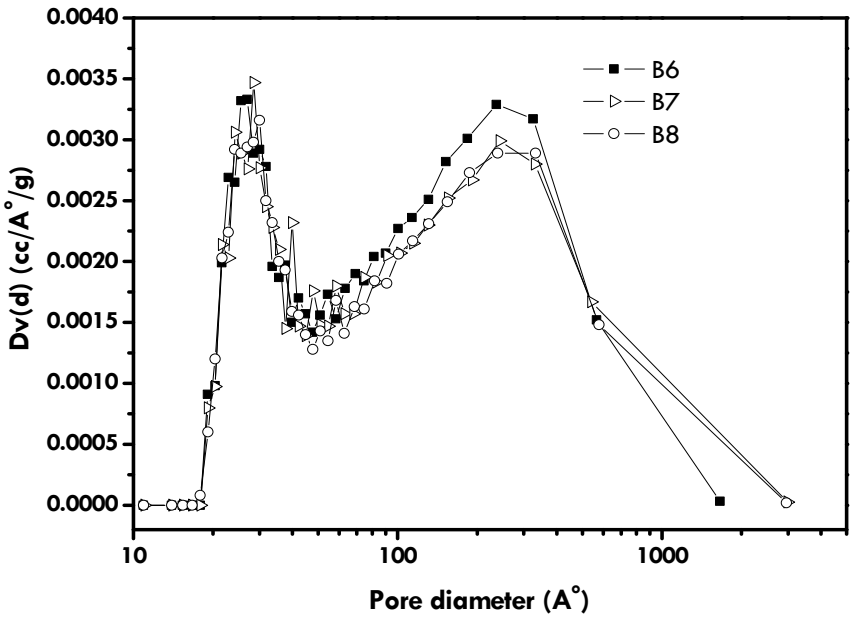

Fig. 4: Pore size distribution of functionalized samples

4. Conclusions

The chemical functionalization of MWCNT by acidic functional groups was successfully performed to enhance mercury(II) removal from aqueous solution. The chemical treatment was successful in anchoring acidic functional groups on the functionalized samples. The optimum condition of treatment was found to be at 200 ^{o}C for 2 hrs that creates the highest number of acidic functional groups on the functionalized samples. At this temperature, the sample (B7) exhibits the highest number of acidic site as compared to other two samples. The IR studies showed the formation of oxygen and sulphur containing functional groups. From the BJH method, the pore size distribution shows the mesopores characteristic for all functionalized samples.

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6. References

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