

## Selective adsorption of soft heavy metal ions with thiolated carbon nanotubes prepared by plasma functionalization

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### Introduction

Functionalized carbon nanotubes have attracted attention in removal of metal ions due to their adsorption properties and functionality [1,2,3]. It is shown that adsorption properties of carbon nanotubes depend extremely on the quantity of functional groups introduced in open ends and defects in graphitized structure of CNTs [4]. So far chemically treated CNTs to create acidic and basic functional groups have been used in heavy metal adsorption. Nevertheless, other studies show that other functionalities can be more effective in adsorption of heavy metals. In this respect, Liu et al. used CNTs functionalized with L-Cysteine as a selective adsorbent for soft metal ions such as cadmium. It is believed that selective behavior of these CNTs is due to soft Lewis base thiol group in cysteine molecules which can form stable bond with soft Lewis acid  $\text{Cd}^{2+}$ . However, the thiolation process was complex and required utilization of hazardous chemicals [5]. To overcome these difficulties, plasma functionalization is a preferred method as a clean and fast technique.

In this investigation we utilized, for the first time, thiolated CNTs functionalized in a dielectric barrier discharge (DBD) plasma reactor for removal of cadmium ions from water.

### Experimental

MWCNTs (Shenzhen Nanotech Port Co., Ltd, China), elemental sulfur and carbon tetrachloride (merck) were used to prepare the thiol functionalized-MWCNTs. CNTs were annealed in helium atmosphere at  $1000^{\circ}\text{C}$  in order to remove any possible functional groups on the CNTs. Annealed nanotubes were impregnated with a solution of sulfur and  $\text{CCl}_4$  and then were dried overnight at  $80^{\circ}\text{C}$ . MWNTs were placed in a DBD reactor for plasma treatment. A high voltage amplifier (TREK 10/40A) was used to generate DBD plasma. A HAMEG 20 MHz oscilloscope was used for monitoring the generated current and phase shift. The DBD plasma reactor consisted of a 4.0 mm thickness quartz tube as a dielectric barrier and a stainless steel rod inner electrode. For each 0.05 g of the impregnated MWCNT sample, a 10.0 sccm flow of 10% hydrogen in helium was passed over the sample. The exposure time to plasma varied in the range of 30 s to 7 min with a 9 kV AC voltage. Samples treated as such were washed with  $\text{CCl}_4$  at  $40^{\circ}\text{C}$  in order to remove any non-reacted sulfur and then dried overnight. To have a basis for comparison some of the annealed MWCNT was treated in a concentrated nitric acid for 4 h under reflux conditions. The solution was then

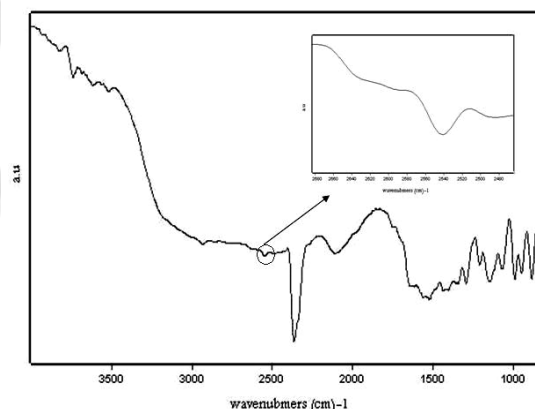
centrifuged and its solid was collected, resuspended in deionized water, centrifuged several times and finally dried overnight.

The functional groups of CNTs were determined via infrared spectroscopy. The quantity of functional groups for each sample was measured and compared by a temperature-programmed chemical reaction (TPR) technique in presence 10% hydrogen in argon atmosphere. The temperature range applied for TPR was  $100\text{-}1000^{\circ}\text{C}$  with a ramp rate of  $10^{\circ}\text{C}/\text{min}$ . The effluent gas from the TPR reactor was analyzed using an online FTIR spectrometer.

Adsorption properties were studied by adding 25.0 mg of functionalized CNTs into 50 ml of  $\text{Cd}^{\text{II}}$  solution with a concentration of 10 ppm.  $\text{NaNO}_3$  were added as the source of  $\text{Na}^+$  ions in concentration ranged from 0 to 20 ppm. After stirring for 6 h, the solid phase was separated and the remained solution was measured for the remaining  $\text{Cd}^{\text{II}}$  ions by atomic absorption spectrometer.

### Results and Discussion

Figure 1 shows the FTIR spectrum of a sample thiolated in plasma atmosphere for 4 min. This spectrum shows a characteristic peak at  $2550\text{ cm}^{-1}$  which is assigned to  $-\text{SH}$  stretching bond linked to CNTs framework [6]. Furthermore a peak at  $1560\text{ cm}^{-1}$  may be assigned to disordered carbon chemical bond in CNTs.



**Fig. 1** FTIR spectrum of a sample thiolated in plasma atmosphere for 4 min.

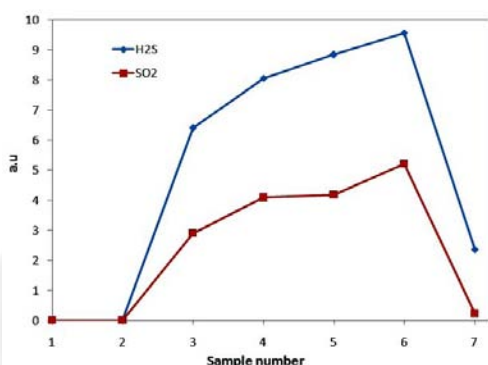
The sulfur containing functional groups was quantified by TPR in hydrogen and argon atmosphere. The treatment conditions for the samples are presented in Table 1. IR spectroscopy performed on the TPR reactor effluents indicate that the functional groups on CNTs were detached in the form of hydrogen disulfide and sulfur dioxide. By integrating the area under the peaks of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in IR spectrum, the amount of evolved gases can be comparatively estimated. The results are shown in Figure 2. As may be observed, the annealed CNTs and the samples washed with the solvent after impregnation, do not show any desorbed sulfur containing

gases. It is obvious that with increasing in the plasma exposure time, the amount of desorbed gases is increased. However,

**Table. 1** Treatment conditions for the samples.

Sample 1	Annealed
Sample 2	Washed with CCl <sub>4</sub> after impregnation
Sample 3	30sec treatment with plasma
Sample 4	1min treatment with plasma
Sample 5	2min treatment with plasma
Sample 6	4min treatment with plasma
Sample 7	7min treatment with plasma

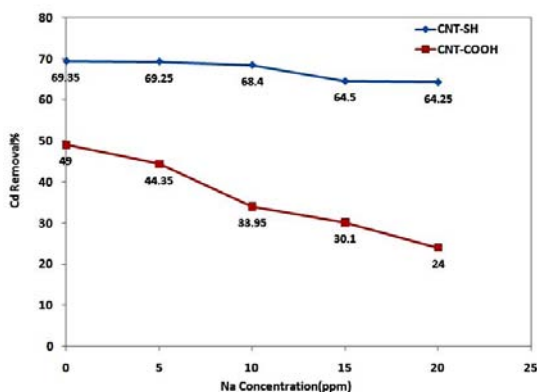
after 4 min exposure to plasma atmosphere the amount of desorbed gases is reduced. This behavior may be attributed to the destruction of chemical bonds linked to the CNTs framework as a result of collision with the high energy species present in the plasma atmosphere.



**Fig. 2** Estimation of evolved H<sub>2</sub>S and SO<sub>2</sub> detected by IR spectroscopy

Although the nanotubes were annealed in argon atmosphere, it seems that some oxygenated groups remains in the course of annealing and these groups react with sulfur and are desorbed mostly in the form of SO<sub>2</sub>.

Figure 3 shows the selective adsorption behavior of the sample treated in plasma for 2 min.



**Fig. 3** Adsorption behavior of thiolated samples in presence of competitive Na<sup>+</sup> ions.

As can be seen the cadmium removal from water for acidified sample, i.e., the sample chosen for comparison, decreases from 49 to 24% as the Na<sup>+</sup> concentration increases from 0 to 20 ppm in the solution. On the other hand, the thiolated CNTs have an almost constant behavior in presence of competitor ions such as Na<sup>+</sup>. In this case the removal percentage of cadmium is slightly reduced from 69 to 64%. The results indicate that the cadmium ions are selectively removed from solution in presence of a metal ion like Na<sup>+</sup>. This behavior may be explained as follows: the soft metal ions such as Cd<sup>2+</sup> can form stable complex with the soft thiol groups on the CNTs, whereas sodium ions have the less affinity toward thiol functional groups because of their relative hardness.

### Conclusions

MWNTs were impregnated with elemental sulfur and were treated with helium and hydrogen plasma in DBD reactor. FTIR studies show chemical reaction of hydrogen and sulfur with carbon and formation of thiol groups. Temperature programmed reaction of CNTs with hydrogen confirmed the presence of sulfur containing functional groups. It was also shown that there is an optimized exposure time to plasma in order to produce maximum amount of the functional groups on CNTs. The results also confirmed that adsorption of a specified concentration of Cd<sup>2+</sup> occurs in presence of sodium ions without a considerable decrease, while concentration of sodium ions increased gradually. In other words plasma functionalization of CNTs results in selective adsorption behavior.

Thus, the plasma method may be considered as a fast and clean method for efficient removal of soft metal ions in wastewater treatment and also in the recovery of precious metals.

### References

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