Removal of Pb by Adsorption of Amidoxime Group Modified Carbon Nanotubes

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Abstract. Multi-walled carbon nanotubes (MWNTs) were modified by amidoxime group, characterized by fourier transform infrared spectrometer (FTIR). The adsorption experiments of Pb(Pb) on raw MWNTs and amidoxime group modified MWNTs(AO-MWNTs) were studied under different conditions. Results showed that, the adsorption capacities of Pb on raw MWNTs and AO-MWNTs primarily increased with the increasing pH, adsorption temperature and the initial Pb concentration. Under the condition of pH=7 and temperature was 50℃, the adsorption capacities reached the maximum. The adsorption equilibrium of raw-MWNTs on Pb reached balance in about 90min and the AO-MWNTs achieved stable in 60min.The adsorption process of AO-MWNTs could be better described by Freundlich model.

Introduction

Carbon nanotube(CNT) has been widely researched since it was found in 1991[1].Carbon nanotubes(CNTs) have seamless, hollow cylinder type structure and they were curly formed by one or multi-layer graphenes. With the unique mechanical and electrical performance, CNTs have broad application prospects in the field of electronics, optics and material[2].In respect of adsorption, CNTs with large specific surface area, the nano-scale pore structure and the surface can be easily modified, they can be widely used to act as adsorption materials[3].

But some bad characteristics of the CNTs greatly limit the application of themselves[4], such as the strong van der Waals force, high surface activity, very easy to reunite and can't be easily dispersed in aqueous solution. Chemical functional groups could be introduced to modified the surface properties of CNTs[5], so as to increase their hydrophilicity and strengthen the ability of removing harmful pollutants in aqueous solution. In this paper, amidoxime group was used to modified the multi-wall carbon nanotube(MWNTs), in order to enhance the dispersion of MWNTs, improve the adsorption properties for metal ions in aqueous solution, and provide a new effective technique for the treatment of heavy metal ions.

Materials and Methods

Materials

MWNTs: Shenzhen NANO Tech. Port. Co. Ltd. (Shenzhen, China), diameter 20-40nm, length >5 m, the purity was more than 97%. Uranium standard solution: 1.1792g U_3O_8 was placed in a beaker of 100mL, added 10mL hydrochloric acid, 3mL H_2O_2 and about two drops of nitric acid. After the severe reaction, heated the beaker until U_3O_8 completely dissolved, and then transferred the liquid to a 1000mL volumetric flask, added distilled water to the scale and shook, per 1mL this solution contained 1mL uranium.

Methods

The 10.0g raw multi-wall carbon nanotube(MWNTs) were refluxed in a strong oxidizing agent (3:1 concentrated H_2SO_4/HNO_3 mixture)[6] at 60℃ for 12 h. Then 100mL of distilled water was added and the mixture was vacuum-filtered through a 0.45μm pore size PTFE filter paper. The filtrate was then washed with distilled water until the eluate reached the neutral pH and dried at 50℃ to obtain carboxylated CNTs(COOH-MWNTs).Second, 9.0g COOH-MWNTs(after granding) were added to a three-necked flask, 2ml dimethyl formamide (DMF) and 70ml dichloride sulfoxide ($SOCl_2$) were added, then heated to 70 ℃and refluxed for 12 h, with tetrahydrofuran (THF) centrifugal washing five times to remove the solvent to yielded acyl chloride-functionalized MWNTs (COCl-MWNTs).Thirdly, according to document[7], 8.0g COCl-MWNTs were added to 100mL 25% ammonia under ice bath condition, then reacted 4h in 10℃ environment, through high-speed centrifugation to get rid of supernatant, washed several times with methanol, dried under 50℃ and obtained the amide carbon nanotubes (NH2-MWNTs).Fourth, 6.0g NH_2-MWNTs were added into the mixed solution of 200ml acetonitrile, 40mL 37% formaldehyde and 40mL acetic acid. Heated to 95℃ and reacted 12h, then the mixture was vacuum-filtered through a 0.45μm pore size PTFE filter paper, the filtrate was washed with methanol. Vacuum drying under 50℃ to obtain the cyano functionalized carbon nanotubes(CN-MWNTs).Afterward, 8.686g hydroxylamine hydrochloride(NH_2OH・HCl) and 250mL distilled water were putted in a flat bottom flask, added 6.625 g Na_2CO_3 while pumped in N_2.Stirring and heating until they dissolved completely.Then 5.0 g CN-MWNTs was added and reacted under magnetic stirring and the temperature of 70℃.Through the vacuum filtration, the filter residue was washed with distilled water several times and got the final product of amidoxime functionalized carbon nanotubes(AO-MWNTs) after dried under 50℃.

Adsorption Experiment

Under the condition of different factors respectively investigated the adsorption effect of Pb on AO-MWNTs. After adsorbed completely, then vacuum-filtered through a 0.45μm pore size PTFE filter paper, the Pb concentration in filtrate was measured by the atomic absorption spectrophotometer.

Results

Suspension Dispersion Stability

Dispersion stability was an important index to evaluate the effect of the modification of carbon nanotubes, collision between the particles in dispersion liquid occurred due to the Brown movement, it was easy to generate attractive interaction between the particles, when attraction was less than repulsion, carbon nanotubes can be relatively stable dispersion in aqueous solution, on the contrary, precipitation was produced. A certain amount of different types of carbon nanotubes were separately dissolved in distilled water and were ultrasonic dispersed 30min, obtained mass concentration of 0.8g/L carbon nanotubes dispersion. The suspensions stabilities of different types of carbon nanotubes were listed in Table1, and the dispersed photos after 1day and 30days were separately shown in Fig.1.From this experiment could find that the liquid dispersion stabilities of COOH-MWNTs and AO-MWNTs were both well, while the stabilities of raw-MWNTs and NH_2-MWNTs were not good.

Tab. 1 The suspension dispersion stability of different CNTs

Carbon nanotube type	Precipitation time
raw-MWNTs	Less than one hour
NH_2-MWNTs	One day
COOH-MWNTs	No precipitation after 30 days
AO-MWNTs	No precipitation after 30 days

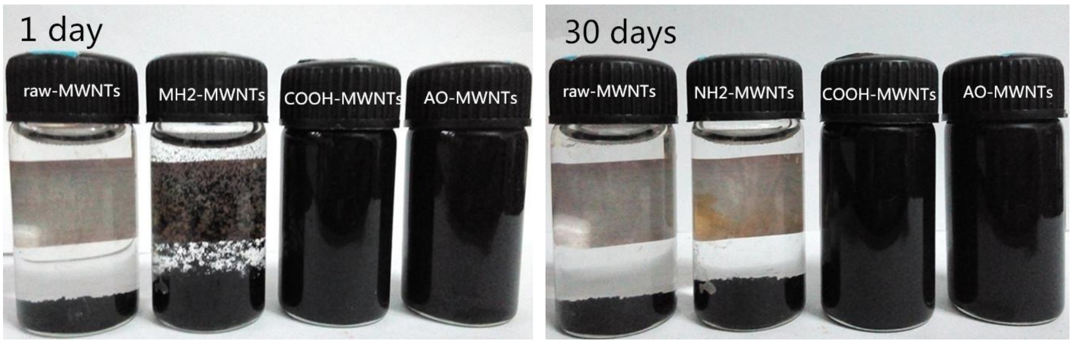
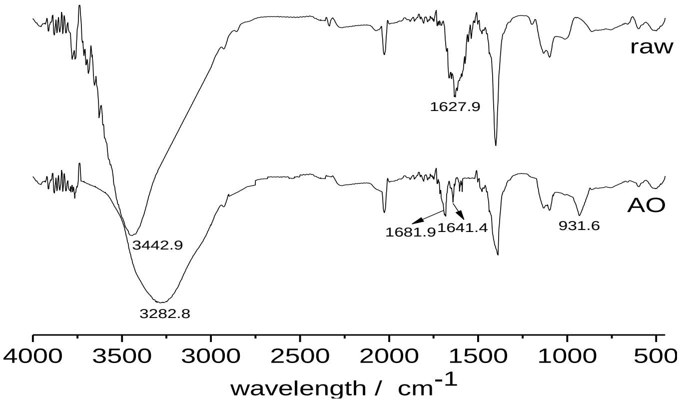


Fig.1 Different times of the suspension dispersed photos of CNTs

FT-IR Spectroscopy

Fig.2 showed the FT-IR spectra of raw-MWNTs(raw) and AO-MWNTs(AO).before modified, band of 1627cm^{-1} was appeared, which was due to C=O stretching vibration, and the strong wide band of 3440cm^{-1} was belonged to the stretching vibration of -OH.Observation can be found that AO-MWNTs appeared the band at 3282cm^{-1}, which corresponded to the stretching vibration of -OH in amidoxime group and the vibration of -NH_2 in primary amine. The C=N(1641cm^{-1})stretching vibration and the vibration of N-O(931cm^{-1}) could also be found, so amidoxime group was introduced to the carbon nanotubes.



raw: raw-MWNTs, AO:AO-MWNTs

Fig.2 Infrared spectra of MWNTs

Effect of pH

The 10mg/L simulated waste water of Pb was prepared, adsorbent dose was 0.5g/L and adjusted the pH in the range of 2-7, under 25 ℃ conditions investigating the absorption influence of pH on amidoxime carbon nanotubes of Pb. The adsorbents were ultrasonic dispersed 15min by ultrasonic cleaning machine firstly, oscillated 1h and vacuum-filtered through 0.45μm microporous membrane, the Pb concentration of filtrate was measured by atomic absorption spectrophotometer. When adjusting pH over 6, Pb gradually precipitated, this may influenced the determination results. While in the process of ultrasonic dispersion, the ultrasonic effect of raw-MWNTs was significantly less than AO-MWNTs.

The results were shown in Fig.3, with the increase of pH, the adsorption capacities of Pb on raw-MWNTs and AO-MWNTs were both increased gradually, it was because the solubility of Pb decreased while the pH value increased, white precipitate could be easily found when pH=7, this may reduce the Pb concentration of filtrate, so in order to achieve the better adsorption of Pb, the pH value was adjusted to 6 in the next experiment.

Effect of Initial Pb Concentration

Under the condition of pH=6, adsorption dosage was 0.5g/L, temperature was 25℃, the initial concentration of Pb were 2, 5, 10, 25, 50, 100mg/L separately. The adsorbents were ultrasonic dispersed 15min by ultrasonic cleaning machine firstly, oscillated 1h and vacuum-filtered through 0.45μm microporous membrane, the Pb concentration of filtrate was measured by atomic absorption spectrophotometer. As shown in Fig.4, with the increase of initial Pb concentration, the adsorption capacities of raw-MWNTs and AO-MWNTs were both increased, but the Pb adsorption effect of AO-MWNTs was significantly better than raw-MWNTs, when initial Pb concentration was 100mg/L, the adsorption capacity of AO-MWNTs could reach 131.4mg/g, this better adsorption effect was due to the better dispersibility of AO-MWNTs.

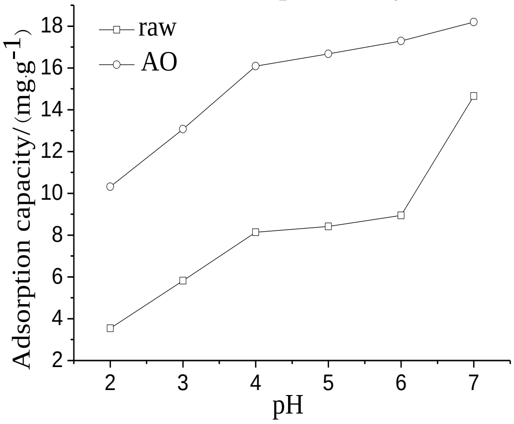


Fig.3 Effect of pH on adsorptivity

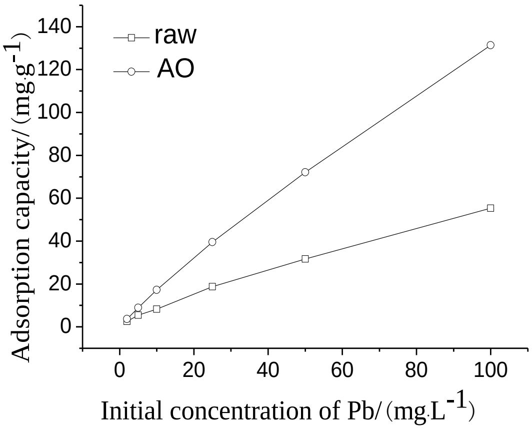


Fig 4 Effect of initial Pb concentration on adsorptivity

Effect of Oscillating Time

When the pH value was 6, adsorbent dosage was 0.5g/L, the concentration of Pb was 10mg/L, under the condition of the temperature of 25℃ to examine the influence of oscillating time on the adsorption capacity. Firstly the adsorbents were ultrasonic dispersed 15min, oscillated and vacuum-filtered through 0.45μm microporous membrane, the residual Pb concentration of filtrate was measured by atomic absorption spectrophotometer. The results were shown in Fig.5, the adsorption capacity of AO-MWNTs on Pb achieved a balance after 30min, while the adsorbing material of raw-MWNTs reached a steady after 60min.

Effect of Temperature

At pH=6, Pb concentration was 10mg/L, adsorbent dosage was 0.5g/L, 15min ultrasonic dispersed and oscillated 1h to investigated the influence that the temperature made on the adsorption process. From Fig.6 can obtained, the adsorption capacities of AO-MWNTs and raw-MWNTs were both gradually increased with the increasing of temperature, the Pb adsorption process of this two adsorbents belonged to endothermic reaction, increasing temperature could make contribution to the process of Pb adsorption.

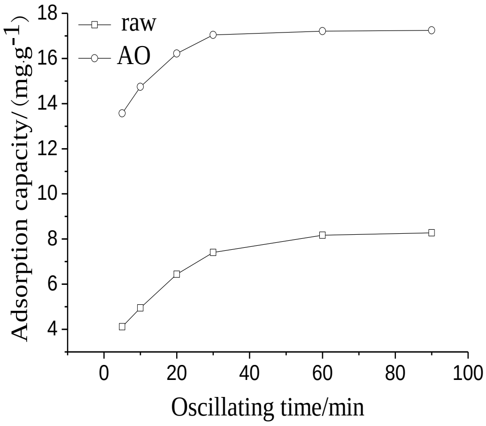


Fig.5 Effect of oscillating time on adsorptivity

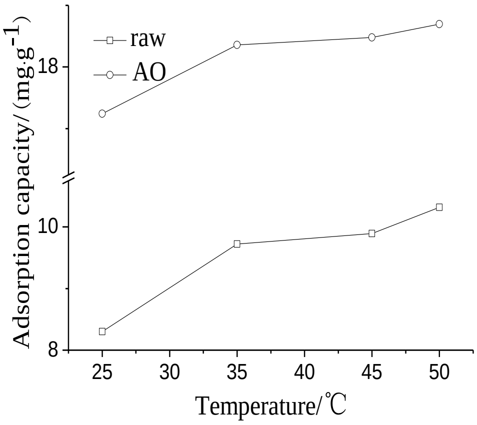


Fig.6 Effect of temperature on adsorptivity

Isothermal Adsorption Model

The adsorption isotherm was described the changing characteristics between adsorption capacity of the adsorbent and adsorbate concentration when reached the adsorption equilibrium under certain temperatures. In this paper, Langmuir and Freundlich model were used to fit the adsorption process of AO-MWNTs on Pb.The results were respectively shown in Fig.7 and Fig.8, the concluded relevant datas were listed in Table 2.From the simulations of this two models to the adsorption process could be seen, the concluded relevant data R^2 of the Freundlich adsorption isotherm model to simulate the adsorption process of AO-MWNTs was more than 99%, better than the Langmuir fitting degree, so the adsorption type of AO-MWNTs on Pb could be better described by Freundlich model, the multilayer adsorption was the main type.

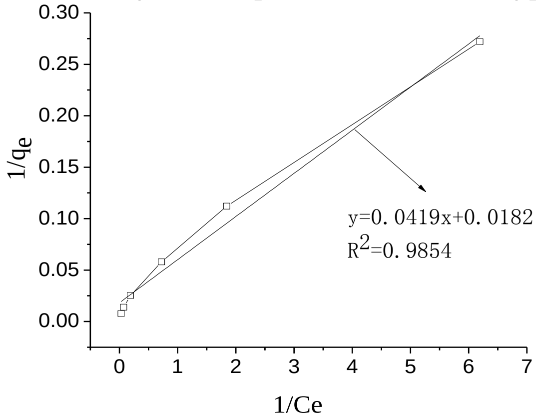


Fig.7 Fitting line of Langmuir adsorption isotherm

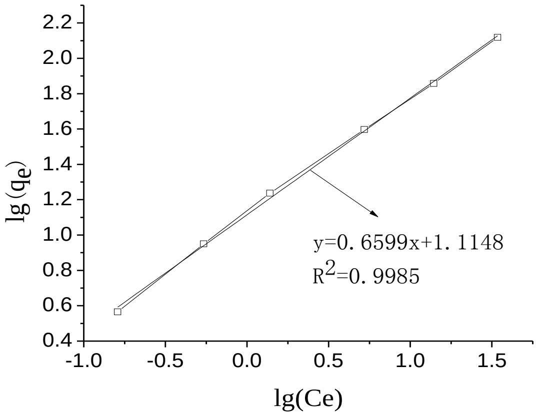


Fig.8 Fitting line of Freundlich adsorption isotherm

Tab. 2 Values of Langmuir and Freundlich constants of AO-MWNTs on the adsorption of Pb

	Langmuir			Freundlich		
	q_{max}	b	R^2	1/n	k	R^2
AO	54.945	0.4344	0.9854	0.6653	3.0158	0.9985

Conclusions

In this work, the cyano group was firstly introduced on CNTs, then amidoxime group was used to modifiy the CN-MWNTs. The detection method of FTIR proved that a novel adsorption material(AO-WMNTs) was produced.This methods improved the dispersion of carbon nanotubes in aqueous solution and enhanced the adsorption capacity of Pb. The adsorption experiments showed that: the Pb adsorption capacities of raw-MWNTs and AO-MWNTs were both gradually increased with the increasing of the pH value, adsorption temperature and initial concentration of Pb. Results also obtained that AO-MWNTs could be used as a good Pb adsorption material, the adsorption capacity of Pb on it was better than raw-MWNTs, and the time it needed to reach the balance was shorter than raw-MWNTs. So, this experiment can make contribution to the better use of carbon nanotubes and provide a better treatment of heavy metal ions.

Acknowledgements

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