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Adsorption of Pyridine from Aqueous Solution by Surface Treated Carbon Nanotubes

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Abstract: The surface treatment of multi-walled carbon nanotubes (MWCNTs) with acid, heat, ultrasonic, and polyvinyl alcohol has been examined. The original CNTs and four treated CNTs were first used as adsorbents to remove pyridine from water and the adsorption isotherms of pyridine on CNTs were studied. At the same time, the effect of pH, temperature, and the adsorption kinetics on the adsorption of pyridine were also evaluated. The experiments show that the adsorption of pyridine on different CNTs is mainly a physical process and the data fit the Freundlich adsorption isotherm well. The short time needed to reach equilibrium as well as the high adsorption capacity of pyridine suggests that CNTs possess highly potential applications for pyridine removal from water.

Keywords: Carbon nanotubes, adsorption, pyridine

INTRODUCTION

Long-term drinking water containing higher concentration pyridine can cause nausea, headache, giddiness, drowsiness, insomnia, increased heart rate and rapid breathing, and liver damage in humans (1). Pyridine contamination in drinking water mainly comes from the industrial process such as the production of pharmaceuticals, dyestuff, disinfector, dynamite and so on. Many methods including chemical reaction, photocatalytic degradation (2), ultrasonic-wave degradation (3), and adsorption have been used to remove

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pyridine from wastewater. Among these methods, adsorption is a cost-effective, simple, and widely used method.

Since their discovery in 1991 (4), carbon nanotubes (CNTs) have attracted great attention because of their unique properties. CNTs can be visualized as a sheet of graphite that has been rolled into a tube and is divided into single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) according to the carbon atom layers in the wall of the nanotubes. With the great progress in the methods of preparing CNTs, large efforts have been devoted to their fields of application. The perceived novel mechanical and electronic properties, large specific surface area, and high thermal stability indicate their tremendous potential for engineering applications. The hexagonal arrays of carbon atoms in graphite sheets of CNTs surfaces have a strong interaction with other molecules or atoms, which make CNTs a promising adsorbent material substituted for activated carbon in many ways. Recently, Long and Yang (5) reported that significantly higher dioxin removal efficiency were found with CNTs than with activated carbon. Li et al. (6) found that CNTs had high lead adsorption capacity and could be used as an adsorbent for lead removal from water. Li et al. (7) showed that CNTs were good fluoride adsorbents and their fluoride removal capability was superior to activated carbon. Peng et al. (8) indicated that CNTs were good adsorbents to remove 1,2-dichlorobenzene from water and could be used in a wide pH range of 3–10. Liang et al. (9) developed a new method using a micro column packed with MWNTs as sorbent for the preconcentration of trace amounts of Cd and Cu prior to their determination by flame atomic absorption spectrometry. The previous studies suggested that CNTs were promising adsorption materials used in environmental protection.

Here we treated CNTs with different methods and characterized their properties with BET N_2 adsorption, laser particle examination. The original CNTs and four treated CNTs were first used as adsorbents to remove pyridine from water and the pyridine adsorption isotherms of the CNTs were studied. At the same time, the effects of pH, temperature, and the adsorption kinetics on the pyridine adsorption were also evaluated.

EXPERIMENTAL

Instrumentation

The specific surface area and pore size distributions of the different CNTs were measured by nitrogen adsorption/desorption at 77 K using BET method by Gemimi V Surface Area and Pore Size Analyzer (U.S.A.), Particle size distributions of the different CNTs were analyzed by laser light scattering with a RISE-2006 (China). The results are volume-based and expressed in terms of equivalent spheres. The filtrates were measured for the unextracted Pyridine by spectrometry (UV-2401PC, Japan).

Reagents

CNTs (LMWNTS-2040) were purchased from Shenzhen Nanotech Port Co., Ltd., Shenzhen, China. Some dosages of the original CNTs were immersed into nitric acid, then the mixture was refluxed at 90°C for 4 h, then filtered and washed (by distilled water) till pH value being neutrality, dried at 100°C for further studies, which was labeled as CNTs-HNO_3; Some dosages of the original CNTs were firstly immersed into nitric acid, then the mixture has been shaken with ultrasonic at 30°C for 1 h, following steps were the same as that for CNTs-HNO_3, which was labeled as CNTs-ULTRA-HNO_3. Some dosages of CNTs-HNO_3 were further heated to 350°C and retained the same temperature for 12 h in air atmosphere, which was labeled as CNTs-HNO_3-OX; Some dosages of CNTs-HNO_3 were immersed into a polyvinyl alcohol solution in the quartz tube, then the mixture was heated to 250°C within 30 min in the air and retained the same temperature for 1 h, which was labeled as CNTs-HNO_3-POLY. Analytical grade pyridine (Honeywell Co., Ltd., China) was used to prepare a stock solution of 1000 mg l^{-1} of pyridine, working solutions were prepared from the stock solutions by stepwise dilution just before use.

Methods

Adsorption kinetics was studied by adding 0.02 g of the original and four treated CNTs into 25 ml of 80 mg l^{-1} of pyridine solutions respectively. The mixture was mechanically shaken for different time at 20°C, then filtered through a 0.45 μm membrane filters respectively. At the same time, another 0.02 g of the original and four treated CNTs were added into 25 ml distilled water respectively, then mechanically shaken and filtered for the determination of blank. The filtrates were immediately measured for the unextracted pyridine against blank by UV spectrometry.

The adsorption isotherms were examined by adding 0.02 g of the original and four treated CNTs into 25 ml of initial concentration from 20 to 80 mg l^{-1} of pyridine solutions at 20°C respectively. After the suspensions were mechanically shaken for 2 h, they were filtered and immediately measured against blank.

To study the effect of pH on pyridine adsorption, 0.02 g of the original and four treated CNTs were dispersed into 25 ml of 80 mg l^{-1} of pyridine solutions at 20°C respectively. The initial pH values of the solution were adjusted from 3.67 to 10.69 with 0.5 mol l^{-1} nitric acid or 0.5 mol l^{-1} sodium hydroxide.

The effect of adsorption temperatures were studied by adding 0.02 g of the original and four treated CNTs into 25 ml of initial concentration from 10 to 80 mg l^{-1} of pyridine solutions respectively. The experiments were carried out at 20°C, 30°C, and 40°C for 120 min respectively.

RESULTS AND DISCUSSION

The specific surface area and pore specific volume of the original and treated CNTs are listed in Table 1. It can be seen that the specific surface areas of the CNTs-HNO_3, CNTs-ULTRA-HNO_3, and CNTs-HNO_3-OX increase from 99.74 (of original CNTs) to 112.88, 113.17, and 117.34 $m^2\ g^{-1}$ respectively, while the specific surface areas of CNTs-HNO_3-POLY decreases from 99.74 to 70.95 $m^2\ g^{-1}$. Thus it can be explained that oxidation with nitric acid can remove the amorphous carbon, carbon black, and carbon nanoparticles introduced by preparation process and probe inner cavities of the CNTs, which expose their internal surface area (10). Carbon can react with air to generate CO_2, the structures with pentagons, heptagons, and amorphous carbonaceous matter have higher reactivities relative to CNTs, so matters containing pentagons, heptagons, or amorphous carbon can be oxidized firstly, which result in the increase of the surface area (11). The reasons for the surface area decrease of CNTs-HNO_3-POLY maybe some pores of the CNTs were blocked by undecomposed polyvinyl alcohol.

Particle size distribution can affect the suspensibility and adsorption property of the adsorbents. Figure 1 shows the comparable results of particle size distributions of the original and treated CNTs by laser light scattering. The particle diameters corresponding to the peak for original CNTs is 31.59 μm, while for the CNTs-HNO_3, CNTs-ULTRA-HNO_3, and CNTs-HNO_3-POLY the particle diameters decrease to 27.15 μm, 31.33 μm, and 23.24 μm, respectively. The phenomenon indicates that oxidation with HNO_3 can partially break up CNTs into small pieces; further treatment with polyvinyl alcohol can increase its suspensibility. But for the CNTs-HNO_3-OX the particle diameters increase to 34.89 μm, which is harmful for the suspensibility.

Adsorption kinetics of pyridine on the CNTs are given in Fig. 2. We can see that the adsorption and desorption of pyridine can attain equilibrium basically about 50 min on different CNTs. The results indicate that the CNTs has a fast uptake kinetics.

The adsorption capacities of pyridine on the CNTs are given in Fig. 3. It is clear that the adsorption capacity of pyridine by original CNTs is 3.8 mg g^{-1} at

Table 1. Porosity and specific surface areas of different CNTs

Sample	S_{BET} ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)
Original-CNTs	99.74	0.35
CNTs-HNO_3	112.88	0.44
CNTs-ULTRA-HNO_3	113.17	1.76
CNTs-HNO_3-OX	117.34	1.17
CNTs-HNO_3-POLY	70.95	0.21

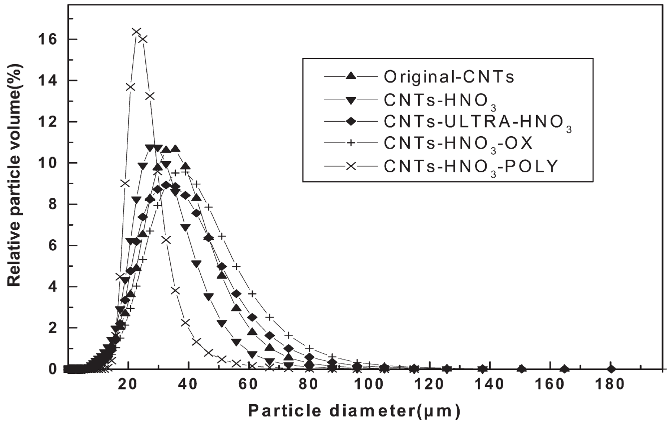

Figure 1. Particle size distribution of CNTs.

80 mg l^{-1} of pyridine concentration while the adsorption capacities increase slightly and reach 4.36, 4.28 and 4.07 mg l^{-1} for the CNTs-ULTRA-HNO_3, CNTs-HNO_3, and CNTs-HNO_3-OX at the same concentration. Compared with the original CNTs, the surface areas and suspensibility of CNTs-ULTRA-HNO_3 and CNTs-HNO_3 adsorption capacities of pyridine increase accordingly. For CNTs-HNO_3-OX, The suspensibility decreases but the surface area increases, so the adsorption capacity of pyridine increases slightly. For CNTs-HNO_3-POLY, the increased suspensibility is favorable for adsorption, but a sharp decrease of its surface area is harmful for adsorption, so the adsorption capacity obviously decreases to 2.58 mg l^{-1}. From the

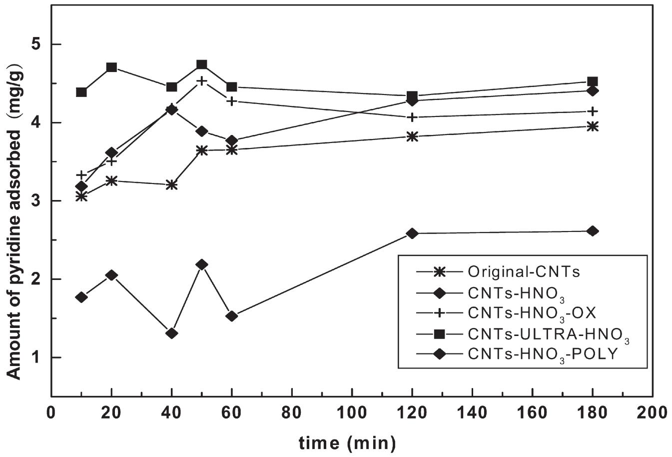

Figure 2. Time effect on the adsorption of pyridine on CNTs.

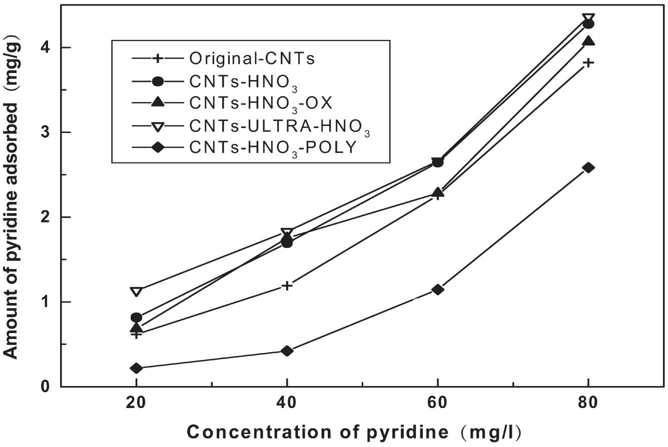

Figure 3. Adsorption isotherms of pyridine on CNTs.

experiment, we can deduce that the surface area of CNTs is a dominant factor on adsorption capacity.

Figure 4 shows the effect of pH values of the solutions on the adsorption capability of pyridine by different CNTs. Below pH 8.55, the amounts of pyridine adsorbed on different CNTs increase with the increase of the pH value. Above pH 8.55, with the increase of the pH value, the adsorptions of pyridine decrease. This indicates that the interaction between pyridine (weak alkaline) and H^+ at strong acidic conditions has an opposite effect on pyridine adsorption on different CNTs. But the surfaces of different CNTs

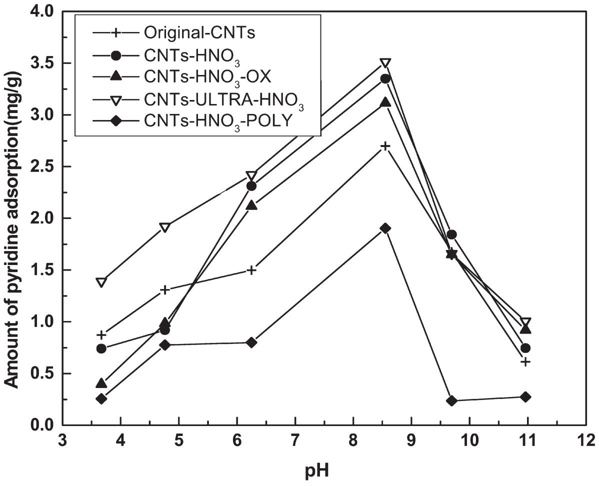

Figure 4. pH effect on the adsorption of pyridine on CNTs.

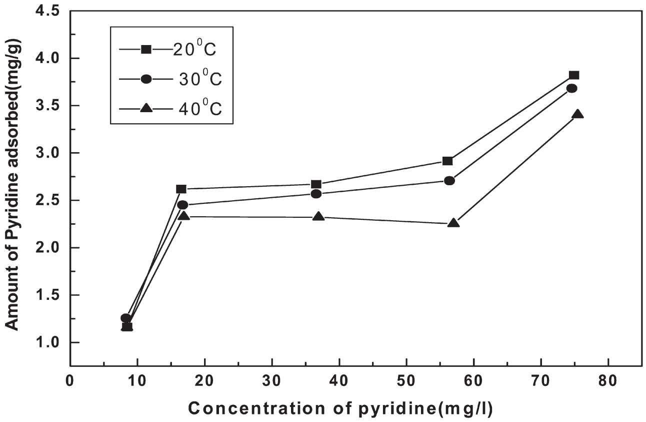

Figure 5. Adsorption isotherm of pyridine on original-CNTs at different temperatures.

become negatively charged at strong basic conditions, which is also harmful for pyridine adsorption. So a weak alkaline solution is an optimum condition for the adsorption of pyridine.

Figure 5 shows the adsorption isotherms of pyridine on the original CNTs at different temperature. It is clear that the adsorption of pyridine on CNTs decrease with the increase of the temperature. Adsorption isotherms of pyridine on the treated CNTs at different temperature are similar to Fig. 5. Therefore, the adsorption of pyridine on original or treated CNTs is mainly

Table 2. Constants of Freundlich adsorption isotherm models for adsorption of pyridine to CNTs

Sample	T/K	$lnq_e = (1/n)lnC_e + lnK$	R^2
Original-CNTs	293	$lnq_e = 0.81508lnC_e$-2.55401	0.9914
	303	$lnq_e = 0.8134lnC_e$-2.55787	0.9913
	313	$lnq_e = 0.81545lnC_e$-2.55882	0.9914
CNTs-HNO_3	293	$lnq_e = 0.81475lnC_e$-2.55307	0.9914
	303	$lnq_e = 0.81255lnC_e$-2.5547	0.9913
	313	$lnq_e = 0.82121lnC_e$-2.57651	0.9918
CNTs-HNO_3-OX	293	$lnq_e = 0.80567lnC_e$-2.51817	0.9907
	303	$lnq_e = 0.81506lnC_e$-2.55395	0.9915
	313	$lnq_e = 0.81505lnC_e$-2.55401	0.9914
CNTs-SULTRA-HNO_3	293	$lnq_e = 0.80281lnC_e$-2.50821	0.9907
	303	$lnq_e = 0.80538lnC_e$-2.5177	0.9910
	313	$lnq_e = 0.80525lnC_e$-2.51861	0.9908
CNTs-HNO_3-POLY	293	$lnq_e = 0.82539lnC_e$-2.59182	0.9918
	303	$lnq_e = 0.82716lnC_e$-2.59904	0.9919
	313	$lnq_e = 0.82498lnC_e$-2.58918	0.9913

a physical process. The Freundlich model was then applied to the analytical data. Freundlich adsorption isotherm represents the relationship between the amount of pyridine adsorbed by per unit mass of adsorbent (q_e) and the concentration of pyridine at equilibrium (Ce):

$$\ln q_e = (1/n)\ln C_e + \ln K, \tag{1}$$

where K and n are constants representing the adsorption capacity and intensity of the adsorption, respectively. Constants of Freundlich adsorption isotherm models for adsorption of pyridine to CNTs are listed in Table 2. As can be seen from Table 2, the data fit the Freundlich adsorption isotherm well.

CONCLUSIONS

CNTs was modified with different methods and characterized with BET N_2 adsorption, laser particle examination and static absorption test. The results showed that modification treatment with HNO_3, ultrasonic and heat can increase the surface area and pore volume which is favorable for adsorption but treatment with polyvinyl alcohol can decrease the surface area and pore volume. The particle sizes decrease due to the fracture at where defects exit for all CNTs except CNTs-HNO_3-OX. The pH value of the solution plays an important role on the adsorption of pyridine. For different CNTs, the optimum pH value for adsorption is about 8.55. The experiments show that the adsorption of pyridine on CNTs is mainly a physical process and the data fit the Freundlich adsorption isotherm well. The short time needed to reach equilibrium as well as the high adsorption capacity of pyridine suggests that CNTs possess highly potential applications for pyridine removal from water.

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