Carbon nanotubes-iron oxides magnetic composites as adsorbent for removal of Pb(II) and Cu(II) from water

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Carbon nanotubes (CNTs), a novel kind of carbon, were first reported by Iijima in 1991 [1]. CNTs can be thought of as cylindrical hollow micro-crystals of graphite [2]. Because they have relatively large specific area, CNTs have attracted researchers' interest as a new type of adsorbent and offer an attractive option for the removal of organic and inorganic contaminants from water. Li et al. found that acid-refluxed CNTs can be good adsorbents for Pb²⁺ and Cd²⁺ [3,4]. Peng et al. reported that CNTs can also be used to remove organic pollutants from water [5].

Because of their relatively large specific area, CNTs can also be used as supports for adsorption materials. Li et al. prepared amorphous Al₂O₃ supported on carbon nanotubes (Al₂O₃/CNTs) and found that it has a much higher adsorption capacity of fluoride than γ -Al₂O₃ [6]. Our previous research has found that ceria nanoparticles supported on carbon nanotubes can be effective adsorbent for the removal of arsenate from water [7].

In this work, a novel kind of magnetic composites based on CNTs was prepared and the obtained composites show good adsorption capacity for Pb(II) and Cu(II) from aqueous solution. CNTs-iron oxide magnetic composites can be used to adsorb contaminants from aqueous effluents and after the adsorption is carried out, the adsorbent can be separated from the medium by a magnetic process. The preparation of carbon-iron oxides magnetic adsorbent based on activated carbon has been reported in the literature [8]. But magnetic adsorbent based on CNTs has not been reported and is the topic of the present study.

CNTs were prepared by catalytic pyrolysis of the propylene-hydrogen (C₃H₆:H₂ = 2:1) mixture at 750 °C in a

ceramic tube furnace using Ni particles as catalysts. The CNTs were then washed with deionized water and ground. The specific area of as-grown CNTs is 134.0 m² g⁻¹. For the preparation of CNTs-iron oxide magnetic composites, CNTs were first immersed in concentrated nitric acid and then hydrofluoric acid for 24 h each to dissolve the catalyst particles. Then they were oxidized by refluxing the as-prepared CNTs with 50% nitric acid at 140 °C for 1 h. The magnetic composites were prepared from a suspension of 1.0 g oxidized CNTs in a 300 ml solution of 0.585 g FeCl₃ · 6H₂O and 0.390 g FeSO₄ · 6H₂O at 70 °C under N₂ atmosphere. NaOH solution (18.7 ml, 0.5 mol l⁻¹) was added dropwise to precipitate the iron oxides. After the addition of NaOH solution, the mixture was adjusted to pH 11.0 and stirred for 30 min. Then the mixture was aged at 70 °C for 2 h and washed 3 times with deionized water. The obtained material were dried in an oven at 45 °C and ground (particle size <0.075 mm).

The magnetic composites were characterized by powder XRD using a D/max-RB X-ray diffractometer (CuK α , λ = 1.540598 Å) and SEM using a Hitachi model S-3000N scanning electron microscope. Magnetization measurements were carried out on a LDJ model 9600 vibrating sample magnetometer at room temperature.

Batch adsorption experiments were performed in glass bottles. To each bottle, 50 ml Pb(II) or Cu(II) solution and 0.03 g adsorbent were added. For the effect of pH on adsorption experiments, 20 mg l⁻¹ Pb(II) or Cu(II) solution was used and the experiments were performed at 20 °C. Adsorption isotherms were obtained by varying the initial Pb(II) and Cu(II) concentration with the initial pH of 5.0 at 20 °C. The pH was adjusted using 1 M HCl or 1 M NaOH. The bottles were capped with glass screws and then were shaken on a HZQ-C shaker for 3 h. After equilibrium the adsorbent was

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separated from the solution by a magnetic process using a permanent magnet made of Nd–Fe–B and the residual concentrations of Pb(II) and Cu(II) in the supernatant solution was analyzed using a Hitachi model Z-6100 atomic absorption spectrophotometer.

Previous study has shown that heavy metal adsorption capacities of CNTs can be significantly enhanced by chemical oxidation and the as-grown CNTs without chemical oxidation have only poor heavy metal adsorption capacities [3,4]. The enhanced adsorption capacity by chemical oxidation is due to the introduction of many oxygen-containing functional groups on the surface of CNTs. Our co-workers measured these groups using Boehm's method and reported that the amount of carboxyl, lactones and phenols on the CNTs treated with nitric acid are 0.76, 1.83 and 1.45 mmol g⁻¹, respectively [4]. These functional groups can be efficient adsorption sites for heavy metals. Moreover, during the preparation of the magnetic composites, these groups can preserve the suspensibility of CNTs in solution and may be beneficial to the adhesion of metal oxide particles on the wall of CNTs [9].

After preparation, a test with the Nd–Fe–B magnet showed that the whole material was magnetic and completely attracted to the magnet. The magnetization measurements showed that the specific saturation magnetization (σ_s) is 17.85 emu g⁻¹ (magnetic field = 20000 Oe). The X-ray diffraction (XRD) pattern of the magnetic composites is shown in Fig. 1. It can be seen that the three peaks corresponding to the structure of CNTs also exist in the XRD pattern of the magnetic composites. Four iron oxides are commonly formed under the reaction conditions employed, i.e. Fe₃O₄ (magnetite), γ -Fe₂O₃ (maghemite), α -Fe₂O₃ (hematite) and α -FeO(OH) (goethite). Among these oxides, only the first two, magnetite and maghemite, are magnetic [10]. The

XRD pattern of the magnetic composites reveals a cubic iron oxide phase ($d = 2.51, 2.93, 2.09$ and 1.61 Å), which can be related to the presence of maghemite or magnetite. Other peaks are also observed at $d = 4.17, 2.68$ and 2.44 Å for the magnetic composites, which may be related to the presence of goethite [8,11].

SEM image of the composites was shown in Fig. 2. It depicts an entangled network of carbon nanotubes with clusters of iron oxides attached to them. SEM studies on many flakes reveal the homogenous distribution of iron oxides agglomerates in the flakes, which indicates the formation of carbon nanotubes-iron oxides composites.

The effect of pH on the adsorption was shown in Fig. 3. The tests were limited to the pH range of 3.8–8.1. It is found from Fig. 3 that under acidic pH conditions, the composites have lower adsorption capacities. The removal of Pb(II) and Cu(II) increases with the increase in pH. For Pb(II) ions, the removal capacity has a maximum value at pH 4.8. For Cu(II) ions, the removal increased with the increase in pH, reaching a high removal rate at around pH 8.1. At higher pH values, metal hydroxides precipitation may account for metal removal. The K_{sp} values for Pb(OH)₂ and Cu(OH)₂ at 20 °C are 1.2×10^{-15} and 5.0×10^{-20} [12], respectively. The concentration used was 20 mg l⁻¹, so the pH after which the hydroxides of Pb(II) and Cu(II) begin to formulate was about 8.5 and 6.1, respectively. Within the pH range studied, no Pb(OH)₂ precipitation occurs and the removal of Pb(II) is due to adsorption. Cu(OH)₂ precipitation occurs when pH > 6.1 and the removal of Cu(II) is due to adsorption when pH < 6.1 and due to surface precipitation when pH > 6.1. At pH values below the point after which the hydroxides precipitation begin to formulate, the decreased adsorption with the decrease of pH maybe is due to positive surface charge caused by the protonation of electron π rich regions

Fig. 1. XRD pattern of the composites and CNTs (G = goethite Mh = maghemite, Mn = magnetite).

Fig. 2. SEM image of the composites.

Fig. 3. The effect of pH on the adsorption of Pb(II) and Cu(II) to the magnetic composites at 20 mg l⁻¹.

on the surface of CNTs. A bond may be established between H₃O⁺ ions and the cloud of π electrons of the aromatic rings of carbon [13,14] and positive surface charge will be formed.

After adsorption, the magnetic separation process using the permanent magnet shows that the magnetic adsorbent can be easily separated from water and a recovery rate of above 98% has been achieved. This indicates that, after adsorption the adsorbent still has magnetic properties.

Fig. 4 shows the adsorption isotherms of Pb(II) and Cu(II) to the magnetic composites. The maximum adsorption capacities for Pb(II) and Cu(II) in the concentration range studied are 0.51 and 0.71 mmol g⁻¹. The Freundlich isotherm model was employed for the adsorption. Freundlich adsorption isotherm represents the relationship between the amount of heavy metal adsorbed by per unit mass of adsorbent (q_e) and the concentration of heavy metal at equilibrium (C_e) [15]:

Fig. 4. Adsorption isotherms of Pb(II) and Cu(II) to the magnetic composites (pH = 5.0, $T = 20^\circ\text{C}$).

$$q_e = KC_e^{\frac{1}{n}} \quad (1)$$

or

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (2)$$

K and n are constants representing the adsorption capacity and intensity of the adsorption, respectively. The experimental data fit Freundlich adsorption isotherm well with correlation coefficients of 0.9794 for Pb(II) and 0.9770 for Cu(II).

Conclusions

- (1) CNTs-iron oxide magnetic composites were successfully prepared and used for the removal of Pb(II) and Cu(II) from water. After adsorption the adsorbent can be separated from the medium by a simple magnetic process and a recovery rate of above 98% has been achieved.
- (2) XRD characterization suggests that the magnetic phase formed is maghemite or magnetite. SEM image shows an entangled network of carbon nanotubes with clusters of iron oxides attached to it and suggest the formation of carbon nanotubes/iron oxides composites.
- (3) The adsorption is pH dependent. The adsorption capacities for Pb(II) and Cu(II) in the concentration range studied at pH 5.0 reach 0.51 and 0.71 mmol g⁻¹, respectively.

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Direct growth of carbon nanotubes on the surface of ceramic fibers

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Carbon nanotubes have been grown on two micro-scale ceramic fibers (SiC and alumina) by a simple chemical vapor deposition (CVD) method. SiC and alumina fibers are two main types of ceramic fibers that have been widely used as high temperature reinforcements in polymer, ceramic and metal matrix composites [1]. Fiber coating was often used to modify their interfacial characteristics, and thus to improve the mechanical behaviours of the composites [2,3]. There are several reports on depositing whisker-like silicon to form a special coating on carbon fibers, and the fiber/matrix interfacial strength is significantly increased [4,5]. Carbon nanotubes were also grown on carbon fibers and formed a nano-scale coating [6–8]. Our experiments showed that multi-wall carbon nanotubes could act as a nanoscale coating on the ceramic fibers. The carbon nanotubes hybridized ceramic fibers should have wide applications in various composites, and the interfacial properties might be modified by forming a carbon nanotubes reinforced interfacial layer [7,8].

Our experimental set-up was an electrical furnace equipped with a quartz tube of 40 mm in diameter. Xylene was used as carbon source, and ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) as catalyst. Continuous Nicalon-NLM-202 SiC fibers and discontinuous Saffil alumina fiber were placed in the center of the quartz reactor. The CVD

growth temperature was 700 °C. The total flow rate of the buffer gas N_2/H_2 (with a ratio of 10/1) was 1650 sccm. The feedstock mixture (with a ferrocene content of 0.02 g/ml in xylene) was injected at a rate of 0.05 ml/min. Generally, the growth time was 10 ~ 30 min. Scanning and transmission electronic microscopy and micro-Raman spectroscopy (DILOR LABRAM with 514.5 nm Ar^+ laser excitation) were used to characterize the products.

Fig. 1 shows four SEM images of typical SiC fibers with a carbon nanotube coating. The CVD growth time is 20 min. At a lower magnification, as shown in Fig. 1a, the surfaces of most of the SiC fibers were covered by new-grown coating. Higher magnification images (Fig. 1b and c) indicated that the coating consists of well-aligned carbon nanotubes, which are nearly normal to the surface of the SiC fibers. The thickness of the aligned carbon nanotube coating is about 10 μm , which indicates that the growth rate of the carbon nanotubes is about 0.5 $\mu\text{m}/\text{min}$. Generally, carbon nanotubes have two kind of growth mode in the chemical vapor deposition method [9]. One is the base growth mode, and metal catalyst particles attach to the substrate; the other is the tip growth mode, where metal catalyst particles do not wet the substrate, and carbon nanotubes push catalysts away from the substrate. Fig. 1d shows that there are some catalyst particles attached to the roots of the carbon nanotubes, indicating that these carbon nanotubes are in the base growth mode. TEM observations also

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