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Rapid and economical synthesis of magnetic multiwalled carbon nanotube/iron oxide composite and its application in preconcentration of U(VI)

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ABSTRACT

Magnetic multiwalled carbon nanotube/iron oxide composite (Fe_3O_4/MWCNT) was synthesized as an adsorbent for the preconcentration of U(VI) from aqueous solutions. The surface properties of Fe_3O_4/MWCNT were characterized via adopting FTIR, SEM and potentiometric acid–base titration. The sorption behaviors of U(VI) on the surface of Fe_3O_4/MWCNT were investigated under environmental conditions by using batch technique, such as pH, ionic strength and contact time. The pH-dependent U(VI) sorption behavior on Fe_3O_4/MWCNT illustrated that sorption mechanism of U(VI) was achieved by outer-sphere surface complexation at low pH values, while the sorption of U(VI) was achieved by inner-sphere surface complexation and simultaneous precipitation at high pH values. Besides, the pH-dependent sorption also demonstrated an optimal and feasible pH value of 7.0 by adopting Fe_3O_4/MWCNT in the preconcentration of U(VI) from aqueous solutions. The sorption kinetic experimental data could be well simulated by using the pseudo-second-order pattern. The Langmuir and Freundlich patterns were employed to simulate sorption isotherms of U(VI) at three different temperatures, the experimental results demonstrated that sorption process was favorable at higher environmental temperature. The maximum sorption capacity of U(VI) on Fe_3O_4/MWCNT was higher than that of major materials reported. Related experimental data further indicated that Fe_3O_4/MWCNT had satisfactory treatment performance for the simulated wastewater. The Fe_3O_4/MWCNT particles having strong magnetism could be favorably and easily separated from aqueous solution under an external magnetic field. The correlative experimental results further demonstrated that the Fe_3O_4/MWCNT composite could be a promising adsorbent for the preconcentration of radionuclides from large volumes of aqueous solution.

1. Introduction

With the rapid development of nuclear techniques and establishment of many nuclear plants, large quantities of hazardous radionuclides have been discharged into aqueous systems by means of various nuclear processes, such as extracting of nuclear fuels, mining industries, nuclear tests and even nuclear plant accidents [1]. The increasing levels of hazardous radionuclides demonstrate detrimental influences to human health, natural environment and living organism [2,3]. In a sense, long-term exposure to radioactive pollutions could cause detrimental sicknesses, such as spasms, leukemia, vomiting, lymphatolysis, diarrhea, neurological disorder, cardiovascular system damage and even cancers [4–7]. In view of human health and ecological environment, the significant task is to exploit high performance materials and advanced techniques for preconcentration and solidification of radioactive wastewater.

Uranium is usually presented in hexavalent oxidation state in subsurface environments and industrial effluent under the aerobic condition [8,9]. Uranium can directly destroy living organisms and lead to generate reactive radicals that subsequently react with bio-molecule when one eats it from radioactive source by mistake, such as particles in air, water and soil. Uranium released into the natural environment systems could be hazardous to public health, which achieves the top of the food chain causing detrimental sickness, such as liver damage, kidney damage and even death [10]. Therefore, it is momentous to immobilize uranium from wastewater before its discharge into aqueous solution systems. Meanwhile, a series of legislations and policies have been suggested in the past two decades to restrict radionuclide concentration in environmental systems. For example, the standard level for uranium concentration in drinking water was recommended to be 30.0 μg/L by the US Environmental Protection Agency (USEPA) [11]. Furthermore, some European Union countries adopted entire referential dosage (i.e., <0.1 mSv/y) as an extra standard level for radionuclide in drinking water [12]. For the sake of public health and ecosystem stability, some high performance materials and advanced techniques are explored to decrease uranium concentration in polluted groundwater systems in order to conform with the abovementioned water quality standards. Conventional techniques comprise coagulation, electrolysis froth flotation,

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chemical precipitation, ion exchange, sorption, liquid–liquid extraction, membrane separation and reverse osmosis for the removal of radionuclides and heavy metal ions [13–16]. Among those approaches, sorption has widely received increasing attention in the environmental protection field owing to its multiple advantages, such as low cost, environmental friendliness, wide adaptability, convenient operation and high efficiency. Many varieties of adsorbents such as coir pith [17], *Ficus carica* fiber [18], montmorillonite [19], coal fly ash [20], clinoptilolite zeolite [21], bio-charcoal [22], heulandite [23] and attapulgite [24] have been proved to be available in the immobilization of U(VI)-bearing wastewater. Nevertheless, the puzzle dilemma in the recovery and separation of those adsorbents has restricted their further application from solution systems. To compensate for the dilemma, the synthesis and preparation of magnetic nanoparticles with high separation performance have become a new research topic of concern during the past two decades [25]. Magnetic nanoparticles would be applied in the ecological conservation field due to their particular characteristics, such as low cost, small size, high magnetism, high separation convenience and high surface area to volume ratio.

Carbon nanotubes, a new shape of carbon family, were first found in 1997 by S. Iijima [26]. Carbon nanotubes could be accounted as the shape of cylindrical hollow microcrystals of graphite. Carbon nanotubes comprise two modes of single-wall and multi-wall nanotubes totally depending on the amount of layers. The carbon nanotubes, possessing remarkable electronic properties, porous structure, large specific surface area, and chemical and mechanical characteristics, have been widely applied in many fields, such as catalyst supports, quantum nanowires, chemical sensors, electron field emitters and hydrogen storage [27,28]. In recent years, multi-wall carbon nanotubes (MWCN) have attracted researchers' and scientists' extensive concern as a new adsorbent for the immobilization of organic/inorganic, radioactive and heavy metal ion contaminants [29–31]. The unique characteristics of adsorbents determine the property of wastewater disposal, comprising post-treatment techniques and sorption capacity (i.e., recovery and/or separation), which accordingly plays a significant role in the environmental pollution disposal. From the present observation and analysis, filtration and ultracentrifugation are primary approaches for separating the solid phase of adsorbents from aqueous solution systems. Nevertheless, the two approaches are dissatisfied because of the fact that high-speed centrifugation will consume plentiful electric energy and filtration process is very liable to leach blockages. Up to now, the magnetic separation technique has been attracting wide attention owing to its speediness and convenience in separation and recovery processes in wastewater disposal [32,33]. What's more, the magnetic adsorbents could be favorably separated under an external magnetic field.

In this work, we have synthesized Fe_3O_4/MWCN from oxidized MWCNT and adopted it as an adsorbent to remove U(VI) ions from aqueous solution. The concrete objectives of this work are: (1) to characterize Fe_3O_4/MWCN using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), magnetization curves and potentiometric acid–base titrations; (2) to determine the sorption kinetic parameters and to explain experimental data by using a pseudo-second-order equation; (3) to investigate the impacts of different experimental conditions on U(VI) sorption by adopting batch technique, such as pH, ionic strength, and contact time; (4) to illustrate sorption isotherms of U(VI) at three different temperatures using Langmuir and Freundlich patterns; and (5) to evaluate the potential application of Fe_3O_4/MWCN in wastewater disposal based on the experimental results.

2. Experimental

2.1. Materials

All of the chemicals with analytical purity were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and were used directly in all experiments without any further purification. The distilled water (Millipore, Bedford, MA, USA) was adopted to prepare all solutions.

2.2. The synthesis of oxidized MWCNT

MWCNT was synthesized by adopting chemical vapor deposition (CVD) of acetylene in hydrogen flow at the temperature of 760 °C adopting Ni–Fe nanoparticles as catalysts [34]. $Ni(NO_3)_2$ and $Fe(NO_3)_2$ were dealt with the sol–gel process and calcinations to obtain NiO and FeO, then deoxidized by H_2 to obtain Ni and Fe nanoparticles. Oxidized MWCNT were synthesized by oxidization using 3.0 mol/L HNO_3. In general, 410 mL 3.0 mol/L HNO_3 solution comprising 2.0 g of MWCNT was ultrasonically stirred for a day, filtrated, and then rinsed using distilled water until the pH of the solution was almost neutral. Such synthesized specimen was dried for 24.0 h in an electrothermal blowing dry box at 85 °C, afterwards calcined at 450 °C for 6.0 h to totally remove amorphous carbon and nitrate ions. ICP-MS analysis experimental results illustrated that the amounts of catalysts of Ni and Fe in the synthesized MWCNT were less than 0.03% and 0.02%, respectively. The characteristics of the oxidized MWCNT applied in this study were listed in Table 1.

2.3. The synthesis of Fe_3O_4/MWCNT

The material of Fe_3O_4/MWCNT was synthesized as follows: 0.50 g MWCNT was added into a 450 mL flask of 0.58 g $FeCl_2 \cdot 4H_2O$ and 1.56 g $FeCl_3 \cdot 6H_2O$ in an oil bath on the base of molar ratio of Fe^{3+} $Fe^{2+} = 2{:}1$ under the protection of nitrogen condition at 95 °C for 10 h. The ammonia solution was progressively dropped into the solution until some iron oxide particles were emerged. The pH of the final solution was adjusted to 11.0 after the addition of ammonia, and then chemical reaction was allowed to keep for 6.5 h. Ultimately, the black solution was rinsed and filtered using distilled water until the pH of filtrated solution reached neutrality, and then dried in an electrothermal blowing dry box at 80 °C for 48 h. The expected product was accounted as Fe_3O_4/MWCNT.

2.4. Characterization

The FTIR analysis of Fe_3O_4/MWCNT was recorded with a Nexus670 FTIR spectrometer (Thermo Nicolet, Madison) with a KBr beam splitter in the scope of 4000–400 cm^{-1}. The spectral resolution was set to 1 cm^{-1}, and then 150 scans were collected for each spectrum. The SEM image was performed on JEOL JSM-6700 model to characterize the morphology of Fe_3O_4/MWCNT. The magnetic measurements of Fe_3O_4/MWCNT composite were performed on a MPMS-XL SQUID magnetometer. The potentiometric acid–base titration of Fe_3O_4/MWCNT was enforced adopting a DL50 Automatic Titrator with a 0.01 mol/L KNO_3 background electrolyte solution under argon conditions. The potentiometric acid–base titration curve of Fe_3O_4/MWCNT was by the Boehm titration approach [35]. Briefly, 0.05 g Fe_3O_4/MWCNT was added into 0.01 mol/L KNO_3 background electrolyte solution at room temperature, and purified with argon gas for 2.5 h to remove atmospheric CO_2 (g). The initial pH of suspension solution was gradually adjusted to pH 3.0 by slowly adding 0.01 mol/L of HNO_3 for 2.5 h under vigorous stirring condition, and then ammonia solution was laggardly titrated into mixture solution, the pH of the final solution was adjusted to 11.0. The data which set of pH versus net consumption of H^+ or OH^- were performed to calculate

Table 1
The characteristic of oxidized MWCNT.

Micropore volume/($cm^3 \cdot g$)	2–100 nm pore volume/($cm^3 \cdot g$)	Specific surface area/($m^2 \cdot g$)	O (%)	C (%)	H (%)
0.0004	0.49	121	8.5	90.0	0.19