

Electrospinning Synthesis of MgO Nanofibers and Properties of Uranium (VI)-sorption

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Summary: Magnesium oxide (MgO) nanofibers were prepared by electrospinning process. The characterizations of the adsorbent were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The obtained nanofibers could be used as adsorbents for the removal of Uranium (VI). The maximum adsorption occurred at pH 6, the equilibrium adsorption amount was about 90mg/g, and the equilibrium time was 120min.

Keywords: Electrospinning; Uranium (VI) adsorption; Magnesium oxide

Introduction

The toxicity and radiation of uranium has brought serious harm to human beings in recent years. The radioactive elements once enter in vivo, it will cause serious damage to organs in the body, and eventually lead to cancer. The increasing presence of uranium in the environment derives mainly from uranium mining, milling and nuclear energy power plants. Uranium can exist in several oxidation states [e.g. U(0), U(III), U(IV), and U(VI)][1], but under aerobic conditions, the predominant oxidation state for uranium is U(VI). Under oxidizing conditions, U (VI) mainly exist in the form of complexed, adsorbed, or precipitated uranyl species[2-4]. The formation of the uranium ions of most species are dependent on the conditions of the aqueous solution, such as temperature, pH, and ion concentration, and so on. Therefore, many methods are used to remove U(VI) from aqueous solutions, for example membrane, chemical precipitation, solvent extraction, etc.[5-7] However, most of these methods have their own shortcomings, such as generation of toxic sludge, incomplete removal of metal ions, and high requirements for energy. So the method of adsorption is widely used. Various substances, such as montmorillonite [8], kaolinite [9], bentonite[10], activated charcoal [11], organosilicon [12] and polymers [13] have been used as adsorbents for the removal of uranium (VI) ions.

MgO, as a remarkable adsorbent, leads to important applications in waste water treatments and

the desulfurization of waste gases [14-15]. However, there are few reports on the removal of uranium by MgO from aqueous environment. Therefore, it is urgent to develop a facile method to fabricate MgO and adopt it as an adsorbent to investigate the performance of U(VI) removal. The objective of the present study was to prepare MgO nanofibers by electrospinning process and find the optimum conditions of uranium (VI) adsorption. Series of experiments to study uranium (VI) adsorption performance on adsorption material were carried out. The following parameters were analyzed: contact time, initial uranium concentration, solution pH, and temperature. These results will help to develop the potential application of metal oxides as adsorbent.

Results and Discussion

Fig. 1 shows XRD patterns of the as-prepared MgO nanofibers and the sample calcined at 500°C. For the as-prepared MgO (Fig. 1a), only one broad band at $2\theta=22^\circ$ can be observed, that is assigned to the diffraction peak of semi-crystalline polyvinylpyrrolidone (PVP). When the sample is calcined at 500°C (Fig 1 b), the broad peak disappears. This indicates the decomposition of PVP under this temperature. From Fig 1 b, several peaks can be observed. These strong peaks may be ascribed to the cubic MgO phase (JCPDS, 45-0946). The diffraction peaks are very sharp, which indicates that the MgO phase is well crystallized.

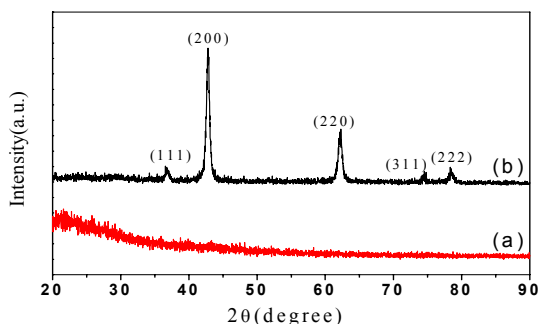


Fig. 1: The XRD spectras of the as-prepared precursor (a) and calcined at 500°C (b).

Fig. 2 shows SEM and TEM images of different samples. As can be seen from Fig. 2a, the surface of precursor nanofibers are smooth, and the particle size range between 450 and 800 nm. After calcined at 500°C for 3 h (Fig. 2b), the MgO samples are obtained, and due to the decomposition of PVP, the particle size ranges from 180 to 260 nm. Fig. 2c shows the TEM image of MgO samples. It can be seen that the MgO nanofibers are comprised of a lot of MgO particles, and the average particle size is about 15 nm.

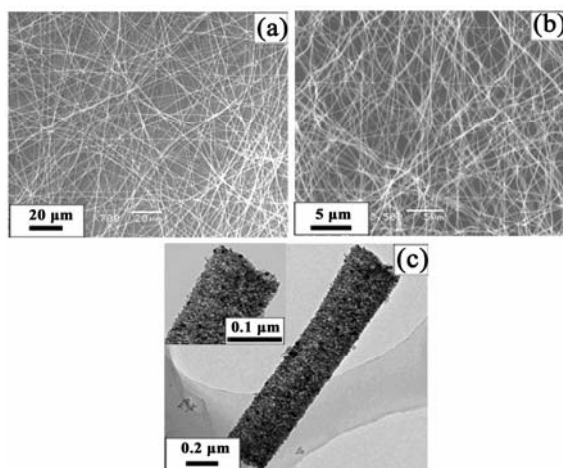


Fig. 2: SEM and TEM images of different samples: (a) SEM image of the as-prepared precursor fibers; (b) SEM image of the as-prepared precursor fibers annealed at 500°C; (c) TEM image of as-prepared precursor fibers after annealed at 500°C

The effect of pH on metal adsorption has been studied by many researchers previously, and the results indicate that the pH is a most significant factor in adsorption of metal ions [16]. In this work, we investigated the effect of pH on adsorption of U (VI) onto MgO nanofibers. It can be seen from Fig. 3a that With the increasing of PH value, the adsorption quantity of uranium increases gradually, and reaches a maximum adsorption at pH=6, and then the adsorption quantity of uranium decreases with the increasing of pH. The adsorption of uranium below pH 5 is lower. This may be due to the reason that the excess hydrogen ions can compete effectively with the active site of U (VI). This condition can take advantage of the desorption of U (VI) ions. At low pH, the adsorbent has a net-positive surface charge and when the pH range from 1 to 5, uranium mainly exists in the form of UO_2^{2+} ions [17]. Since both adsorbent surface and adsorbate are positively charged below pH 6, the adsorption amount decreases. However, with further increase of the pH value, the adsorption percent decrease. The formation of stable $[\text{UO}_2(\text{OH})]^+$, $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$ and $[(\text{UO}_2)_3(\text{OH})_5]^+$ complexes [18] should be the main reason for the decline of the adsorption capacity. These results indicate that the influence of pH on the adsorption of uranium are associated with protons of the active sites on the surface of the adsorbent.

Fig. 3b shows the effect of contact time. It can be seen from Fig. 3b, the adsorption capacity of U (VI) increased rapidly at the beginning; then it becomes slow due to the diffusion of uranium from the surface to the interlayer [19]. It means that the adsorption of U (VI) ions on the adsorbent reaches the equilibrium after 120 mins, and according to the formula of the adsorption capacity (Eq.(1)) the equilibrium adsorption amount is about 90 mg/g. Uranium adsorption Kinetics consists of two stages: an initial rapid stage and a slower second stage. At the initial stage of adsorption, due to more active sites and the higher concentration of uranium, the adsorption rate is very quickly. As the active sites gradually occupied, uranium concentration gradually decreases, the adsorption rate is reduced until equilibrium obtains.

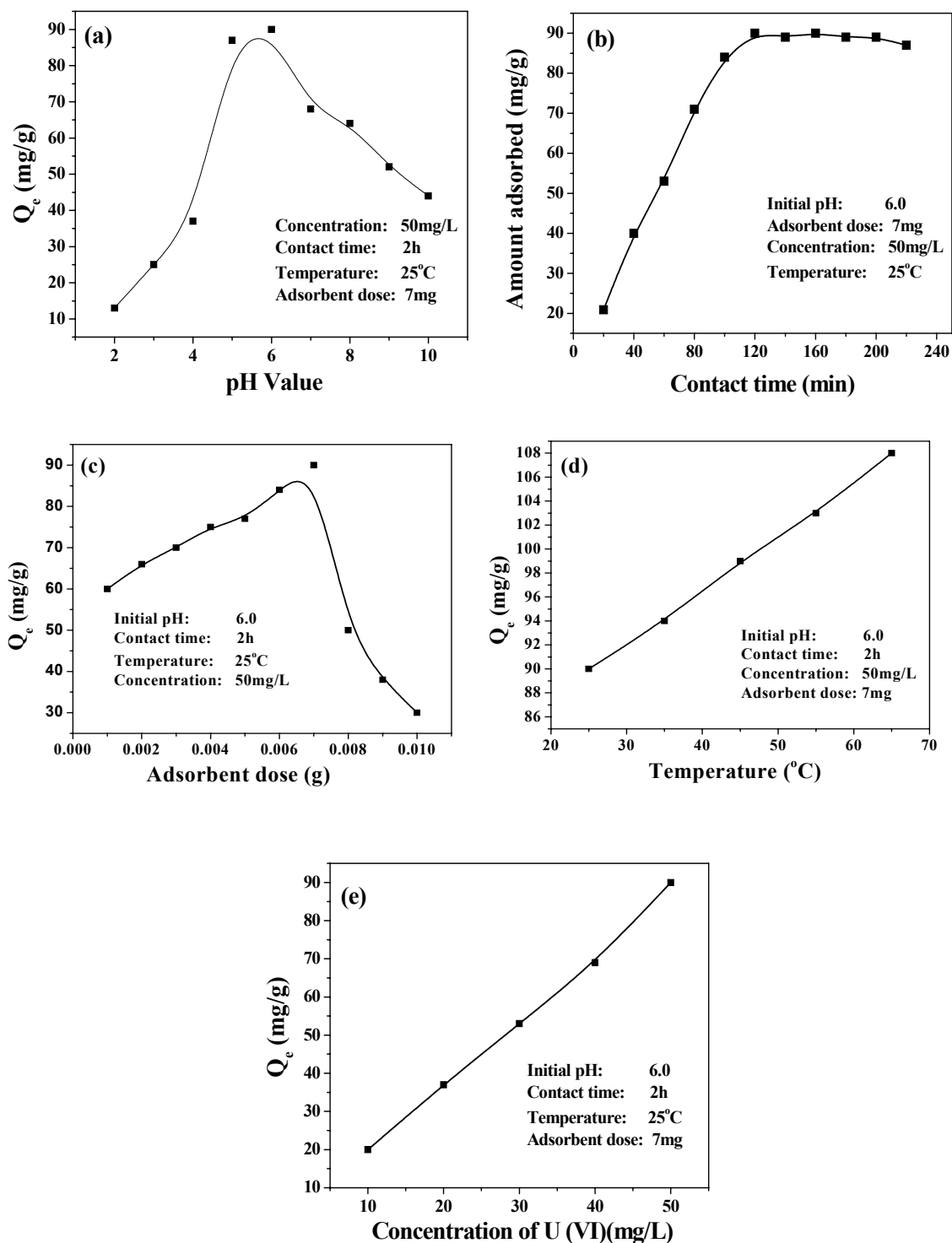


Fig. 3: Effect of the react conditions : (a) U (VI) adsorption on MgO at different pH; (b) U (VI) adsorption on MgO nanofibers at different times; (c) U (VI) adsorption on different amount MgO nanofibers; (d) Effect of reaction temperature; (e) Effect of the concentration of U (VI).

Adsorbent dosage is another factor affecting adsorption equilibrium. In order to verify the adsorbent dosage effect on adsorption equilibrium, the various amounts of nanofibers from 1 to 10 mg were used. It can be seen from Fig. 3c that the adsorption capacity of uranium(VI) increases rapidly with increasing dosage of MgO nanofibers, and then increases unobviously at $m > 7$ mg. With the increasing content of MgO nanofibers, the surface area is enlarged and more sorption sites are provided for the adsorption of uranium ions. But considering the economical point, adsorption dosage of 7mg is selected for the following studies.

The adsorptions of U (VI) on MgO nanofibers at different temperatures were conducted and depicted in Fig. 3d. The uptake of U (VI) is found to increase with the increasing temperatures, indicating the U (VI) adsorption on MgO nanofibers is endothermic. When the temperature is raised from 25 to 65 °C, the corresponding adsorption amount of U (VI) is increased from 90mg/g to 108 mg/g. This may also be explained by the increased adsorption sites which are activated and thermally motive to the adsorbed species with temperature, resulting in the increase of the U (VI) adsorption capacity with raising temperature.

To study the equilibrium of the sorption, a range of initial U (VI) solutions (10, 20, 30, 40 and 50 mg/L) are kept in contact with a fixed mass of MgO nanofibers (7mg) at a fixed temperature (25 °C) and initial pH 6.0, and the results are depicted in Fig. 3e. As shown in Fig. 3e, adsorption amount of U (VI) increases with the increasing of the initial U (VI) concentration. It can be explained that more targets of U (VI) can provide higher driving force to facilitate the ions diffusion from the solution to active sites assembly [20-21]. Moreover, the enhanced adsorption may be ascribed to either the increasing number active binding sites which is available for the adsorption on the adsorbent surface or due to the decreasing in the thickness of boundary layer, and there by decreased boundary layer mass transfer resistance. At U(VI) concentration of 50 mg/L, the adsorption amount gets up to a maximum and the U(VI) adsorption amount of MgO nanofibers is determined to be 90 mg/g.

Experimental

Chemicals and Materials

Polyvinylpyrrolidone (PVP, $M_w=1,300,000$) were purchased from Aldrich. Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$ A.R.) was purchased from Tianjin

Yongda Chemical Company. Ethanol was purchased from Beijing Fine Chemical Company. The U (VI) solution was prepared by dissolving an appropriate amount of $UO_2(NO_3)_2 \cdot 6H_2O$ in nitric acid solution.

Synthesis

Magnesium oxide nanofibers were fabricated by a electrospinning method. The magnesium nitrate was mixed with water/ethanol (final volume ratio of water to ethanol was 3:7), 0.7g PVP and 0.2g P123. The mixture was stirred at room temperature for 6 h, a homogeneous sol which was used for electrospinning was obtained. The distance was maintained at 15 cm, and the voltage was 15 kV, the spinning rate was 1 ml/h. Then the precursor was prepared after calcined at 500°C, the MgO nanofibers was obtained.

The Adsorption of Uranium (VI)

Series of experiments were operated at room Temperature. A mount (5 ml, 10 ml, 15 ml, 20 ml) of U (VI) with different concentration (10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L) were added to the 100 mL conical flasks, and then the as-prepared magnesium oxide was added to the conical flasks. The conical flasks were capped tightly and placed on a constant temperature oscillator with the maximum shaking rate of 200 rpm at 25°C. After several hours(2 h,4 h,6 h,8 h,10 h,12 h), the conical flasks were centrifuged. The centrifuged solutions were analyzed by WGJ-III trace uranium analyzer to determine the final aqueous concentrations of U (VI). The adsorption capacity Q_e (mg/g) was calculated as following:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 is the initial concentration of U (VI) (mg/L), C_e is the equilibrium concentration of U (VI) (mg/L), V is the volume of the testing solution (L), and m is the weight of sorbent (g). All the adsorption experiments were operated at least three times and the results given were the average values. For measurements of the pH value, the pH values were adjusted with 0.1 M NaOH or 0.1 M HNO_3 until the required pH was obtained.

Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-IIIIB

diffractometer using Cu K α radiation ($\lambda=1.5406 \text{ \AA}$). Transmission electron microscopy (TEM) and images were obtained from a FEI Tecnai G2 S-Twin transmission electron microscope with a field emission gun operating at 200 kV. Scanning electron microscopic (SEM) observation was performed on a JEOL SM-6480A scanning electron microscope.

Conclusion

The present study indicated that MgO nanofibers prepared by electrospinning was an effective adsorbent for the removal of U (VI) ions from aqueous solution, and it may have a promising application in metal ion wastewater treatment. The XRD results indicated that the MgO nanofibers was well crystallized; The SEM and TEM images showed that the nanofibers were comprised of many MgO particles. Series of experiments were operated. The results indicated that the maximum adsorption occurred at pH 6, the equilibrium adsorption amount was about 90mg/g, and the equilibrium time was 120min.

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