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Research Article

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Synthesis of MnO_2 nanowires and its adsorption property to lead ion in water

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ABSTRACT

MnO_2 nanowire was prepared by the hydrothermal synthesis route with $MnSO_4$ used as manganese source. In addition, it was investigated that the effects of the reaction temperature and reactant ratio on the morphology, crystal structure and adsorption performance of MnO_2 nanowires. And, the as-prepared MnO_2 nanowire was characterized by a series of techniques, including scanning electron microscopy (SEM), X-ray powder diffraction (XRD). The results indicated that the best hydrothermal reaction temperature is 200 ℃, the optimum ratio of potassium sulfate, potassium persulfate and manganese sulfate is 1:2:1. The as-prepared MnO_2 is nano-linear which stretches evenly, and the adsorption effect is good. The adsorption properties of the MnO_2 nanowire were studied by changing the amount of adsorbent, the pH of the solution, Pb^{2+} initial concentration. The equilibrium of adsorption was achieved within 100 min. Under the conditions of 65 ℃, the concentration of Pb^{2+} is 23.66 mg/L, the adsorption percentage of adsorption Pb^{2+} was 93.17%, and the adsorption capacity was 22.05 mg/g.

Keywords: manganese dioxide, nanowires; preparation, adsorption, lead ions

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INTRODUCTION

Environmental pollution is the common concerned problem we are facing. Recently, the adsorption and catalytic properties of nanostructured metal oxides have been applied for environment pollution removal. Because of their huger specific surface area and many unsaturated atoms on surface，the adsorbability of nanomaterials to metal ions was very strong. Because the price of nanomaterials metal oxides was vile and their preparation was easy, the study on the adsorption of metal ions on nanometer metal oxides was attended in recent years. Manganese oxides and related materials are of considerable importance in many technological applications such as giant magneto resistance devices, catalysts, and rechargeable lithium batteries. Recently, nanosized manganese oxides have attracted increasing attention in view of their applications in batteries, molecular sieves, catalysts, and adsorbents by virtue of their superior properties as compared to conventional bulk materials [1-3]. Lead is a heavy metal of particular concern in the environment, and its fate has always attracted extensive attention. Adsorption of metal ions by birnessites in aqueous phases is a critical process for the environmental application of birnessites in water treatment as well as for the environmental assessment of physicochemical behaviors of metal ions on birnessites. Manganese oxides are extensively distributed in soils, sediments and ocean manganese nodules [4-7]. A great deal of research activity has been undertaken in recent years in the field of nanotechnology which deals with synthesis, characterization and applications of materials with dimension less than 100 nanometers. Metal oxides is typically thought to be the most important adsorbent for removal of heavy metals in aqueous solution due to their relatively high surface area, microporous structure, and OH functional groups adsorbing the metal cations [8]. In this paper, MnO_2 nanowire was prepared by the hydrothermal method and its adsorption property to lead ion in water also was studied.

EXPERIMENTAL SECTION

2.1 Materials
All chemicals used in this experiment were purchased in analytical purity and used directly without any further purification.

2.2 Methods
Preparation of MnO_2 nanowire: The starting materials were composed by potassium sulphate, potassium peroxydisulfate and manganese sulfate monohydrate ($MnSO_4$ H_2O) in defined ratio in 30ml of deionized water. The mixture was transferred to a Teflon vessel held in a stainless steel vessel. The sealed vessel was placed in an oven and heated at 200 ℃ for 24 h. The resulting solid was then resuspended in 500 ml of deionized water and stirred vigorously overnight to yield a homogeneous suspension. The suspension was filtered and washed many times until all soluble impurities were removed from the solid. The nanowire was produced by dispersing the precursor, casting the suspension on a Teflon substrate placed in an oven, and subsequently heating at 85 ℃ for 24 h. Characterization of the samples: The crystalline structure of the samples was characterized using an X–ray diffraction analyzer (D/MAX–2500/PC), the surface morphology of the samples was monitored with SEM (S-4800).

2.3 Sorption experiments
Stock solutions of lead reagents were prepared by dissolving lead nitrate in deionized water. The concentration of Pb (II) in the aqueous solution was analyzed by using AA-6800 atomic absorption spectrometer (Shimadzu Corporation). All adsorption experiments were estimated in batch equilibrium mode. All the experiments were carried out by mixing 100mL of aqueous Pb(II) solutions with 0.15 g of MnO_2 nanowire under ambient conditions. The pH values of initial Pb(II) solutions were adjusted with dilute aqueous solution of HNO_3 by pHs-3C meter. The mixtures were shaken in a thermostatic shaker bath (THZ-98A mechanical shaker) with 150 rpm at different temperature for a given time, and then the suspensions were centrifuged at 3000 rpm for 10min. For adsorption studies the initial concentration of Pb(II) solution was chosen as 20mg/L of Pb (II) solution. Adsorption time of 12 h was chosen to allow attainment of equilibrium at constant temperatures.The amount of Pb^{2+} adsorbed at equilibrium, q_e was calculated by Eq. (1).

$$q_e = \frac{(C_o - C_e)\ V}{m} \quad (1)$$

where q_e is the adsorption capacity (mg/g) at equilibrium, C_o and C_e are the initial concentration and the equilibrium concentration (mg/L), respectively. V is the volume (mL) of solution and m is the mass (g) of adsorbent used.

RESULTS AND DISCUSSION

3.1 Characterization of the sample
As seen from Fig.1, the sample is a linear morphology with one dimension, many nanowires are in the form of some root of bundles, and MnO_2 nanowires unfold loose.

In Fig.2, there are characteristic peaks at 28 °, 37 ° and 57 ° for sample synthetized at 200 ℃, fitted well standard card (PDF65-2821), and the characteristic peaks of sample synthetized at 150 ℃ are more good agreement for standard card (PDF24-0735) than that of sample synthetized at 200 ℃. The peaks of sample synthetized are sharp shape and orderliness, less noise, the diffraction angles variation of same diffraction peaks is not big, spectral peaks are good symmetry, present a strong characteristics diffraction peak, diffraction peaks are narrow and high strength peak, it is shown that MnO_2 nanowires are high crystallinity. Compared with two temperatures of the samples synthetized at 150 ℃ and 200 ℃, according to the test results on adsorption Pb^{2+} with the samples synthetized at 150 ℃ and 200 ℃, the follow-up experiments are still using the samples synthetized at 200 ℃. And the peaks of analytically pure MnO_2 are blunt, a steamed bread peak appeared, and are also in good agreement with standard card (PDF30-0820).

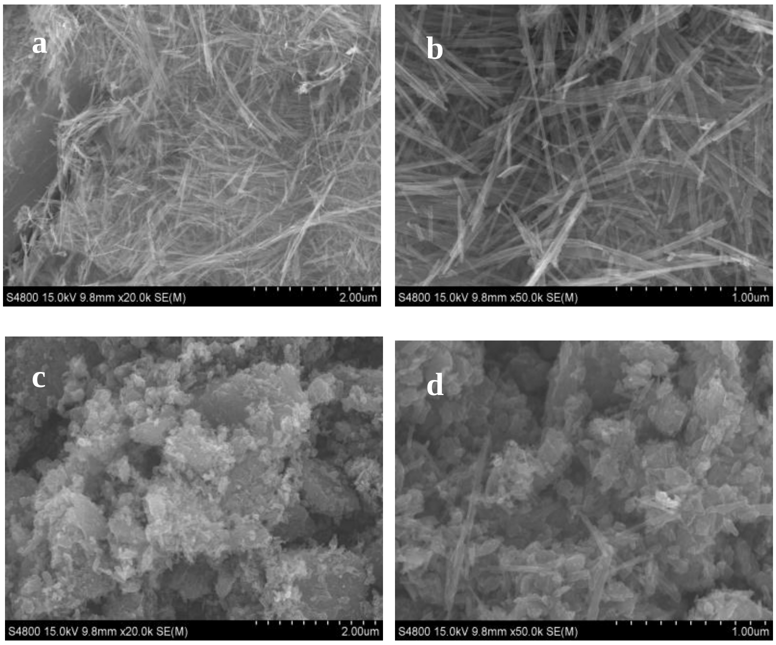

Fig.1 SEM images of MnO_2 nanowire (a, b) and MnO_2 reagent (c, d)

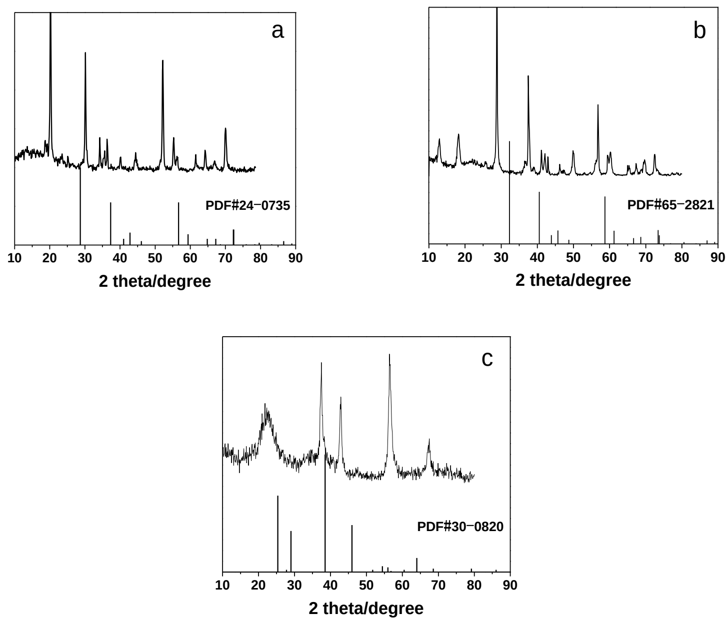

Fig.2 XRD patterns of the samples
a. synthetized at 150 ℃, b. synthetized at 200 ℃, c. reagent

3.2 Effect of synthetized temperature

At room temperature, five different synthetized temperature samples (100 ℃, 125 ℃, 150 ℃, 175 ℃ and 200 ℃) were taken 0.15 g, respectively, lead ions concentration is 20 mg/L, adsorption time is 12 h, after centrifugal separation, Pb^{2+} concentration was measured with atomic absorption spectrophotometer, and the adsorption capacity and removal rate were calculated over MnO_2 on adsorption Pb^{2+}, explored the effect of reaction temperature on the preparation of MnO_2 nanowire for adsorption performance, the results were seen in Fig. 3. In Fig. 3, the adsorption performance of sample synthetized at 150 ℃ is the worst, removal rate only 42.58%. However, the samples synthetized at 100 ℃ and 200 ℃ have well adsorption capacity, and the removal rate is up to 75%.

3.3 Effect of adsorbent dosage

In order to study the effect of the adsorbent dosage for fluoride removal, the experiments were carried out with the initial Pb^{2+} concentration 20 mg/L by varying the adsorbent dosage between 0.05g and 0.25 g at adsorption temperature of 25 ℃, and the results are shown in Fig. 4. The dosage of the adsorbent MnO_2 nanowires had a great influence on the effect of the adsorption of Pb^{2+} in Fig.4, it was shown that removal rate can reach 93.07% when MnO_2 dosage was added 0.15 g , therefore adsorbent dosage is 0.15 g in subsequent adsorption experiments.

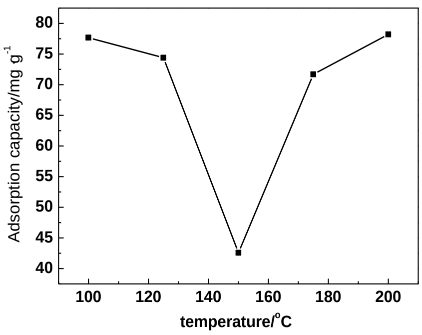

Fig.3 Effect of temperature on adsorption capacity

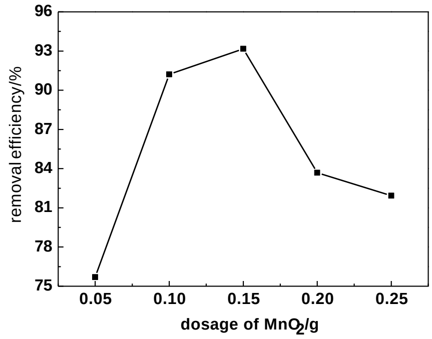

Fig.4 Effect of adsorbent dosage

3.4 Effect of solution pH

The heavy metal ions adsorption was strictly pH dependent, and the pH of the aqueous solution is an important controlling parameter in the heavy metal ions adsorption process. To investigate the effect of pH, the initial pH of the solutions was varied from 2 to 10 with an increment of 0.5 pH unit. The effect of changing pH on Pb(Ⅱ) sorption by MnO_2 nanowires is shown in Fig. 5. It is known that lead species present in the forms of Pb (Ⅱ), $Pb(OH)^+$, $Pb(OH)_2^0$, $Pb(OH)_3^-$ at different pH values [9]. The species of Pb in solution at different pH values is most important for the removal of Pb from aqueous solution to as-prepared MnO_2. At pH<6, the predominant lead specie is Pb(Ⅱ) and the removal of Pb(Ⅱ) is mainly accomplished by sorption reaction. When pH value is low (<3), a high concentration of positively charged protons compete with Pb(Ⅱ) for exchangeable cations on the surface of as-prepared MnO_2. As pH value is higher, there would be a dissociation of weak acid, which could make the adsorbent surface negatively charged to attract the positively charged metal ions, and hence the opportunity of heavy metal binding on adsorbents also increased, resulting in a rapid increase in the adsorption of heavy metal ions.

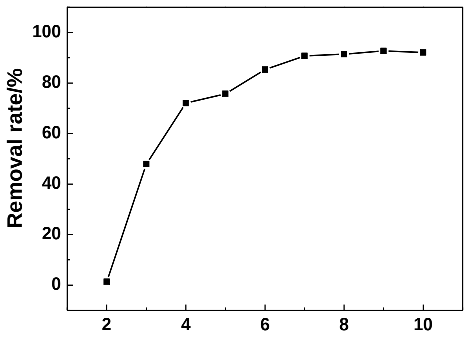

Fig.5 Effect of pH on removal rate

3.5 Effect of initial concentration of Pb^{2+}

In order to understand the effects of the initial concentration of Pb^{2+} on adsorption capacity, adsorption experiment was carried out for 10 group different concentrations of Pb^{2+} solution, and kept the adsorption temperature at 65 ℃, explored effect of the initial concentration of Pb^{2+} on adsorption capacity and removal rate.

As seen in Fig.6, in measuring range, with the increase of lead ion concentration, the adsorption capacity is increased and the removal rate is increases at first and then decreases. So adsorption medium concentration of lead ion is relatively appropriate with MnO_2 nanowires. For too low or high concentration of lead ion solution, the adsorption efficiency is low.

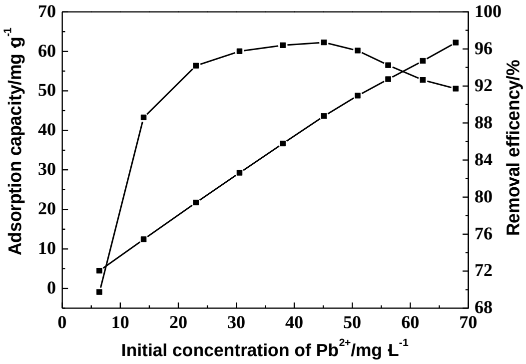

Fig.6 Effect of initial concentration of Pb^{2+}

3.6 Effect of adsorption temperature

The adsorption of Pb^{2+} onto MnO_2 nanowires as a function of temperature is shown in Fig. 7, with the increase of the concentration of Pb^{2+} in aqueous solution, the total amount of Pb^{2+} adsorbed by MnO_2 nanowires increased successively. In addition, the adsorption capacity increased with increasing temperature, which indicated that the adsorption process between MnO_2 nanowires and Pb^{2+} is endothermic.

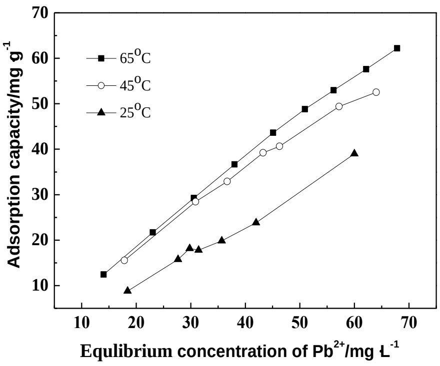

Fig.7 Adsorption capacity at different temperature

3.7 Effect of adsorption time

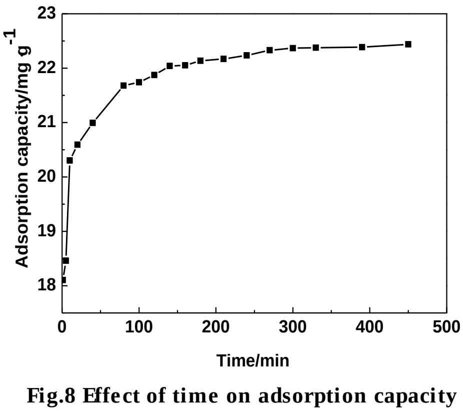

Fig.8 Effect of time on adsorption capacity

As shown in Fig.8, the adsorption capacity of lead ion in aqueous solution with MnO_2 nanowires increases with time, around 100 min, adsorption capacity is 21.74 mg/g, the removal rate of 91.87%, after adsorption160 min, adsorption quantity is 22.05 mg/g, and removal efficiency is 93.17%

CONCLUSION

（1）MnO_2 nanowire was prepared by the hydrothermal synthesis route with $MnSO_4$ as manganese source. The best hydrothermal reaction temperature is 200 ℃, the best ratio of potassium sulfate, potassium persulfate and manganese sulfate is 1:2:1, the as-prepared MnO_2 is nano-linear which stretches evenly, and the adsorption effect is good.

（2）The results of adsorption performance were shown that the pH of solution, adsorbent dosage, adsorption time and initial concentration of Pb^{2+} have a great influence on the adsorption performance.The best single factor conditions for adsorption experiment were as fellows: MnO_2 dosage: 0.15 g, pH of solution: 7, initial concentration of Pb^{2+}: 45 mg/L, adsorption time: 160 min, heating is conducive to the adsorption.

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