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Removal of Chromium Cr(VI) by Fe_3O_4 Hollow Spheres from Wastewater†

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In present work, Fe_3O_4 hollow spheres were prepared and characterized. The adsorption properties of Cr(VI) on Fe_3O_4 hollow spheres have been studied and the effects of varying the dosage and pH on the adsorption process have been investigated. The reproducibility of the adsorption process and the adsorption mechanism were also studied. It was found that the removal ratio of Cr(VI) increased with increasing dosage of Fe_3O_4 hollow spheres. The optimal pH value was found to be 4. Adsorption isotherm was consistent with the Langmuir equation. The adsorption process was mainly physical one and redox reaction was also involved. It was suggested that the Fe_3O_4 hollow spheres is a promising adsorbent for Cr(VI).

Key Words: Chromium, Fe_3O_4, Hollow spheres, Adsorption.

INTRODUCTION

Nowadays, adsorption has become by far the most versatile and widely used technology to check heavy metals pollution. In the past years, the materials based on iron-oxide have been studied for Cr(VI) adsorption because of their natural abundance. And another special property of some iron-oxide based materials (Fe_3O_4), magnetism, came to be realized[1,2]. Utilizing the magnetic properties of these adsorbents, magnetic separation has been combined with adsorption for heavy metal removal from contaminated water at laboratory scales. The specific objectives of the study are (1) to synthesize Fe_3O_4 hollow spheres and (2) to evaluate the Cr(VI) removal effectiveness. The adsorption isotherm is also studied.

EXPERIMENTAL

All the chemicals used were analytical grade. A chromium stock solution of 1000 mg/L Cr(VI) was prepared by dissolving 2.829 g of $K_2Cr_2O_7$ in 1000 mL deionized water. All working concentrations were obtained by diluting the stock solution with deionized water.

Preparation of Fe_3O_4 hollow spheres: 0.5 g polystyrene (PS, 300 nm) was mixed 100 mL of 0.3 mol/L $FeCl_3$ solutions and dispersed 20 min by ultrasound[3]. The pH of this solution was adjusted to 6 values with 24 % (v/v) $NH_3{\cdot}H_2O$ slowly. Deposition was filtered and dried at 80 ºC for 3 h. The dry powder was then heated at 600 ºC in H_2 for 3 h to obtain Fe_3O_4 hollow spheres.

Adsorption experiments: Batch Cr(VI) adsorption studies were performed by mixing 0.05 g of Fe_3O_4 hollow spheres with 100 mL of solution of varying Cr(VI) concentrations (5-100 mg/L). The adsorption of Cr(VI) was carried out in a shaking machine at room temperature. After adsorption reached its equilibrium, samples were collected at suitable time intervals. The adsorbent was separated by using a hand-held permanent magnet and the supernatant was collected for Cr(VI) and total Cr concentration measurements.

Analysis: The absorbance of Cr(VI) in aqueous phase was measured by the 1,5-diphenyl carbazide method[4]. Total Cr concentration was determined by ammonium persulfate method[5]. Cr(VI) removal efficiency was calculated according to the following equation:

$$\text{Cr(VI) removal efficiency (\%)} = \frac{(C_i - C_f)\times 100}{C_i}$$

where C_i is the initial Cr(VI) concentration (mg/L); C_f is the final concentration (mg/L).

RESULTS AND DISCUSSION

Characteristics of Fe_3O_4 hollow spheres: TEM image (Fig. 1) shows that the Fe_3O_4 hollow spheres synthesized were multi-dispersed with an average diameter of around 250 nm.

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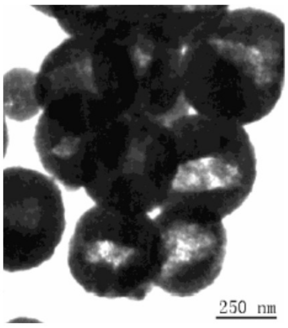

Fig. 1. TEM image of Fe_3O_4 hollow spheres

The identity and purity of the Fe_3O_4 particles were verified by XRD (Fig. 2), with the XRD peaks of the crystallite matching well with standard Fe_3O_4 and without other crystalline phases detected. The saturation moment of synthesized particles from the hysteresis loop measured from VSM was 63.6 emu/g. Therefore, the prepared Fe_3O_4 are expected to respond well to magnetic fields without any permanent magnetization and making the solid and liquid phases separate easily.

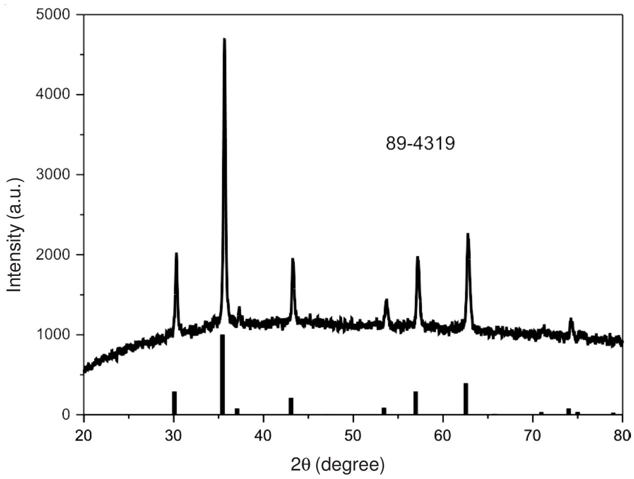

Fig. 2. XRD patterns of Fe_3O_4 hollow spheres

Effect of initial solution pH: pH value is an important parameter affecting the removal of Cr(VI) in wastewaters. As shown in Fig. 3, an appropriate pH variation was 3.0-4.0. Many studies showed that the solution pH of wastewaters containing chromium was generally acidic and the complete removal of Cr(VI) was observed only at higher acidic pH. The Cr(VI) removal was decreased with the increase of pH value. These phenomena may be explained by low pH the iron-oxide surface are protonated so that the net surface charge is positive, which enhances the adsorption of the negatively charged oxyanionic Cr(VI) (CrO_4^-, $Cr_2O_7^{2-}$) species.

Effect of adsorbent dose: As shown in Fig. 4, the removal efficiency of Cr(VI) by Fe_3O_4 hollow spheres increased sharply as the adsorbent dose increased from 0.2-0.5 g/L, then reached an almost constant value. The removal efficiency was 53.2 % when the Fe_3O_4 hollow spheres dose was 0.5 g/L, beyond which the removal was not significantly increased, so 0.5 g/L was chosen as the optimum adsorbent dose for further experiments.

Cr(VI) reduction: It was suggested that Cr(VI) was removed from aqueous solutions through a reduction process[2], so some experiments have been done. Two test solutions were

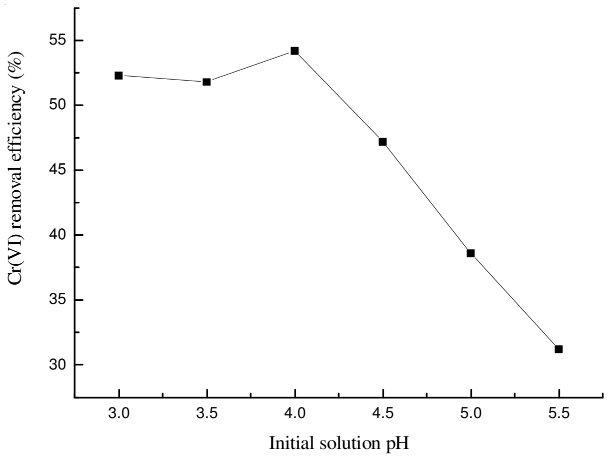

Fig. 3. Effect of initial solution pH on Cr(VI) removal efficiency

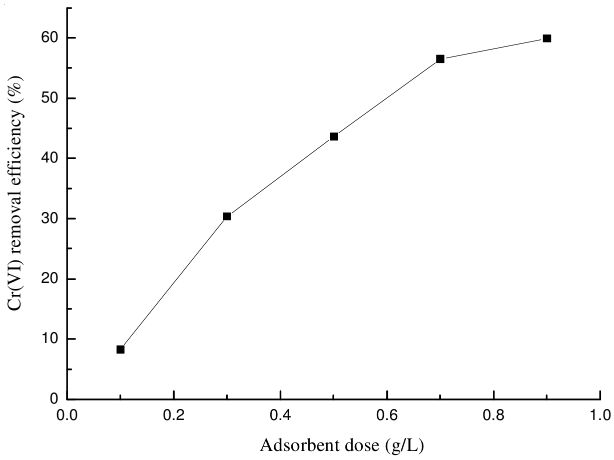

Fig. 4. Effect of adsorbent dose on Cr(VI) removal efficiency

prepared and the result shown in Fig. 5. Cr(III) concentration was obtained the difference between total Cr and Cr(VI) concentration. Comparing with these dates, Cr(VI) could be reduced to Cr(III) in acid conditions.

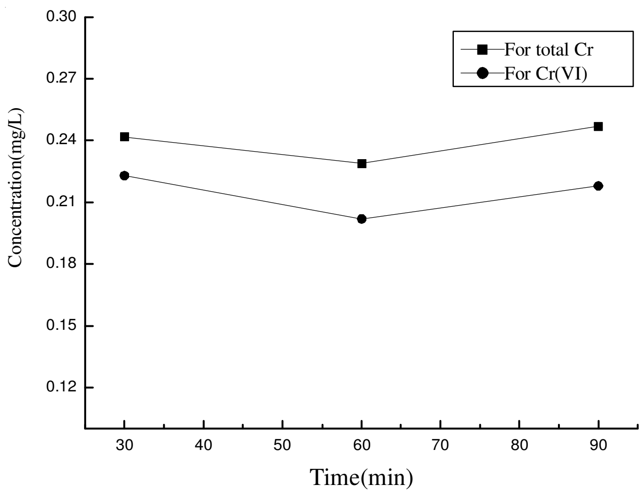

Fig. 5. Test of Cr(VI) reduction

Amount of the reduction of Cr(VI) to Cr(III) is about 10 % of total Cr(VI) removal by calculation at this pH. It's clear evidence that the reduction of Cr(VI) to Cr(III) occurs after Cr(VI) is adsorbed with the magnetite surface while oxidation of Fe(II) to Fe(III)[6].

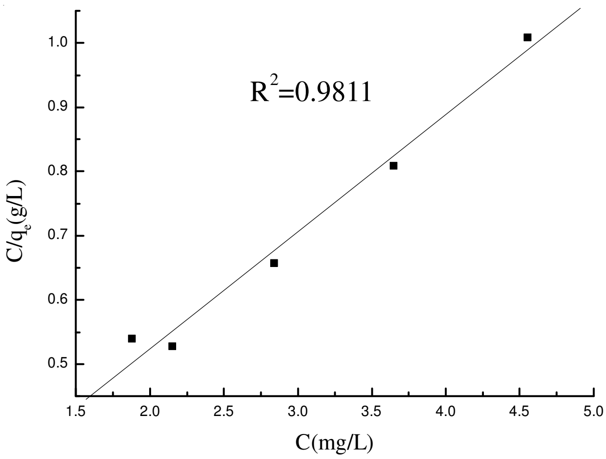

Fig. 6. Langmuir isotherm of Cr(VI) on magnetite particles

Adsorption isotherm: The equation from the experiment dates was $C_e/Q_e = 0.18225\ C_e + 0.15967$, $R^2 = 0.9811$. Here C_e is the equilibrium concentration of the adsorbate in solution (mg/L), Q_e the equilibrium loading of sorbate on sorbent (mg/g). As indicated by the adsorption coefficients computed from above equation, the adsorption isotherms of Fe_3O_4 hollow spheres well fit the Langmuir model.

Conclusion

In this study, Fe_3O_4 hollow spheres was synthesized and characterized. Batch experiments were conducted to remove Cr(VI) from aqueous solution using the Fe_3O_4 hollow spheres with an average diameter of around 250 nm as adsorbent. Nearly 55 % of the initial Cr(VI) (5 mg/L) was adsorbed or reduced to Cr(III) with in the first 10 min at pH 4.0. And adsorbent could be separated easily. The adsorption data fit well with the Langmuir isotherm equation. Fe_3O_4 hollow spheres has proved to be a promising sorbent, as well as a reductant, for Cr(VI) removal from aqueous environment.

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