Adsorption Behavior of Fe_3O_4 / Poly(Acrylate Methyl Ester-co-Divinylbenzene) Microspheres Toward Metal Ions

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Abstract: The Fe_3O_4/ (acrylate methyl ester-co-divinylbenzene) magnetic microspheres were prepared by suspension polymerization. The application of these microspheres as an adsorbent for metal ions adsorption was examined. The results showed that the diameter of the magnetic adsorbent was 35 ~ 55 μm and the amount of Fe_3O_4 was 18%. The adsorbent showed high efficiency for the removal of metal ions. The maximum adsorption capacity (q_m) obtained by the Langmuir isotherm was 2.3 mmol/g for Hg^{2+}, 2.2 mmol/g for Cu^{2+} and 1.1 mmol/g for Ni^{2+}. The adsorption rate constant calculated by Lagergrent equation was 0.023 min^{-1} for Hg^{2+}, 0.034 min^{-1} for Cu^{2+} and 0.036 min^{-1} for Ni^{2+}. Regeneration of the adsorbent was achieved using 1 mol/L H_2SO_4.

Key words: magnetic adsorbent; acrylate-based resin; Fe_3O_4; metal ions
CLC number: O647.3 Document code: A Article ID: 0529-6579 (2007) S1-0154-02

The application of magnetic adsorbent technology to solve environmental problems have received considerable attention in recent years[1-5]. Some examples of this technology are the use of polymer coated magnetic particles for the adsorption of organic dyes and magnetic polymer beads for the removal of metal ions[1-2]. In this work, Fe_3O_4/poly(acrylate methyl ester/divinylbenzene) was prepared as an adsorbent for the removal of metal ions from aqueous solutions. This adorbent was modified by ethylenediamine to improve its adsorption capacity.

1 Experimental

1.1 Preparation of magnetic microspheres

Acrylate methyl ester and divinylbenzene (molar ratio 17∶1, total volume 10 mL) were mixed well with 0.1 g benzoyl peroxide. Then 1 mL isopropyl alcohol and 12.6 mL cyclohexane were added. The contents are then poured into a flask containing 73 mL of 1% polyvinyl alcohol and 0.5 g Fe_3O_4 nanoparticles. The reaction mixture was stirred at 75 ~ 80℃ for 6 h. The formed precipitate was filtered off, subsequently washed and then dried. The adsorbent obtained was referred by FAD.

Four 4 g of ethylenediamine were dissolved in 12 mL dimethylamide, then 1 g of FAD microshperes was added. The reaction mixture was heated at 75 ~ 80℃ for 72 h. The product was filtered off, subsequently washed and dried. The adsorbent obtained was referred by FADA.

1.2 Adsorption experiments

The adsorption of metal ions by FADA was investigated at pH 1 ~ 8. 0.05 g adsorbent was added to 50 mL metal ions solution at initial concentration of 5 mmol/L. After adsorption for 2 h, the adsorbent was removed magnetically from the solution. The concentrations of metal ions were measured using a model GGX—9 atomic absorption spectrometer.

2 Results and discussion

2.1 Effect of pH on adsorption capacity

The higher uptake capacity was achieved around the netural pH for all metal ions. The observed lower uptake in acidic medium may be due to the partial protonation of the amino group of the magnetic adsorbent. At pH < 2, no appreciable uptake was detected for the three metal ions, indicating complete protonation of the active sites.

2.2 Adsorption isotherm

The adsorption data of metal ions on FADA at pH 6.0 fitted the Langmuir model very well (Fig. 1). The maximum adsorption capacity (q_m) values are 2.3

①收稿日期: 2007-01-10
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mmol·g⁻¹ for Hg^{2+}, 2.2 mmol·g⁻¹ for Cu^{2+} and 1.1 mmol·g⁻¹ for Ni^{2+}. The adsorption equilibrium constant (K) values are 1.38 L·mmol⁻¹ for Hg^{2+}, 0.56 L·mmol⁻¹ for Cu^{2+} and 1.24 L·mmol⁻¹ for Ni^{2+}, respectively. The uptake of the metal ions at neutral pH may be explained to proceed via complex formation. The higher value of q_m for Hg^{2+} reflects the higher soft acid/soft base interaction between Hg^{2+} and amino groups.

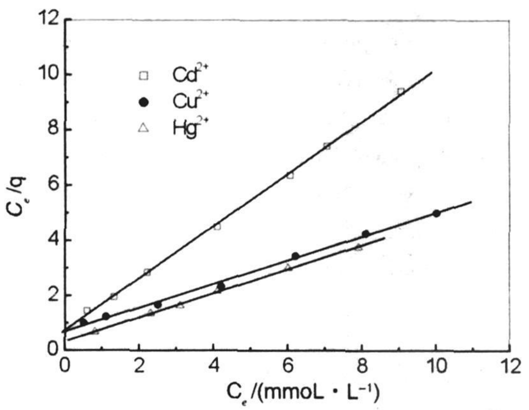

Fig.1 Langmuir curves for Hg^{2+}, Cu^{2+} and Ni^{2+} adsorption

2.3 Kinetics

The rate constants for adsorption of metal ions were determined using the Lagergrent equation: $\ln(q_e - q) = \ln q_e - K_{ad} t$, where q_e and q (mmol/g) is the adsorption capacity at equilibrium and at time t (min), respectively. K_{ad} is the rate constant (min⁻¹). The plot of $\log(q_e - q)$ vs t yielded straight lines. K_{ad} (min⁻¹) values calculated from the slope were 0.023 min⁻¹ for Hg^{2+}, 0.034 min⁻¹ for Cu^{2+} and 0.036 min⁻¹ for Ni^{2+}, respectively.

3 Conclusions

FADA magnetic microspheres of 35~55 μm were obtained by suspension polymerization. The maximum adsorption capacity (q_m) values were 2.3 mmol/g for Hg^{2+}, 2.2 mmol/g for Cu^{2+} and 1.1 mmol/g for Ni^{2+}, respectively. The kinetic data was well described by the Lagergrent equation. K_{ad} values was 0.023 min⁻¹ for Hg^{2+}, 0.034 min⁻¹ for Cu^{2+} and 0.036 min⁻¹ for Ni^{2+}, respectively. Regeneration of the adsorbent was achieved using 1 mol/L H_2SO_4 with efficiency of more than 95% for all of the metal ions.

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Fe_3O_4/聚（丙烯酸甲酯—二乙烯苯）微球对金属离子的吸附

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摘 要：通过悬浮聚合制备 Fe_3O_4/聚（丙烯酸甲酯—二乙烯苯）磁性微球，考察了微球对金属离子的吸附性能。结果表明，磁性吸附剂粒径 35~55μm，Fe_3O_4 质量分数 18%，能有效吸附金属离子。由 Langmuir模型得到的饱和吸附容量分别为：Hg^{2+} 2.3 mmol/g，Cu^{2+} 2.2 mmol/g，Ni^{2+} 1.1 mmol/g。由 Lagergrent方程计算的吸附速率常数分别为：Hg^{2+} 0.023 min⁻¹，Cu^{2+} 0.034 min⁻¹，Ni^{2+} 0.036 min⁻¹。吸附剂可用 1mol/L H_2SO_4 再生。

关键词：磁性吸附剂；丙烯酸树脂；Fe_3O_4；金属离子

中图分类号：O647.3