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Short Communication

Gellan gel beads containing magnetic nanoparticles: An effective biosorbent for the removal of heavy metals from aqueous system

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ABSTRACT

This study describes an efficient adsorbent consisting of magnetic Fe_3O_4 and gellan gum, which couples magnetic separation with ionic exchange for heavy metal removal. Adsorption kinetics analysis showed that the adsorption capacities were in an order of $Pb^{2+} > Cr^{3+} > Mn^{2+}$. Different experimental parameters studies indicated that adsorbent dosage, initial metal concentration, temperature and initial pH played important roles in adsorption process. Additionally, the Freundlich model gave a better fit to the experimental data than the Langmuir model. Chemical analysis of calcium ions released into the bulk solutions demonstrated that carboxyl group is critical for binding Pb^{2+}, Mn^{2+} and Cr^{3+}. Furthermore, a high desorption efficiency was obtained by sodium citrate.

1. Introduction

Heavy metals released into the environment have posed a significant threat to the environment and public health because of their toxicity and persistence in environment, and therefore, must be removed from water. Various conventional processes (precipitation, electrochemical processes and/or membrane processes) have been employed to treat industrial effluents (Gavrilescu, 2004). However, these applications are often limited by technical and economical issues.

The integrated process, which couples magnetic separation with surface complexation adsorption and ionic exchange, is especially effective in remediation of heavy metals (Ngomsik et al., 2006; Yantasee et al., 2007). This system has several advantages that the process does not generate secondary waste and the materials involved can be recycled and facilely used on an industrial scale, and furthermore that the magnetic particles can be tailored to fix specific metal species in water, waste or slurries (Ngomsik et al., 2006; Li et al., 2008).

In our present work, a composition of gellan gum and Fe_3O_4 nanoparticles was employed as a unique adsorbent for heavy metal removal in aqueous solutions. The effects of different experimental parameters were investigated. In addition, the experimental data were correlated to the kinetic and equilibrium model to evaluate the bioaccumulation capacities of magnetic particles.

2. Methods

2.1. Biosorption experiments

Magnetic gel beads were prepared by previous method (Wang et al., 2007), and the final concentration of Fe_3O_4 nanoparticles was 12 mg/mL. All batch adsorption experiments were performed in 300 mL flasks, containing 20 mL heavy metal mixture solution with shaking at 200 rpm on a rotary shaker for a desired time at 30 °C. Magnetic gel beads made by 40 mg gellan gum were used as the adsorbents in all experiments (except for the experiment of measuring the effect of adsorbent dosage). The metal uptake q (mg/g) was determined by the following equation:

$$q = \frac{(C_0 - C_t) \times V}{m}, \tag{1}$$

where C_0 and C_t are the initial and final metal ion concentrations (mg/L), respectively; V is the volume of solution (mL), and m is the mass (g) of the adsorbents used. The metal concentration of supernatant was determined by Inductively Coupled Plasma Atomic Emission spectroscopy (IRIS Intrepid II, Thermo Electron, USA).

2.2. Effects of different experimental parameters

The effects of different experimental parameters such as absorbent dosage (1, 2, 3 and 4 g/L), initial pH (1.5, 3.5 and 5.5), temperature (10, 20, 30 and 60 °C) and initial concentrations of heavy metal solution (from 30 to 500 mg/L for Cr^{3+}; from 20 to

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500 mg/L for Mn^{2+}; from 50 to 1000 mg/L for Pb^{2+}) on the adsorption kinetics were evaluated, respectively.

2.3. Desorption experiments

After each batch adsorption, magnetic gel beads were washed twice with sterile distilled water and suspended in 20 mL sodium citrate solution (100 mM) at 30 °C with shaking at 200 rpm for 4 h, and then the supernatant was collected to determine the amount of heavy metals.

2.4. Model to experimental data

Adsorption kinetics analysis was calculated using the pseudo second-order rate equation as (Ho and Mckay, 2004):

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e}, \tag{2}$$

where K is the pseudo second-order rate constant (g/mg/min); q_e and q_t are the metal uptake (mg/g) at equilibrium and at time t, respectively.

The Langmuir equation can be represented by Al-Degs et al. (2006):

$$q_e = \frac{bq_{\max}C_e}{1 + bC_e}, \tag{3}$$

where C_e is the equilibrium concentration of the remaining metals in the solution (mg/L); $q_{\max}$ is the amount of adsorbate to form complete monolayer coverage (mg/g); b is a constant relevant to the heat of adsorption.

The Freundlich isotherm model has the following form as (Al-Degs et al., 2006):

$$q_e = kC_e^n, \tag{4}$$

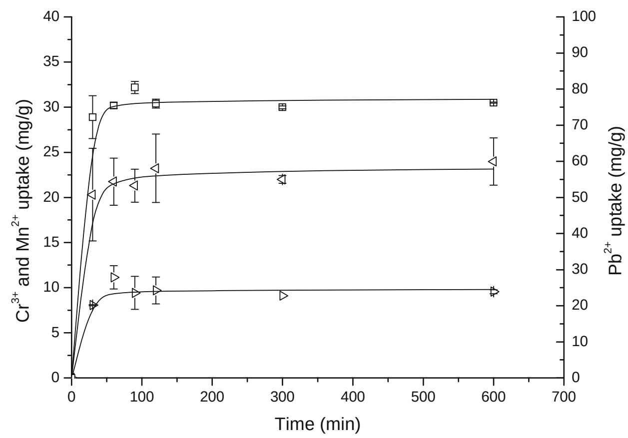

Fig. 1. Adsorption kinetics of Pb^{2+}, Mn^{2+} and Cr^{3+} by magnetic gel beads. Symbols are Pb^{2+} (□), Cr^{3+} (◁), Mn^{2+} (▷). The full lines are model prediction.

where k (mg) represents the adsorption capacity when metal equilibrium concentration equals 1, and n represents the degree of dependence of adsorption with equilibrium concentration.

3. Results and discussion

3.1. Adsorption kinetics

In this study, we constructed a composite system of gellan gum/Fe_3O_4 to couple magnetic separation with surface complexation adsorption and ionic exchange for the remediation of heavy metals. The magnetic gel beads with super-paramagnetic properties (16 emu/g) could be easily concentrated to tailor various applications by external magnetic field. From Fig. 1, a sharp increase of

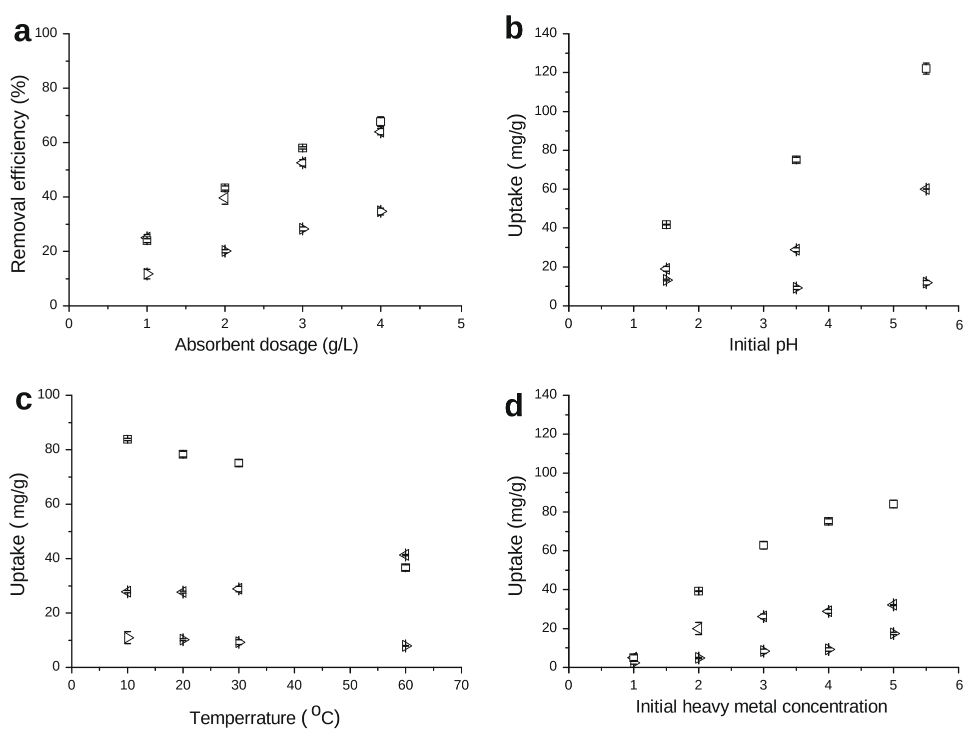

Fig. 2. Effects of different experimental parameters on the adsorption capacities of Pb^{2+}, Mn^{2+} and Cr^{3+}. Symbols are Pb^{2+} (□), Cr^{3+} (◁), Mn^{2+} (▷). a is for the absorbent; b is for the initial pH; c is for the temperature; d is for the initial heavy metal concentration, and 1–5 are samples with different initial concentrations of Pb^{2+}, Mn^{2+} and Cr^{3+}.