



## Short Communication

# Novel complex gel beads composed of hydrolyzed polyacrylamide and chitosan: An effective adsorbent for the removal of heavy metal from aqueous solution

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## ABSTRACT

A novel kind of complex gel beads containing HPAM (hydrolyzed polyacrylamide) and chitosan components (HPAM-chitosan gel beads) was prepared and applied in the removal of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  ions from aqueous solutions. These gel beads exhibited a good performance for heavy metal removal. Moreover, the average diameter of these gel beads was about 1 mm, which could be appropriate for use in column system. The removal order was  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Hg}^{2+}$  under the same conditions. The effects of different experimental parameters, such as adsorbent dosage, initial pH, temperature, and initial metal concentration, on the adsorption capacities were studied. The Freundlich model gave a better fit to the experimental data than the Langmuir model in adsorption isotherm study. Desorption study indicated that the gel beads were easy to be regenerated.

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## 1. Introduction

As a result of industrialization and urbanization, the presence of heavy metal ions in water streams has readily increased in the last 50 years. Heavy metals are considered to be non-biodegradable and have great environmental, public health, and economic impacts. In the removal of heavy metals, adsorption process seems to be most versatile and effective method if combined with appropriate regeneration steps (Park and Chae, 2004; Wang et al., 2009).

In the removal of heavy metal ions from aqueous solutions, both synthetic polymers containing carboxylic, sulfonic, amide, amine and imino groups, and semi-natural polymers have been used (Alves and Mano, 2008; Rivas et al., 2006; Wan Ngah and Hanafiah, 2008). Functional groups presenting in the polymer structure can provide binding sites to remove the metal ions from aqueous solutions.

In this paper, we established a novel method to prepare complex HPAM-chitosan gel beads. In these gel beads there are a lot of functional groups such as  $-\text{COO}^-$ ,  $-\text{NH}_3^+$ ,  $-\text{OH}$ ,  $-\text{CONH}_2$ , and  $-\text{NH}_2$ . Moreover, the crosslinking point of physical complex gel has higher tendency to dissociate in saline solutions than that of common chemical gel. And the diameter of gel beads is about 1 mm, which could be appropriate for use in column system for

heavy metal removal. As a result, the efficiencies of the gel beads on the removal of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  ions were studied.

## 2. Methods

### 2.1. Materials

The average molecular weight of HPAM was  $4.3 \times 10^6$  g/mol and the hydrolysis degree of it was 46%. The average molecular weight of chitosan was  $9.1 \times 10^5$  g/mol and the deacetylation degree of it was 71%. Other materials were analytical reagent and used as received.

### 2.2. Preparation of HPAM-chitosan gel beads

Chitosan was dissolved in 0.1 mol/L HCl solution in order to obtain a concentration of 0.6 wt.%. HPAM aqueous solution (8 g, 1 wt.%) was extruded dropwise through a syringe fitted with a 25 gauge needle into  $\text{AlCl}_3$  solution (30 mL, 0.2 mol/L) at room temperature under gently stirring at 100 rpm, and then gel beads were allowed to be cured for 2 h. These gel beads were washed with distilled water for three times and immersed into chitosan solution (20 mL) for 24 h. These gel beads were dried under reduced pressure at 50 °C for 48 h and were labeled HPAM-chitosan gel beads. From FTIR analysis, the presence of chitosan and HPAM components in gel beads were indicated by the peak at  $1105 \text{ cm}^{-1}$ , which was classically assigned to the polysaccharide molecule backbone

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vibrations, and the peak at  $1730\text{ cm}^{-1}$ , which was assigned to the absorption band of  $-\text{COOH}$  in HPAM molecules, respectively.

### 2.3. Adsorption experiments

Non-competitive removal of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  ions onto the gel beads was carried out by batch method and the influence of contact time (from 15 to 600 min), initial pH (2.0, 4.2, and 5.5), temperature (10, 20, 30, and  $60\text{ }^\circ\text{C}$ ), adsorbent dosage (0.1, 0.2, 0.3, 0.4, 0.5 g/L) and initial metal ion concentration (from 0.2 to 1.8 mmol/L) were studied. For each experimental run, 40 mL of metal solution of known concentration, which contained only one kind of metal ion, was taken in a 100 mL stoppered reagent bottle. The solution was stirred by a magnetic stirrer continuously during the adsorption experiment. About 8 mg of gel beads was used as the adsorbents in all experiments except for the experiment of measuring the effect of adsorbent dosage. The metal uptake  $q$  (mmol/g) was determined by the following equation:

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

where  $C_0$  and  $C_t$  are the initial and final metal ion concentrations (mmol/L), respectively;  $V$  is the volume of solution (L), and  $m$  is the mass (g) of the adsorbents used. The metal concentration of solution was determined by atomic adsorption spectrophotometer (Varian Spectra HP 3510).

### 2.4. Desorption experiments

After being immersed into metal ion solution (1 mmol/L, pH 4.2) for 5 h, the adsorbents were taken out from the metal ion solution, and blotted the beads with filter paper to remove adsorbed solution on the surface. The adsorbed metal ions were removed by stirring the adsorbents in 10 mL of HCl (0.1 mol/L) solution for 30 min. After thorough washing, they were reused for the next new metal ion solution (40 mL, 1 mmol/L). The adsorption–desorption test of the gel beads was repeated 10 consecutive times.

### 2.5. Model to experimental data

Adsorption kinetics analysis was calculated using the pseudo-second-order rate equation as (Hamadi et al., 2001)

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \left(\frac{1}{q_e}\right)t \quad (2)$$

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 sorption isotherm equation is given below (Al-Dege et al., 2006)

$$q_e = \frac{bq_{\max}C_e}{1 + bC_e} \quad (3)$$

where  $C_e$  is the concentration of heavy metal ion solution at equilibrium (mg/L);  $q_{\max}$  signifies the adsorption capacity (mg/g) and  $b$  is related to the energy of adsorption.

The Freundlich sorption isotherm equation is given below (Al-Dege et al., 2006)

$$q_e = kC_e^n \quad (4)$$

where  $k$  ( $\text{mg}^{1-n}\text{L}^n/\text{g}$ ) 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

The removal capacities of the HPAM-chitosan gel beads for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  ions are shown as a function of time in Fig. 1. The removal of metal ions occurs in the order of  $\text{Pb}^{2+}$  (1.69 mmol/g) >  $\text{Cu}^{2+}$  (0.69 mmol/g) >  $\text{Hg}^{2+}$  (0.51 mmol/g). From the results, it is indicated that the gel beads have a good performance for heavy metal removal, especially for  $\text{Pb}^{2+}$  ion removal. It is also indicated that a sharp increase of the adsorption for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  was obtained during the first hour of contact time, followed by a slow increase until an equilibrium state was reached. Very high correlation between the experimental data and the pseudo-second-order model ( $R^2 > 0.963$ ) was obtained in our experiment. The numerical results of  $K$  for each ion are 0.00311 ( $\text{Cu}^{2+}$ ), 0.00013 ( $\text{Pb}^{2+}$ ), and 0.00101 ( $\text{Hg}^{2+}$ ), respectively.

### 3.2. Effects of different experimental parameters

The effects of adsorbent dosage, initial pH, temperature, and initial heavy metal concentration on the removal efficiency or uptake of the gel beads are shown in Fig. 2. As shown in Fig. 2a, when the amount of adsorbent dosage increased from 0.1 to 0.5 g/L, the removal efficiency of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  increased from 11.5% to 24.3%, 19.7% to 50.4%, 6.3% to 15.1%, respectively. However, the adsorption capacities of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  at equilibrium decreased from 1.01 to 0.42 mmol/g, 1.84 to 0.94 mmol/g, and 0.66 to 0.31 mmol/g. This is consistent with other materials and could be due to the increase of binding sites for the adsorption of heavy metals (Naiya et al., 2009; Wang et al., 2009). As shown in Fig. 2b, at low initial pH, the adsorption capacities for all three ions were insignificant and when it increased from 2.0 to 4.2, sharp increases of adsorption capacities were observed for all three ions. This might be mainly due to the dissociation of carboxyl groups in the process. When initial pH increased from 4.2 to 5.5, there were no remarkable differences in the adsorption capacities for  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ , which is rather different from that of the  $\text{Pb}^{2+}$  case. This could attribute to the solvation and hydrolysis of metal ions in the aqueous solution (Naiya et al., 2009). The effect of temperature on the adsorption capacities was shown in Fig. 2c. The adsorption capacity for  $\text{Hg}^{2+}$  remained approximately the same when the temperature increased from 10 to  $60\text{ }^\circ\text{C}$ . In contrast, the adsorption capacities for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  increased with the increase of temperature. The variation of adsorption capacity against temperature is due to the strengthening or weakening of adsorptive forces between the active sites of the adsorbents and adsorbate species (Naiya et al.,

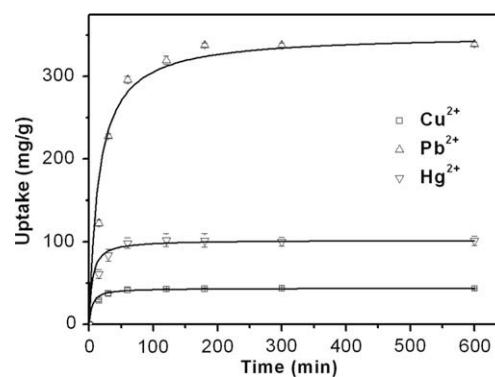


Fig. 1. Adsorption kinetics of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  by HPAM-chitosan gel beads ( $30\text{ }^\circ\text{C}$ ; pH 4.2; initial metal concentration 1 mmol/L). The full lines are model prediction.

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