Screening of algae material as a filter for heavy metals in drinking water

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ABSTRACT

Calcium alginate beads generated from alginic acid sodium salt from brown algae were used to explore the adsorption processes of lead and copper ions in water. The main parameters in the experiment were initial pH, equilibrium time, and concentration of metal ions. The adsorption processes of lead and copper were carried out under specific pH values. Moreover, the multiple adsorption of lead and copper was carried out to study the competition of two metal ions. It was found that the highest adsorption percentage of lead and copper was achieved under the optimum pH respectively. Meanwhile, the highest adsorption percentage of multiple adsorptions was lower than that of single metal adsorption under pH of 4. The optimum pH was utilized in the kinetic experiment and equilibrium experiment. The pseudo-second-order kinetic equations would fit the experimental data well. The maximum amounts of adsorption for lead and copper based on Langmuir models were 250 mg/g and 62.5 mg/g respectively.

1. Introduction

The security of water is the basic requirement and important to health for human. More and more sources of fresh water such as rivers and ground water have been polluted by human activities. Among all of the contaminants in water, lead is one of the most serious polluted components which must be controlled below the maximum limits [7]. It tends to generate bioaccumulation effect in living systems and cause nervous disease to offspring [10]. Copper is a common kind of heavy metal that has been widely used for productions in many industries. The large amount of copper-based wastes from different processes would release into water which would cause serious pollution. Therefore, the treatment of lead and copper ions from water is significant to ensure the quality of drinking water.

The Algae are available in fresh water and seawater; they could be found almost everywhere in water environment systems. The algae have larger surface area with high binding affinity than other materials [8]. Thus, algae become cost-effective materials for removal of toxic compounds. Among different kinds of algae biomass, the dried brown marine algal biomass has been considered one of the potential biomass materials for removing toxic metals. The nature of the adsorption of heavy metals is that the special structures of cell wall in algal biomass which contains many functional groups such as carboxyl, amino, hydroxyl and sulphate that can bind heavy metal at a certain pH value [3].

In this project, the aim is to investigate the capacity of algal adsorption for the two target metal ions for drinking water. The adsorption

effect of lead and copper would be examined with different parameters such as pH, equilibrium time and the initial concentration of metal ions. The equilibrium adsorption data would be evaluated with kinetic model and Langmuir isotherm model.

2. Materials and methods

2.1. Biomass preparation

A 2% solution of Alginic acid sodium salt from brown algae (Sigma) was dripped into 0.05 mol/L $CaCl_2$ solution with the gentle magnetic stirring to form calcium alginate beads. In order to stabilize the beads, the Ca-alginate beads in $CaCl_2$ solution would be stored in a fridge at 4 °C for 24 h. Then the beads were filtered and washed several times with deionized water to remove the excess $CaCl_2$ solution. Finally, the beads were dried in an oven at 50 °C for 24 h to form the dried Ca-alginate beads which would be used as biomass materials in the experiments. The dried beads would be stored in a clean and dry bottle for further experiments.

2.2. Reagents and equipments

All of the chemical reagents were analytical grade and without further purification. The solid $CuSO_4 \cdot 5H_2O$ and $Pb(NO_3)_2$ (Fisher Scientific Company) would be used to generate 1000 mg/L standard stock of lead solution and copper solution that would be diluted to different concentrations for experiments. HNO_3 and NaOH solutions with the same concentration of 0.1 mol/L were respectively prepared to adjust pH value in the batch experiment. Meanwhile, a Perkin Elmer AAnalyst

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200 flame atomic adsorption spectrometer (FAAS) was used to measure the concentration of lead and copper in the batch experiments.

2.3. Effect of initial pH

In this experiment, 50 mg/L lead solution and 50 mg/L copper solution were respectively used to study the effect of pH to the adsorption of heavy metals on Ca-alginate beads. The adsorption effect of 25 mL of solution sample and 0.05 g alginate beads were tested under different pH of 4, 6 and 8 in the batch experiments. The samples were triplicate in order to obtain the average concentration of the sample solution. All of the solution samples were under rotary shaker at 140 rpm at room temperature for 24 h. The metal concentration for solution samples was determined by FAAS. The adsorption percentage under different pH values would be compared to test the optimum pH values for adsorption of lead and copper separately.

The percentage of metal adsorption on Ca-alginate beads was calculated as the equation below:

$$\text{Adsorption } (\%) = \frac{(C_i - C_f)}{C_i} \times 100\% \tag{2.1}$$

where, C_i is the initial concentration of metal; and C_f is the final concentration of the metal.

2.4. Effect of multiple adsorption

In order to study the metal adsorption on Ca-alginate beads, the multiple adsorptions for lead and copper were carried out under pH of 4 and 6. The initial concentration of the lead and copper solution used in this experiment were 25 mg/L, 50 mg/L and 100 mg/L, respectively. In the batch experiments, 50 mL of the mixing solution with the same initial concentration of lead and copper solution and 0.1 g Ca-alginate beads were tested under the rotary shaker at 140 rpm for 2 h. Then the solution and beads would be filtered and the filtrate was prepared to measure the concentration with FAAS. The percentage of multiple adsorptions would be calculated as well.

2.5. Equilibrium experiments

In equilibrium experiments, all of the solution samples were adjusted to optimum pH of 4. The solution samples for lead and copper were respectively diluted to different concentrations from 10 mg/L to 400 mg/L. And then, 50 mL of solution sample and 0.1 g Ca-alginate dried beads were tested under the rotary shaker at 140 rpm for different contact times from 30 min to 48 h. The equilibrium time would be determined from FAAS according to the results of solution concentration before and after experiment. The kinetic models and Langmuir isotherm models for lead and copper adsorptions would be discussed in details in following sections.

3. Discussion

3.1. Characterization of Ca-alginate beads

The weight measurement showed that the wet beads contained about 95% w/w water. The density for wet beads was 0.9512 g/cm³. The particle sizes were determined by a sieving mesh system. The diameter for most wet beads was in the range of 4 mm, while the dried beads showed the maximum diameter of 2 mm. It was shown that the volume of the beads after drying decreases rapidly. Even though the porosity of the two types of beads was not examined, the previous study showed that wet beads were with little pores while the dried beads were with a large ratio of porosity and the roughness of the dried beads increased the surface area which was valuable for binding heavy metal ions [5].
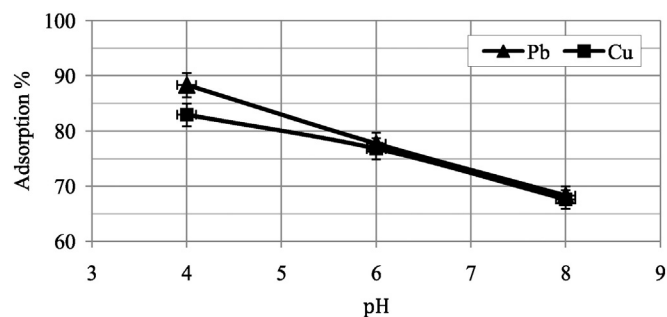

Fig. 3.1. Effect of pH for adsorption of 50 mg/L lead and copper solution onto dried Ca-alginate beads for 24 h.

3.2. Effect of initial pH

According to the adsorption percentage results in Fig. 3.1, both lead and copper solution samples achieved the highest adsorption performance under pH of 4. With increasing of pH, the adsorption percentage of metal ions decreased. This result demonstrated that the dried Ca-alginate beads indeed had the capacity of adsorbing heavy metals under proper pH conditions.

In the carboxyl groups, the main functional groups on Ca-alginate beads were dependent on pH values. Moreover, the initial pH would affect the mechanism of metal chemistry and the functional groups on alginate materials. The surface of Ca-alginate beads was positively charged under low pH so that the metal ions were not able to bind to functional groups on alginate biomass due to the competition between hydrogen ions and the metal ions. With the increasing of pH, more ligands with binding sites on the surfaces of beads particles released, as the surface of the particles was negatively charged and the metal ions would be able to bind the functional groups on the bead particles. Therefore, the optimum pH for adsorption of lead and copper was pH of 4. The reason was that under pH of 4 the solution was not extremely protonated and suitable for the weak acidic nature of binding sites so that the metal ions could bind to the functional groups carboxyl acid groups. The highest percentage of adsorption for lead was about 88% while the best adsorption for copper under pH of 4 was about 83%. The similar results were obtained from literatures. The highest percentages of lead and copper adsorption with Ca-alginate were respectively around 90% and 80% [9]. Therefore, pH of 4 would be used as optimum pH for further experiments.

3.3. Effect of multiple adsorption

Fig. 3.2 showed that the highest adsorption percentage for lead and copper was achieved under pH of 4. The highest adsorption percentage for lead and copper were 72% and 68% under pH of 4. The adsorption
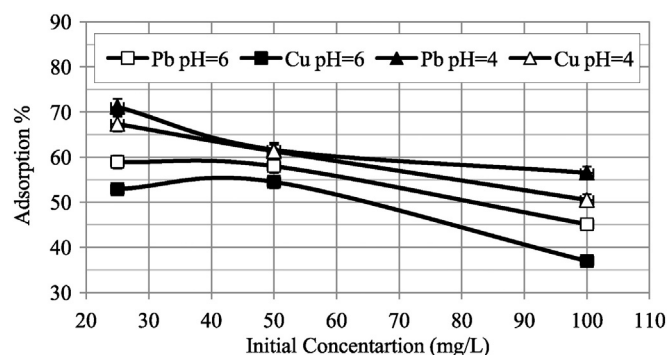

Fig. 3.2. Effect of pH for adsorption of multiple metal solution of different initial concentrations under pH of 4 and 6.