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Screening of Algae Material as a Filter for Heavy Metals in Drinking Water

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.

Keywords: Heavy metals adsorption; Biosorption; Dry Ca-alginate beads; Kinetic; Isotherm

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 (Saleh & Gupta, 2012). It tends to generate bioaccumulation effect in living systems and cause nervous disease to offspring (Tiwari & Tripathi, 2012). 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 (Sari & Tuzen, 2008). Thus, algae become cost-effective materials for removal of toxic compounds. Among different kinds of algae biomass, the dry 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 (Gupta & Rastogi, 2008).

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 dry Ca-alginate beads which would be used as biomass materials in the experiments. The dry 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 concentration for experiments. 0.1 mol/L HNO_3 and 0.1 mol/L NaOH was prepared to adjust pH value in the batch experiment. Meanwhile, a Perkin Elmer AAnalyst 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

50 mg/L lead solution and 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:

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

Where, C_i is the initial concentration of metal; 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 was respectively 25 mg/L, 50 mg/L and 100 mg/L. 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 concentration from 10 mg/L to 400 mg/L. 50 mL of solution sample and 0.1 g Ca-alginate dry beads were tested under the rotary shaker at 140 rpm for different contact time from 30 minutes 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/cm^3. The particle sizes were determined by a sieving mesh system. The diameter for most wet beads was in the range of 4mm, while the dry beads showed the maximum diameter of 2 mm. It was shown that the volume of the beads after drying decrease rapidly. Even though the porosity of the two types of beads were not examined, the previous study showed that wet beads were with little pores while the dry beads were with a large ratio of porosity and the roughness of the dry beads increased the surface area which were valuable for binding heavy metal ions.(Lagoa & Rodrigues, 2009).

3.2 Effect of Initial pH

According to the adsorption percentage results in Figure 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 dry Ca-alginate beads indeed had the capacity of adsorbing heavy metals under proper pH conditions.

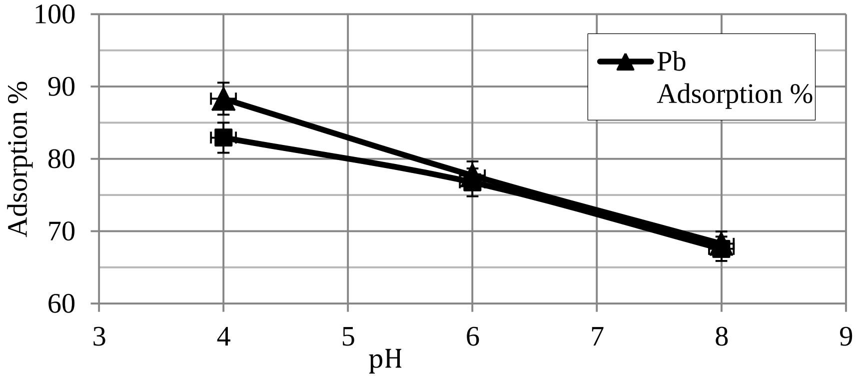

Figure 3.1 Effect of pH for Adsorption of 50 mg/L Lead and Copper Solution onto dry Ca-alginate Beads for 24 h.

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 were 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 were 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% (Sheng et al., 2004). Therefore, pH of 4 would be used as optimum pH for further experiments.

3.3 Effect of Multiple Adsorption

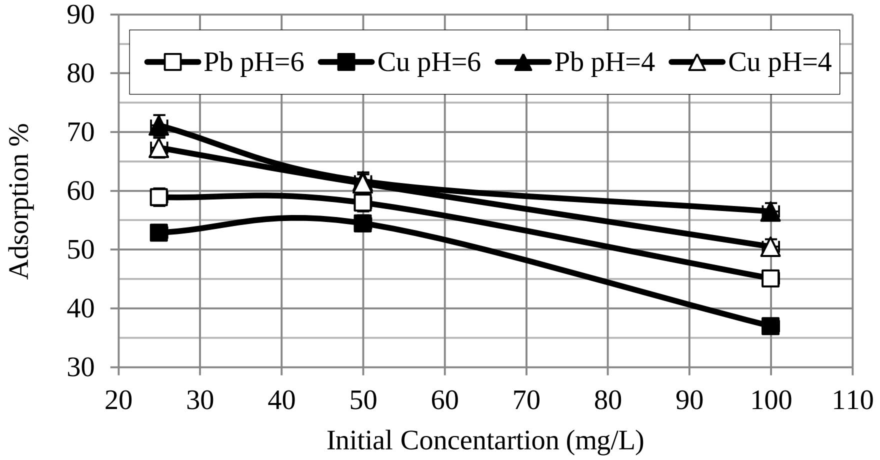

Figure 3.2 Effect of pH for Adsorption of Multiple Metal Solution of Different Initial Concentration under pH of 4 and 6.

Figure 3.2 showed that the highest adsorption percentage for lead and copper were achieved under pH of 4. The highest adsorption percentage for lead and copper were 72% and 68% under pH of 4. The adsorption percentage decreased compared to the single adsorption systems. It was found that the functional groups preferred to lead ions. The lead ions could be able to bind with carboxyl groups that offered negatively charged sites and coordinative interaction better, these ions tended to have more affinity to the functional groups on alginate beads. Meanwhile, the lead ions had larger radii than that of copper ions (Chong & Volesky, 1995). The ions with large radii in the “egg box” would be stable. The other properties such as the softness of the ions and electron negativity, electrode potentials for various ions also could contribute to the competition for multiple metal adsorptions (Yun, 2004).

3.4 Kinetic Adsorption Experiments

Figure 3.3 and 3.4 showed that the concentration of lead and copper decreased rapidly within 2 h and finally reached the equilibrium concentration for 24 h respectively. The previous studies showed that equilibrium time were various as the reaction conditions were different. However, the equilibrium time for this experiment was a little long compared with other results in the literatures which demonstrated that the equilibrium time was only several hours for metal adsorption (Jalali et al., 2002). The long equilibrium time would restrain the application for treating toxic metal ions significantly.

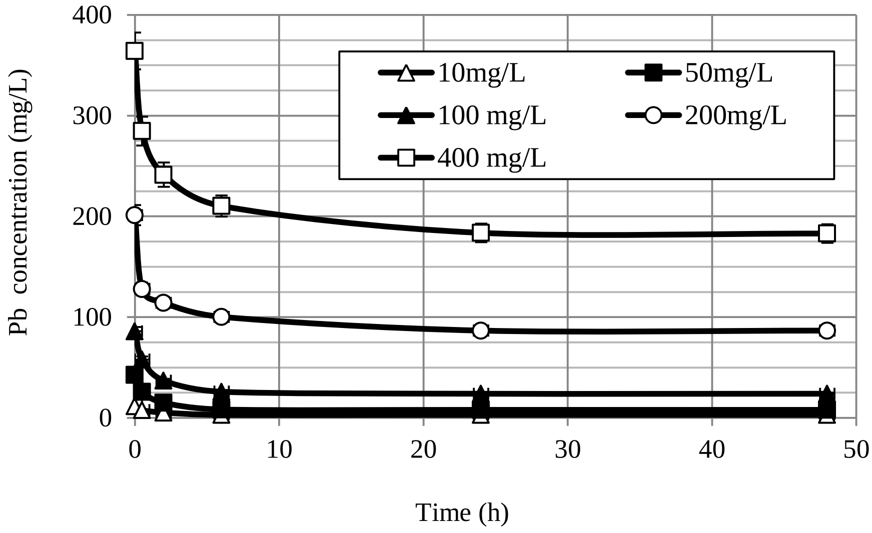

Figure 3.3 Kinetic Adsorption for Lead with Different Initial Concentration under pH of 4.

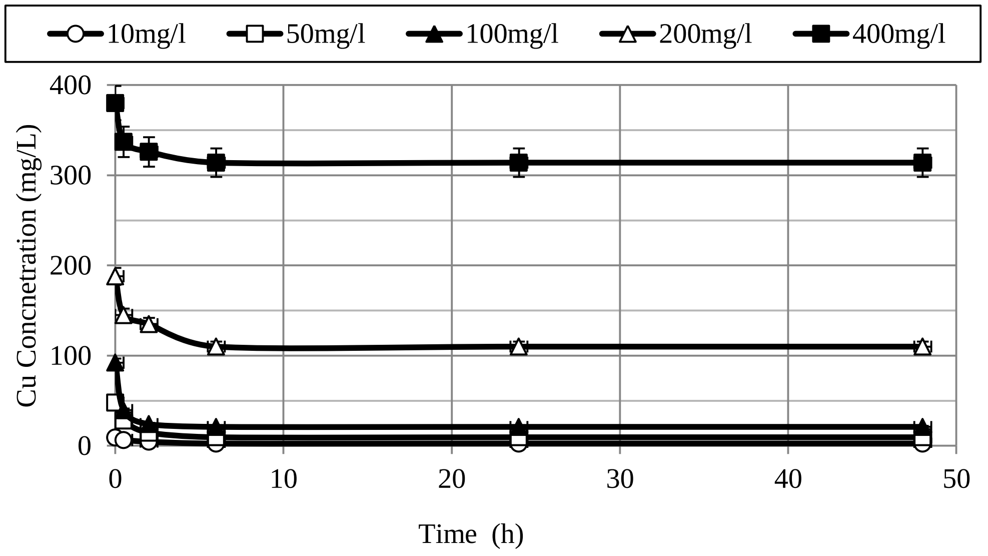

Figure 3.4 Kinetic Adsorption for Copper with Different Initial Concentration under pH of 4.

The kinetic models were useful to examine the quantitative description of the adsorption process dynamics. The pseudo-second-order model was used in this experiment. The linear equation for pseudo-second-order kinetic model was given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + (\frac{1}{q_e})t \qquad \text{Eq. 3.1}$$

Where, q_t (mg/g) is the amount of adsorption at a given time t (h); q_e (mg/g) is the amount of adsorption at equilibrium time; k_2 (g/mg h) is the rate constant of pseudo-second-order kinetic equation.

According to the results in Table 3.1, the correlation coefficients for both lead and copper solutions indicated that the pseudo-second-order model could fit the concentration of lead and copper solutions well. With the increasing of the initial concentration, the rate constants for lead adsorption were from 0.206 to 0.005 g/mg h while the constants for copper adsorption were from 0.119 to 0.022 g/mg h. It was found that with the increasing of concentration, the rate constants decreased evidently. The rate constants for lead adsorption were generally higher than that of copper adsorption. This result indicated that the Ca-alginate beads would bind with lead ions faster. However, when the capacity of adsorption was reached, the rate of adsorption would decrease seriously. According to previous studies, the results of rate constant in this experiment were not comparable with some results from previous studies (Deng et al., 2006). The main reason was the various experiment conditions, including different temperature, beads dosage, equilibrium time, and initial concentrations for different metal ions.

Table 3.1 the Kinetic Constants of Pseudo-Second-Order Equation for Adsorption.

Cu mg/L	K_2 g/mg h	R^2	Pb mg/L	K_2 g/mg h	R^2
10	0.119	0.997	10	0.206	0.999

Cu mg/L	K_2 g/mg h	R^2	Pb mg/L	K_2 g/mg h	R^2
50	0.057	0.999	50	0.065	0.998
100	0.098	0.999	100	0.028	0.999
200	0.012	0.998	200	0.021	0.999
400	0.022	0.999	400	0.005	0.999

3.5 Equilibrium Isotherm Models

The Langmuir isotherm was a widely used model to test the capacity of the biosorbents to heavy metals. The assumption of Langmuir model was that the rate of occurring metal adsorption at each binding sites of the beads was equal to each other. The linear equation for Langmuir isotherm model was represented as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad \text{Eq. 3.2}$$

Where, q_e is the equilibrium concentration for metal ion on the Ca-alginate beads (mg/g); C_e is the equilibrium concentration for metal ion in the solution (mg/L); q_m is the maximum adsorption capacity for the calcium alginate beads (mg/g); K_L is the Langmuir adsorption constant (L/mg).

The correlation coefficients for lead and copper adsorptions were 0.960 and 0.989 respectively which indicated the Langmuir models would fit the data well. The maximum capacities for adsorptions were 250 mg/g and 62.5 mg/g for lead and copper respectively. According to the intercepts of the equations, the equilibrium constants would be determined and the values were 1.3×10^{-1} L/mg for lead adsorption and K_L 1.7×10^{-2} L/mg for copper adsorption. The constants were related to the affinity of binding sites (Deng et al., 2006). The capacity of adsorption for lead was evidently higher than that of copper adsorption. The adsorption capacity order was: Pb > Cu.

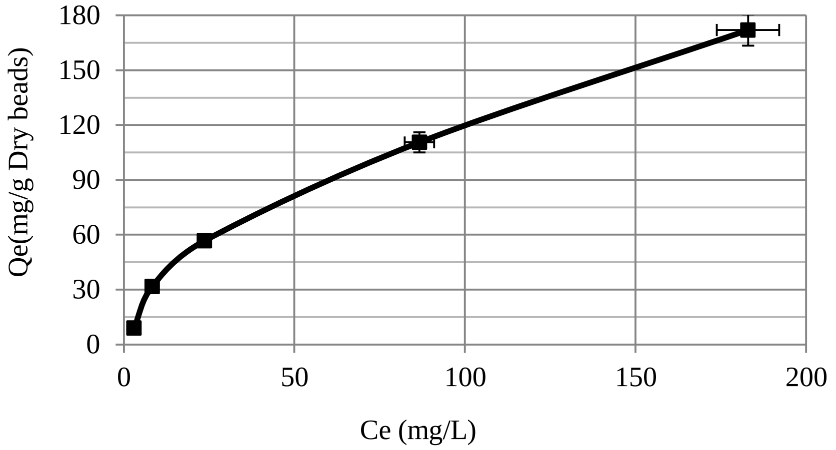

Figure 3.5 Langmuir Isotherms for Adsorption of Lead with Dry Ca-alginate Beads (Initial Concentration from 10 mg/L to 400 mg/L, pH=4, 48h)

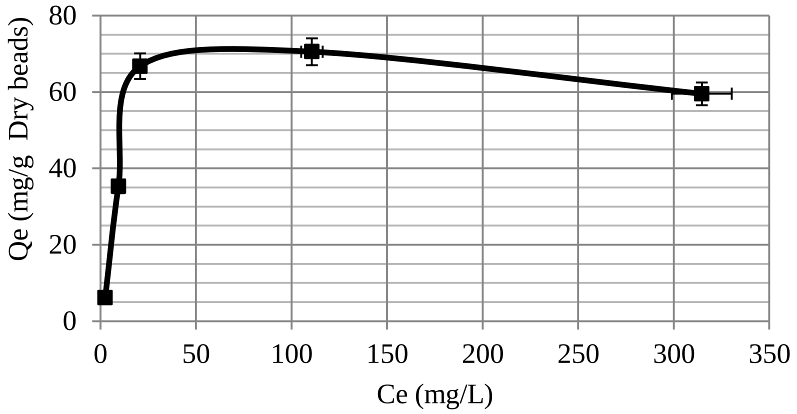

Figure 3.6 Langmuir Isotherms for Absorption of Copper with Dry Calcium-alginate Beads (Initial Concentration from 10 mg/L to 400 mg/L, pH=4, 48 h)

According to Figure 3.5 and Figure 3.6, it was found that the amount of lead adsorption on beads would not reach the maximum capacity while the capacity of copper adsorption on beads had reached its maximum capacity for saturated state; therefore, the beads could not adsorb copper ions any more. It was observed through the copper adsorption that after equilibrium, the amount of copper adsorption on beads decreased with the increasing of initial concentration in solution. Due to the chemical property of copper ions, the affinity of binding copper ions to Ca-alginate beads may be not strong enough and the reaction would proceed towards the opposite direction which cause the occurrence of desorption for copper ions. The order was similar to the result from previous literatures that demonstrated the affinity order was Pb > Cd > Cu > Ba > Sr > Ca > Co > Ni (Papageorgiou et al., 2006). The result also indicated that the active binding sites were preferred to metal ions with larger radii that would form a more stable structure with the coordination of oxygen atoms.

4. CONCLUSIONS

As a whole, the optimum initial pH for adsorption of lead and copper ions in solution were both 4. In the multiple adsorption systems, the adsorption percentage of both lead and copper decreased compared with the results of single adsorption experiments. It was found that the pseudo-second-order model was appropriate to fit the experimental data. According to Langmuir model, the maximum capacity of adsorption for lead and copper were 250 mg/g and 62.5 mg/g respectively which indicated the potential ability for removing heavy metals in water.

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