

Influence of surfactant entrapment to dried alginate beads on sorption and removal of Cu^{2+} ions

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Abstract

The removal of heavy metals has been investigated widely in recent years due to their potential health risk to human beings. In this study, the removals of copper from aqueous phase by alginate and SDBS entrapped alginate was investigated. First, a series of equilibrium sorption experiments were conducted at different initial pH values. Both equilibrium copper concentration and final pH values were observed. Then, a series of kinetic experiments were conducted and a second order rate relationship was fit to the experimental data. Equilibrium sorption experiments showed that the sorption of Cu^{2+} ions by 2% of SDBS entrapped alginate beads were greater than the plain and 0.5% of SDBS entrapped alginate beads. More H^+ ion exchange occurred with the 2% of SDBS entrapped alginate beads, which was attributed to the increased number of the exchange sites on the alginate due to the sorption of surfactant to the beads. Kinetic sorption experiments showed that the equilibrium was reached faster for 2% of SDBS entrapped alginate beads. Results were successfully represented using second order kinetic model. Both equilibrium and kinetic experiments showed that the sorption of Cu^{2+} ions increased as the pH of the aqueous solution increased.

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1. Introduction

The removal or the recovery of heavy metals from water and industrial wastewater has been the main focus of some studies for quite some time. Precipitation [1–3], electrokinetics adsorption [4–6] and ion exchange methods [7–10] are the few of the techniques that have been investigated significantly. Each method has its own advantageous and disadvantageous in terms of efficiency and cost. Precipitation yield high levels of removal; however, it showed limited efficiencies especially at the removal of low concentrations of metals. Electrokinetic methods are not cost effective. Adsorption and ion exchange showed promising results. In recent years, the sorption of metals to dead biological materials or to the materials that have been derived from living organisms has been widely investigated due to their low cost and the capacity of high removal of heavy metals [9,10]. Biosorption is a process in which metal uptake occurs by micro-

bial cells through adsorption, ion exchange, co-ordination and/or complexation [10,11]. Among biological materials alginates has become one of the important group of adsorbent because of their unique properties. Alginate has great affinity to divalent cations. Viscous alginate solution forms gelation when it contacts with a divalent cation. Alginate, which is mainly obtained from brown algae, is a biopolymer composed of varying compositions of β -1,4-D-mannuronic and L-guluronic acids [12]. Sorption of various heavy metals by alginate beads has been investigated and sorption models were developed [13–17]. An excellent review of the biosorption of heavy metals by brown algae (including alginate) is presented by Davies et al. [12]. Recently, the influence of the changes in the preparation of alginate beads on the efficiency of removal of heavy metals has been studied. Relatively greater adsorption capacity of Pb^{2+} was observed for alginate coated cotton capsules then for alginate beads [18]. Metal sorption capacity of covalently cross-linked and un-cross-linked alginate beads were almost the same, resulting, no significant change as a result of cross linkage [19]. In order to increase the efficiency of alginate beads dead organisms have been entrapped and removal of heavy metals were investigated [20,21]. The effect of humic

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acid entrapment on the sorption of heavy metals to alginate was also investigated [22].

The surface modification/enhancement using surfactants have not been studied for alginates despite the known positive effect of surfactants on removal of heavy metals [23]. Furthermore, the majority of the studies in the literature were conducted using alginate gels, which are problematic in terms of handling and storage. Using dried alginates provides advantages in scale up applications. The main objective of this study was to investigate the removals of copper from aqueous phase by alginate and surfactant entrapped dried alginate beads. An anionic surfactant, sodium dodecylbenzene sulfonate (SDBS), was chosen as the model surfactant. Plain, 0.5% of SDBS and 2% of SDBS entrapped alginate beads were used in all experiments. First, a series of equilibrium sorption experiments were conducted at different initial pH values. Both equilibrium copper concentration and final pH values were observed. Then, a series of kinetic experiments were conducted and a second order rate relationship was fit to the experimental data.

2. Materials and methods

2.1. Materials

Low density sodium alginate was obtained from Sigma Chemical Co. (St. Louis, MO). The viscosity of alginic acid used in the experiments was 2%. SDBS was obtained from Sigma Chemical Co. and used as received. Cu^{2+} solutions were prepared using analytical grade of CuCl_2 obtained from Merck (Darmstadt, Germany). CaCl_2 was also obtained from Merck.

2.2. Experimental methods

2.2.1. Preparation of alginate beads

An amount of 2% of sodium alginate solution was prepared by dissolving 20 g of low density sodium alginate beads in 100 mL of distilled (DI) water. A magnetic stirrer and a heater were used to accelerate the dissolution of alginate. Prepared alginate solution was rested for 24 h to remove the air bubbles from the solution. An amount of 0.5 and 2.0 g of SDBS was added to 1 L of DI water in addition to sodium alginate for the preparation of the solutions of 0.5% and 2% entrapped SDBS, respectively. The solutions of plain (0%), 0.5% of SDBS entrapped and 2% of SDBS entrapped sodium alginate solutions were dropped into 20% of CaCl_2 , 20% of $\text{CaCl}_2 + 0.5 \text{ g/L}$ of SDBS, 20% of $\text{CaCl}_2 + 2 \text{ g/L}$ of SDBS solutions using a peristaltic pump, respectively. CaCl_2 solutions were mixed using a magnetic stirrer while the drops were falling into the solution. The bead formation started as soon as the alginate and calcium solutions contacted. Almost circular beads were formed and they were left in the calcium solution for another day for calcium to complete the diffusion to inside the beads. Once the wet beads formed they were taken out of solution and washed with DI water thoroughly to remove excess calcium in the beads. After washing, the beads were air dried and then dried in an oven at 60°C for a day.

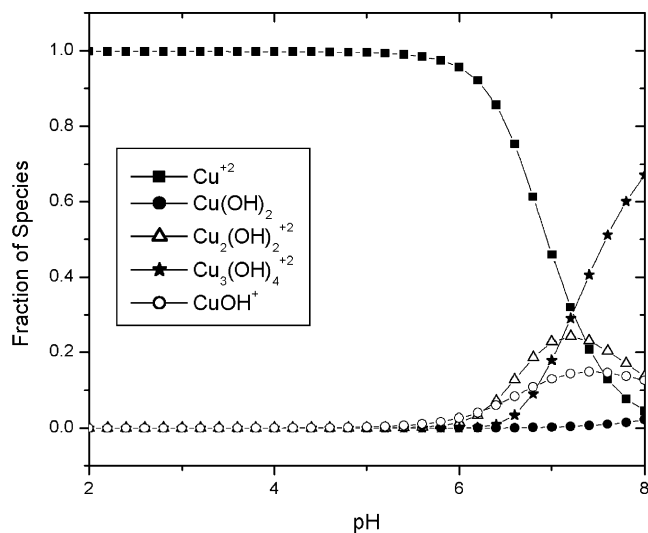


Fig. 1. The effect of pH on the speciation of copper.

2.2.2. Equilibrium sorption experiments

Sorption of Cu^{2+} ions to alginate beads was investigated at Cu^{2+} concentrations varying from 1 to 40 mg/L using 100 mL of glass flasks. Three different adsorbent were used in the experiments: plain (0%), 0.5% of SDBS entrapped and 2% of SDBS entrapped calcium alginate beads. A different set of experiment was conducted at the pH value of 3.0 and 2.0 using all three alginate beads as adsorbent. It was determined that at pH of 5.8 or below the dominant copper species was to be divalent form (Cu^{2+}) and precipitation could not happen. Speciation of copper by the addition of 40 mg/L of CaCl_2 into DI water with pH is constructed using MINTEQA2 (EPA) and presented in Fig. 1. An amount of 100 mL of Cu^{2+} solution was added to each flask and pH was adjusted to the prescribed value using 0.1 M of HCl and NaOH solutions. Then 0.5 g of alginate beads was added to the solution, and the mixture was equilibrated for 24 h at 25°C using an orbital shaker equipped with an incubator (Edmund Buhler, KS-15). Preliminary experiments showed that the sorption of Cu^{2+} reached equilibrium in less than 24 h. After equilibrium reached, final pH measurements were made, and supernatant was taken and analyzed for Cu^{2+} using an atomic adsorption spectrophotometer equipped with a graphite furnace (Perkin-Elmer, SIMAA, 6000).

2.2.3. Kinetic sorption experiments

The sorption kinetic experiments were conducted using 500 mL of flask at different pH values and temperatures. An amount of 500 mL of 40 mg/L of Cu^{2+} solution was added to the flask and pH was adjusted to a prescribed value. Then, 2.5 g of alginate beads were added and the solution was shaken with an orbital shaker at constant temperature. Samples (1 mL) were taken at times between 0 and 120 min and analyzed for Cu^{2+} . The samples taken from the mixture was assumed not causing significant changes in adsorption since the amount of sample was too small (1 mL) compared to the total volume of the solution (500 mL).

3. Results and discussion

3.1. Equilibrium sorption experiments

The results of equilibrium sorption experiments are presented in Fig. 2. Typical sorption isotherms of metals to alginate beads are Langmuir type. However, in this study the maximum initial concentration was low (only 40 mg/L of Cu²⁺), therefore the plateau at which maximum sorption occurs was not observed. The results were fit to a Freundlich type isotherm:

$$S = KC^n \tag{1}$$

where *S* is the sorbed Cu²⁺ mass (mg/g), *C* the aqueous phase concentration of Cu²⁺, and *K* and *n* are the Freundlich coefficient and exponent, respectively. The results obtained fitting experimental data to Freundlich isotherm is presented in Table 1.

The results clearly demonstrated that 2% of SDBS entrapped alginate beads were much better adsorbent than the plain and 0.5% of SDBS entrapped beads. SDBS interacted with alginate and extent its head to the bulk solution, resulting more exchange

Table 1
The Freundlich coefficients and exponents

pH	Concentration of SDBS (%)	<i>K</i>	<i>n</i>	<i>R</i> ²
3	0	2.197	0.72	0.991
3	0.5	1.264	0.997	0.988
3	2.0	3.417	0.997	0.994
2	0	0.671	0.72	0.94
2	0.5	0.386	1.34	0.997
2	2.0	1.182	0.98	0.989

sites for Cu²⁺ ions. The sorption of Cu²⁺ to the plain and 0.5% of SDBS entrapped alginate beads were similar suggesting that 0.5% of SDBS did not improve the sorption. The results also showed that that the sorption of Cu²⁺ was greater at pH of 3 than those observed at pH of 2 for all alginate types. At lower pH values, more acidic conditions prevailed, therefore Cu²⁺ ions remain in solution in greater concentration.

The change of pH values in equilibrium sorption studies are presented in Fig. 3. Initially all the pH values were the same

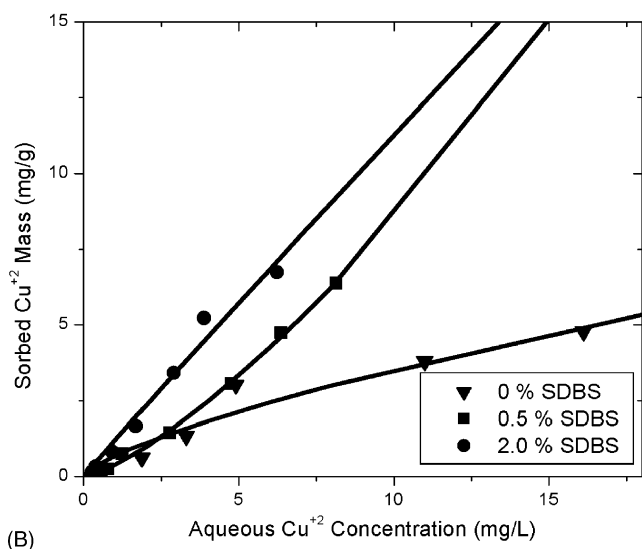
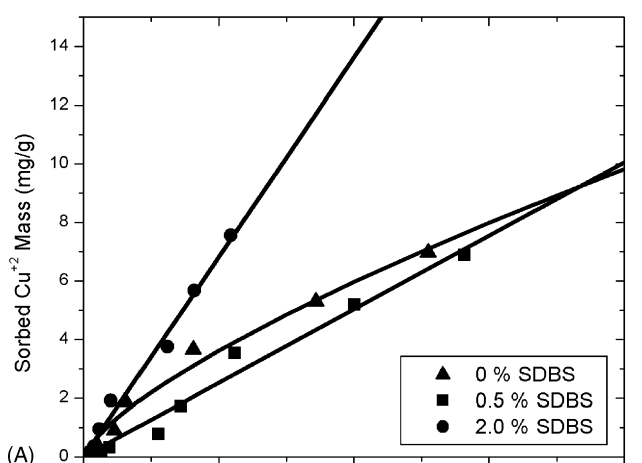


Fig. 2. Freundlich isotherms of Cu²⁺ sorption. (A) Initial pH 3.0, (B) initial pH 2.0.

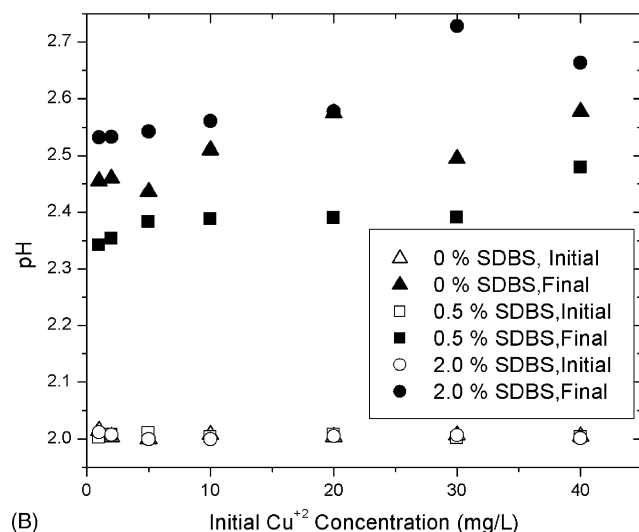
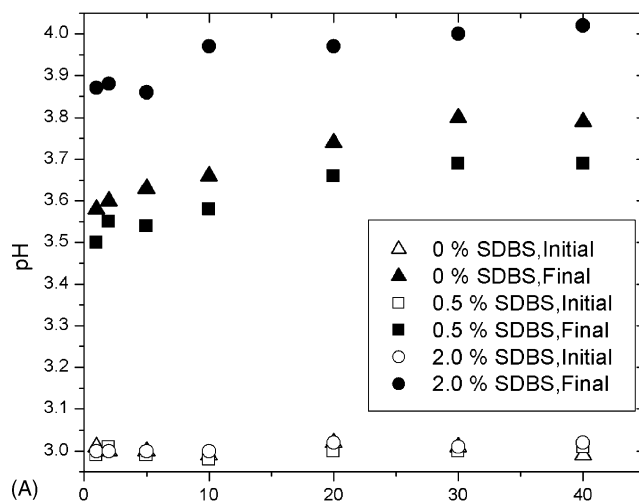


Fig. 3. Change of pH with initial Cu²⁺ concentration. (A) Initial pH 3.0, (B) initial pH 2.0.

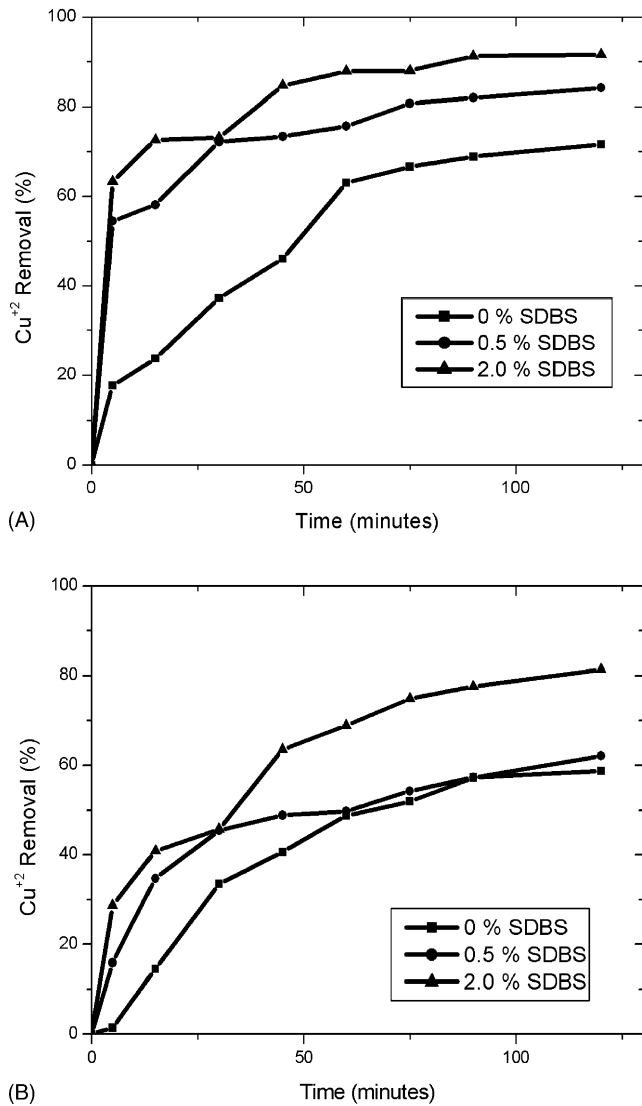


Fig. 4. Removal efficiency of Cu^{2+} ions with time. (A) Initial pH 5.0, (B) initial pH 3.0.

(± 0.1). The pH values in both experiments (pH of 3.0 and 2.0) increased substantially indicating H^+ exchange with the sides available in alginate (COO^- groups) and SDBS. H^+ is a very mobile ion and therefore exchange easily with other cations (i.e. Ca^{2+}). In Fig. 3A, the pH values increased from 3 to 3.5–3.6 for plain alginate, to 3.6–3.7 for 0.5% of SDBS entrapped alginate beads and 3.9–4.0 for 2% of SDBS entrapped alginate beads. Approximately $(5\text{--}10) \times 10^{-4}$ M of H^+ is removed from the solution. The increase in the exchange of H^+ as the increase of SDBS concentration was attributed to the increased number of available exchange sites in the presence of SDBS. Similar results were obtained at the experiment conducted with initial pH of 2.0. pH values increased to 2.35 and 2.7 values depending on the alginate type. The decrease in pH corresponded approximately five times more hydrogen exchange. Higher hydrogen exchange might be one of the factors causing less sorption of Cu^{2+} ions to the beads in addition to the other factors mentioned above.

3.2. Kinetic sorption experiments

In Fig. 4A and B removal (sorption) of Cu^{2+} ions are presented as a function of time. Removal of Cu^{2+} at pH 5.0 is much faster than that observed at pH 3.0. Specifically, both 0.5% and 2% of SDBS entrapped alginate beads reached the equilibrium faster at 3.0 compared to the plain alginate beads. The fast kinetic may be attributed to the presence of surfactants. On the surface of alginate beads SDBS extend its head to the bulk solution. Exchange to the groups on the surface is much easier than diffusion within the beads. Another reason maybe the fact that the sizes of the beads were different. Since SDBS reduced the surface tension of alginate solution, the slightly smaller drops formed, therefore higher surface area per gram of alginate beads obtained for SDBS entrapped alginate beads. Hence, faster adsorption occurred. The effect of the size of the beads should not have an important impact on equilibrium sorption since the equilibrium sorption of Cu^{2+} ions to plain and 0.5% of SDBS entrapped beads were comparable despite the differences in their size.

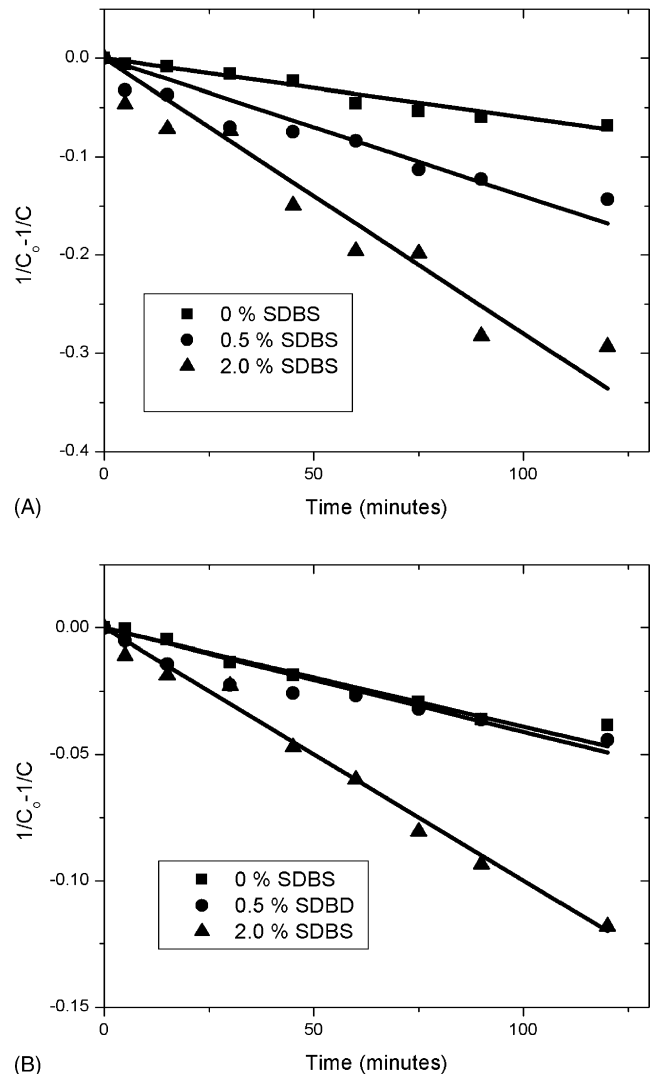


Fig. 5. Second order model fit to experimental data. (A) Initial pH 5.0, (B) initial pH 3.0.

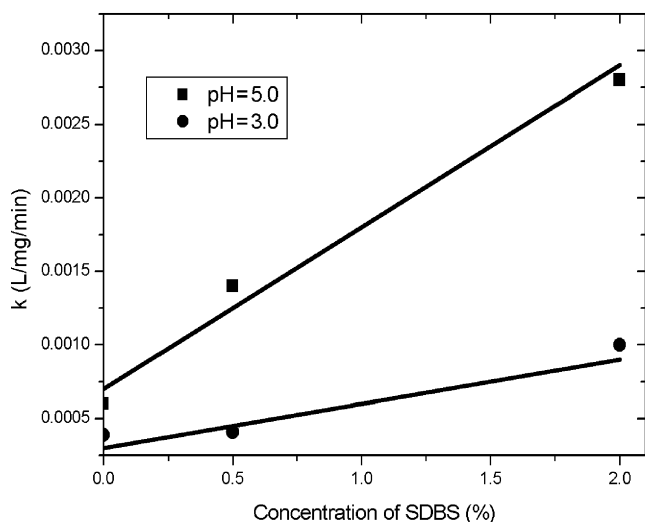


Fig. 6. Change of rate coefficient with SDBS concentration.

The results of kinetic experiments were fit to second order rate equation. The linearized form of second order kinetic:

$$\frac{1}{C_0} - \frac{1}{C} = -kC \quad (2)$$

where, k is the second order rate coefficient (L/mg/min) and C and C_0 are the aqueous and initial Cu^{2+} concentrations (mg/L), respectively. The results are presented in Fig. 5A and B. Experimental data was well described with second order kinetic. In Fig. 6, the second order rate coefficients are presented as a function of SDBS concentration for the initial pH values of 5.0 and 3.0. The rate coefficients increased almost linearly as the SDBS concentration increased. The rate of sorption increases as the SDBS concentration increased. The rate of sorption was much faster at pH of 3.0 than the rates obtained at pH of 2.0.

4. Conclusion

Equilibrium sorption experiments showed that the sorption of Cu^{2+} ions by 2% of SDBS entrapped alginate beads were greater

than the plain and 0.5% of SDBS entrapped alginate beads. pH of the solution increased throughout the equilibrium studies suggesting the significance of H^+ exchange between alginate beads and aqueous solution. More H^+ ion exchange occurred with the 2% of SDBS entrapped alginate beads, which was attributed to the increased number of the exchange sites on the alginate due to the surfactant. Kinetic sorption experiments also showed that the equilibrium was reached faster for 2% of SDBS entrapped alginate beads. Results were successfully represented using second order kinetic model. Both equilibrium and kinetic experiments showed that the sorption of Cu^{2+} ions increased as the pH of the aqueous solution increased.

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