Kasetsart J. (Nat. Sci.) 43 : 326 - 332 (2009)

Biosorption of Copper by Spent Yeast Immobilized in Sodium Alginate Beads

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ABSTRACT

Spent yeast from the brewing industry was immobilized with sodium alginate and used in a study on biosorption of Cu(II). Kinetic models were developed using pseudo-first and -second order equations and tested for the sorption of Cu(II). The results showed that the sorption of Cu(II) onto immobilized spent yeast in sodium alginate beads could be described by a pseudo-second order model, which had high correlation coefficients (r^2). The rate constant (k_2) and the initial sorption rate (h) were calculated. The values of the rate constants were found to decrease from 0.208 to 0.037 g/mg min with an increase in the initial concentration of Cu(II) from 20 to 80 ppm. The initial sorption rate increased from 0.014 to 0.037 mg/g min as the initial concentration of Cu(II) was varied from 20 to 80 ppm. The observed dependence of the sorption rate on the initial concentration of Cu(II) indicated that the removal of Cu(II) was more rapid when the initial concentration of the solution was high.

Key words: biosorption, spent yeast, sodium alginate, copper

INTRODUCTION

Many industrial processes generate wastewater containing heavy metals which can contaminate the environment. There have been several reports on the use of microbial biomass, including dead and immobilized cells, as sorbents for the removal of various toxicants including heavy metals and radioactive elements from various sources of wastewater (de Rome and Gadd, 1991; Tsezos and Deutschmann, 1992). These systems are less expensive than the traditional physicochemical processes (Araújo and Teixeira, 1997).

Moreover, immobilization of microorganisms seemed to give a higher uptake of metal ions as suggested by de Rome and Gadd (1991), Jang *et al*. (1991) and Kuhn and Pfister (1989). The application of immobilized biomass has many advantages including: easy separation of cells and effluents, minimal clogging, high biomass loading and repeated use of biomass (Brady and Duncan, 1994).

As discussed by Ho and McKay (1999b), the study of sorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions. In addition, kinetics describes the solute uptake rate, which in turn controls the residence time of sorbate uptake

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at the solid-solution interface. It is important to be able to predict the rate at which a pollutant is removed from an aqueous solution, in order to design appropriate sorption treatment plants. Therefore, this study aimed to use immobilized spent yeast entrapped with sodium alginate as sorbent to evaluate the influence of initial concentrations of a metal ion on the uptake of Cu(II) from the solution. Two simplified kinetic models, including pseudo-first order and pseudo-second order equations, were used to describe the biosorption mechanism.

MATERIALS AND METHODS

Source of spent yeast

Spent yeast was obtained from the Thai Amarit Brewery Ltd. (Thailand). It was dried at 80°C for 24 hours and stored in sealed bags at room temperature until use.

Immobilization method

Immobilized spent yeast in sodium alginate beads was prepared by mixing 5 g of dried spent yeast in 100 ml of 1% sodium alginate. The mixture was stirred thoroughly to ensure complete mixing before dropping into 0.1 M $CaCl_2$ solution, to form sodium alginate beads. The beads were hardened for 30 min and then collected and washed with deionized water.

Biosorption studies

Cu(II) biosorption was carried out in triplicate in 500 ml Erlenmeyer flasks containing 150 ml of each heavy metal solution. Initial concentrations of Cu(II) of 20, 40, 60 and 80 ppm at an initial pH value of 4 were used. An amount of 9.5 g dried weight of immobilized spent yeast in sodium alginate beads was added. All flasks were shaken at 200 rpm for 8 h at 35°C. The concentration of Cu(II) ions was monitored before and after the sorption period.

Analysis of heavy metal

Cu(II) concentrations in solution were determined using an atomic absorption spectrophotometer (GBC, Model Avanta 1.33) calibrated with standard solutions prepared from 1,000 mg/l certified reference solutions (Merck).

Kinetic studies

In order to investigate the mechanism of sorption, the rate constants for the sorption of Cu(II) were determined using some kinetic models. A simple kinetic analysis of adsorption can be obtained from the pseudo-first-order equation of Lagergren (Sarkar and Chattoraj, 1993; Ho and McKay, 1999a) (Equation 1):

$$dq_t / dt = k_1 (q_e - q_t) \quad (1)$$

where k_1 is the rate constant of pseudo-first-order adsorption, q_t is the amount of solute sorbed on the surface of the sorbent at any time t (mg/g) and q_e is the amount of adsorption at equilibrium.

After integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (1) becomes Equation 2:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (2)$$

where q_e must be obtained beforehand from the equilibrium experiments.

On the other hand, a pseudo-second-order equation based on adsorption capacity can also be expressed in the form of Equation 3 (Ho and McKay, 1999a and 1999b):

$$dq_t / dt = k_2 (q_e - q_t)^2 \quad (3)$$

where k_2 is the rate constant of pseudo-second-order adsorption and q_e is the amount of adsorption at equilibrium.

Integration of Equation 3 and applying the initial conditions produces Equation 4:

$$t / q_t = (1 / k_2 q_e^2) + (1/q_e) t \quad (4)$$

It is noted that k_2 and q_e in Equation 4 can be obtained from the intercept and slope of the plot of (t / q_t) vs. t and there is no need to know any parameter beforehand. In Equation 4, the initial rate of adsorption, h (mg/g.min), is given by Equation 5:

$$h = k_2 q_e^2 \quad (5)$$

RESULTS AND DISCUSSION

Copper biosorption

The rate of Cu(II) sorption was determined as a function of the initial Cu(II) concentration that varied from 20 to 80 ppm. Figure 1 shows the kinetics of the Cu(II) uptake by immobilized spent yeast in sodium alginate beads. The sorption rate was rapid at the beginning of the period. It was observed that the equilibrium uptake of Cu(II) by immobilized spent yeast was established after 2 h.

Donmez and Aksu (1999) reported that the metal ion uptake in yeasts is known to involve an initial rapid binding of metal ions to negatively-charged sites on the cell wall, which is a multi-laminate, microfibrillar structure consisting of up to 90% polysaccharide (biosorption), followed by a slower, energy-dependent entry. The outer mannan-protein layer of the yeast cell wall, as well as the inner glucan-chitin layer, is important for heavy metal accumulation. Another metal deposition mechanism can be hypothesized based on the active transport of metal ions.

As explained by several researchers, metal ion binding to non-living cells occurs rapidly by cell surface (passive) adsorption and is called “biosorption”. The non-viable microbial biomass frequently exhibits a higher affinity for metal ions compared with viable biomass, probably due to the absence of competing protons produced during metabolism (Sag and Kutsal, 2000). This mechanism was suggested by Strandberg *et al.* (1981).

From this experiment, the immobilization of yeast should be more advantageous than a non immobilization method. As reported by de Rome and Gadd (1991), it was observed that little biosorption of uranium occurred in the alginate beads and when immobilized yeast beads containing a high proportion of yeast were used, the value of uranium uptake increased. Kuhn and Pfister (1989) also suggested that the immobilization of *Zoogloea ramigera* in Ca-alginate could increase adsorption of a variety of metals (Cd, Zn, Mn, Cu, Sr, and Pb) from diluted

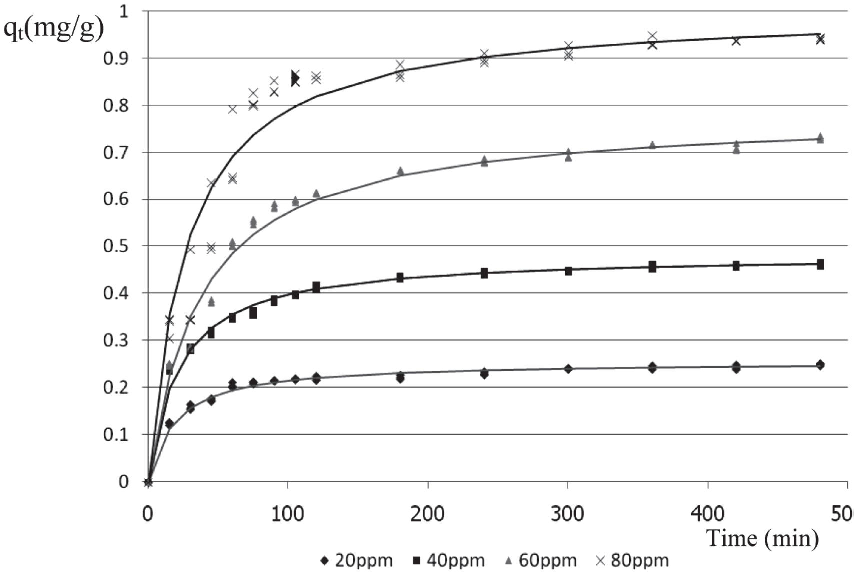

Figure 1 Plot of sorbtion capacity versus time for different initial concentrations of Cu(II) onto immobilized spent yeast in sodium alginate beads.

and concentrated solutions to an amount higher than when Ca-alginate beads alone were used as sorbent.

Sorption kinetics

To investigate the sorption mechanism, the sorption constants were determined using the pseudo-first and the pseudo-second order equations. For evaluation of Cu(II) biosorption, plots of $ln(q_e\text{-}q_t)$ and $t/\ q_t$ against time were used as shown in Figures 2 and 3, respectively. All data were tested against both models.

Table 1 shows a comparison of the applicability of the pseudo-first and the pseudo-second order kinetic models. The results showed that the correlation coefficients obtained from the pseudo-first order equation were significantly lower than the equivalent pseudo-second order correlation coefficients. Moreover, the pseudo-first order equation was only applicable for the first 2 h of biosorption. This strongly suggested that the sorption of divalent metal ions onto immobilized spent yeast in sodium alginate beads was most appropriately represented by a pseudo-second order rate process. Quek *et al.* (1998) and Ho and McKay (1999b) suggested that the pseudo-second order model be used in adsorption.

Table 2 shows the calculated results from the pseudo-first and the pseudo-second order adsorptions. The linear plots are shown in Figure 2 as $ln(q_e–q_t)$ versus time t for the sorption of Cu(II) ions. The gradients, k, were determined from Figure 2 and are listed in Table 2. The pseudo-first order equation showed that the rate constant

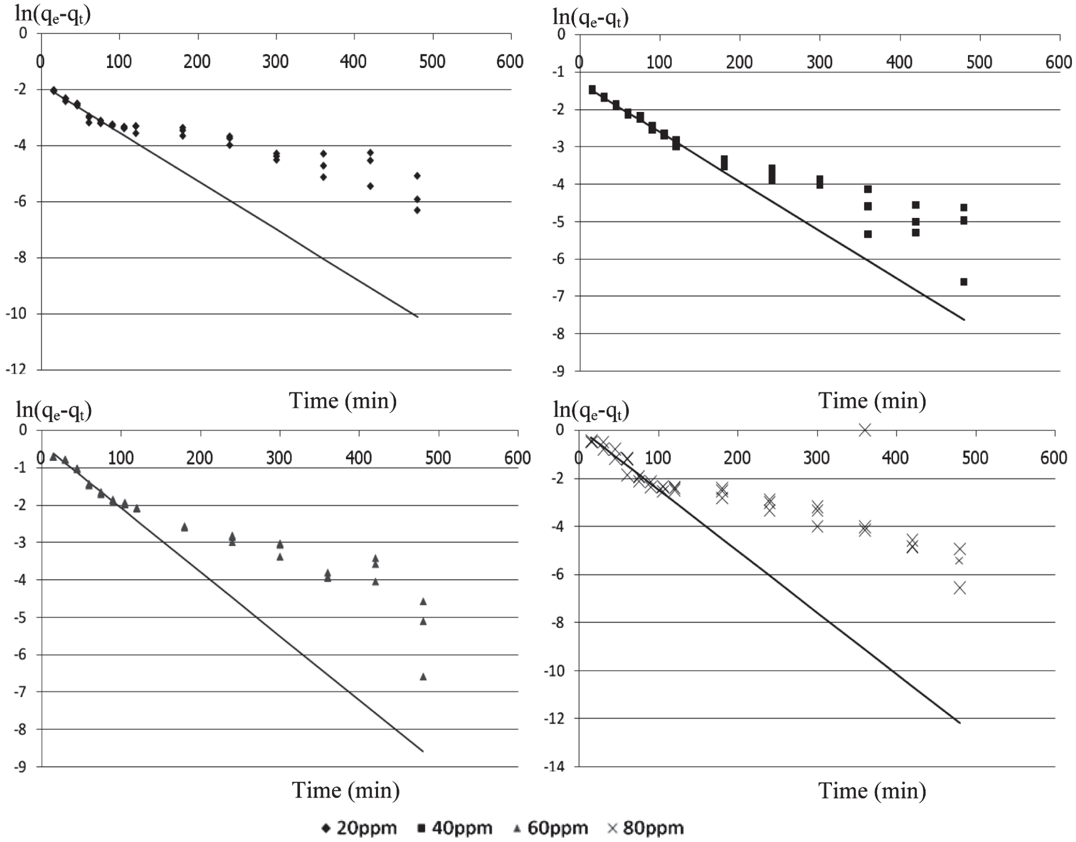

Figure 2 Pseudo-first order sorption kinetics of Cu(II) onto immobilized spent yeast in sodium alginate beads at various initial concentrations.

(k_1) tended to be constant with little fluctuation from 0.017 to 0.025 min^{-1} with an increase in the initial concentration of Cu(II) from 20 to 80 ppm.

The initial rates of adsorption (h, mg/g.min) were calculated from the intercept and the slope of the straight line of the pseudo-second order equation (Figure 3) and are listed in Table 2. The initial sorption rate increased with an increase in the initial concentration of Cu(II). The initial sorption rate varied from 0.014 to 0.037

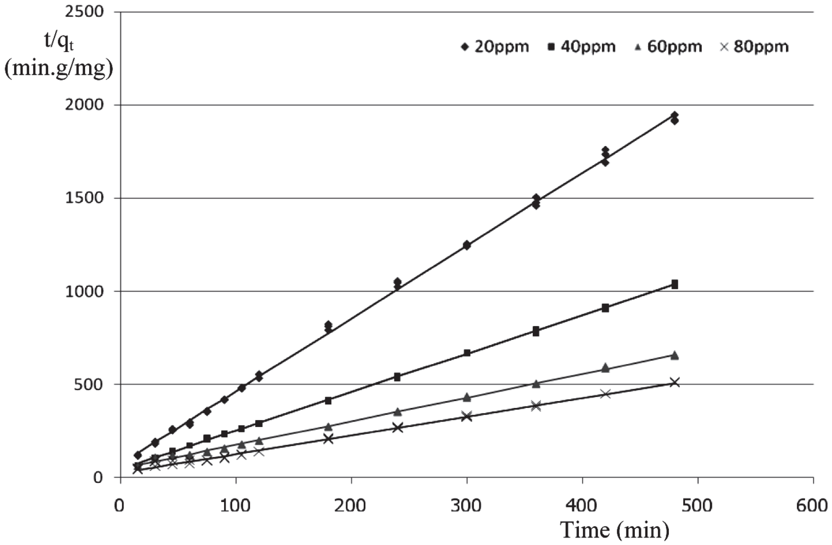

Figure 3 Pseudo-second order sorption kinetics of Cu(II) onto immobilized spent yeast in sodium alginate beads at various initial concentrations.

Table 1 A comparison of the applicability of the pseudo-first and -second order kinetic models.

Initial concentration	Coefficient of determination*, R^2	
	First order	Second order
20 ppm	0.946 ± 0.034	0.999 ± 0.000
40 ppm	0.987 ± 0.003	0.999 ± 0.000
60 ppm	0.971 ± 0.003	0.998 ± 0.000
80 ppm	0.948 ± 0.248	0.996 ± 0.002

* Values are mean ± standard deviation (SD).

Table 2 Kinetic parameters for sorption of Cu(II) by immobilized spent yeast in sodium alginate beads at various initial concentrations.

Initial concentration	First-order*		Second-order*		
	q_e (mg/g)	k_1 (min^{-1})	q_e (mg/g)	k_2 (g/mg.min)	h (mg/g.min)
20 ppm	0.253±0.002	0.017±0.001	0.256±0.003	0.208±0.012	0.014±0.001
40 ppm	0.468±0.004	0.013±0.001	0.483±0.004	0.096±0.006	0.023±0.001
60 ppm	0.737±0.004	0.017±0.001	0.785±0.006	0.035±0.001	0.021±0.001
80 ppm	0.945±0.003	0.025±0.001	1.004±0.014	0.037±0.011	0.037±0.010

* Values are mean ± SD.

mg/g min as the initial concentration of Cu(II) varied from 20 to 80 ppm. The values of the rate constants were found to decrease from 0.208 to 0.037 g/mg min with an increase in the initial concentration of Cu(II) from 20 to 80 ppm. The observed dependence of the rate on the initial concentration of Cu(II) indicated that removal of Cu(II) was more rapid from solutions with higher initial metal concentration.

Figure 3 shows the strongly linear variation of t/q_t with time t, for a large initial fraction of the sorption period. The figure shows a good linearization of the experimental data, thereby supporting the hypothesis that chemical sorption is the rate-limiting step and that the mechanism follows a pseudo-second order reaction. This suggested that the sorption system is not a first order reaction and that the pseudo-second order model provides the best correlation with the data (Ho and McKay, 1999b), (based on the assumption that the rate-limiting step is the chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate),. The pseudo-second order kinetic expression has been applied to the sorption of lead ions onto peat (Ho and McKay, 1998) and the sorption of lead, copper and nickel ions onto sphagnum moss peat (Ho *et al.,* 2000). The current study has demonstrated the successful application of a pseudo-second order rate expression to Cu(II) sorption systems.

CONCLUSIONS

A kinetic model was developed and fitted for the sorption of Cu(II) onto immobilized spent yeast in sodium alginate beads. The results showed that the sorption of Cu(II) under the experimental conditions of the study could be described by a pseudo-second order model, based on the assumption that the rate-limiting step was chemical sorption involving valency forces through sharing or exchange of electrons between the sorbent and sorbate. The equilibrium sorption capacity, q_e, which is a function of the initial Cu(II) concentration, had a major influence on the kinetics of the sorption reaction.

ACKNOWLEDGEMENTS

The authors are grateful to Ms Monrudee Kitpaiboonwattana for providing original experimental data for the adsorption of Cu(II) on immobilized spent yeast in sodium alginate beads.

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