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Kinetic Modeling of Biosorption of Heavy Metals by Loofa-sponge Immobilized Phanerochaete chrysosporium From Aqueous Solution

M. Nikazar, P. Namiranian, F. Vahabzadeh
Chemical Engineering Faculty of Amirkabir University of Tehran, Iran
Center of Excellency for Petrochemical Engineering
E-mail address : nikazar@ aut.ac.ir

Mat of mycelia of Phanerochaete chrysosporium were immobilized on loofa-sponge discs, as an inert support, to obtain a suitable biosorbent .Mean amount of immobilized P.chrysosporium on loofa-sponge was 376 mgg^{-1} of dry loofa-sponge. In this study immobilized P.chrysosporium and naked loofa-sponge discs were used as biosorbent to remove Pb (II) and Cd (II) from aqueous solution .At kinetic study residual concentration of metal ions was determined after contacting for up to 120 min. Equilibrium was established in about 60 min for both metals. The maximum uptake of Pb and Cd was 88.9 mgg^{-1} and 63.1mgg^{-1} for immobilized P.chrysosporium and 21.6mgg^{-1} and 16.5 $mgg^{-1}$for naked loofa-sponge, respectively. In order to examine the controlling mechanism of biosorption process, kinetic models were used to test the experimental data and kinetics was found to be best-fit pseudo-second-order equation.

Key words: Cadmium; Lead; Phanerochaete chrysosporium; Wastewater; Biosorption;

1. Introduction

The increase in usage of heavy metals in industrial activities has caused the existence of them in waste water. For example lead and cadmium which the wastewater of industries such as electroplating , plastic and paint manufacturing , mining , metallurgical process , petrochemical process , batteries , paper and pulp contains them (Iqbal and Edvean,2004, Iqbal and Edvean,2005).

According to the toxicity of these metals and their dangerous effects on the environment and human health, many attemptions have been done to remove them from waste water and environment.

Conventional chemical and physical methods such as chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, reverse osmosis, membrane technology and evaporation, exit to remove heavy metals from wastewater (Iqbal and Edvean,2004, Ahluwalia and Goyal,2007).
But, these technologies are often expensive, generating toxic and non eco-friendly sludge or are ineffective when the metals concentration are low (range 1-100ppm)

(Iqbal and Edvean,2004, Ahluwalia and Goyal,2007). So that, considerable attention has been given to biological technologies, such as biosorption, which is the ability of microorganisms such as algae, fungi, bacteria and yeasts to bind heavy metals non-metabolically (Iqbal and Edvean,2004, Iqbal and Edvean,2005, Ahluwalia and Goyal,2007).But commercial application of biomass is reduced by problems associated with their physical characteristics such as low rigidity, low density, low mechanical strength, small particle size and difficulty in separation of biomass from liquid-phase. Due to these problems considerable attention has been given to immobilization of biomass (Iqbal and Edvean, 2004, Iqbal and Edvean, 2005).

Several immobilization media have been used. According to above problems a suitable matrix for immobilization which has low cost, high porosity and easy usage seems necessary.

In this study mat of mycelium of a known basidiomycete fungus, Phanerochaete chrysosporium was used to immobilized on loofa-sponge due to its low cost, physical strength, rigidity and high porosity .(Iqbal and Edvean,2004, Iqbal and Edvean,2005,Ahmadi et al, 2006)
This study looks at single removal of lead and cadmium from aqueous solution in batch system. Biosorption efficiency of immobilized fungi compared with naked loofa sponge is reported for removal of Pb (II) and Cd (II) in single biosorption.

2. Materials and Methods

2.1. Microorganism and culture medium

The white-rot fungus, P.chrysosporium (ATCC 24725) was maintained by sub culturing on 1/5% YMG agar slants (yeast extract 4 gr, malt extract 10 gr, and D-glucose 6 gr per liter of distilled water). The growth medium consisted of (gr per liter of distilled water); D-glucose, 10.0; KH2PO4, 2.0; MgSO4.7H2O, 0.5; NH4Cl, 0.1; CaCl2 .H2O, 0.1; thiamine, 0.001; yeast extract, 0.1gr;

2.2. Immobilization

The loofa sponge was obtained on removing hard pericarp tissue of the ripened dried fruit of Luffa cylindrica. The fibrous sponge was cut into discs of approximately 2.5 cm diameter, 2-4 mm thick, soaked in boiling water for 30 min, washed under tap water, and left for 24 hr in distilled water, changed 3 - 4 times. The sponge discs were oven dried at 70 ^{0}c.

Preparation of the inoculum was as follows: The fungus was grown on YMG agar for 5 days at 27^{0}c and for preparation of an aqueous fungal suspension the spores were transferred to 150 ml of YMG broth in a 500 ml Erlenmeyer flask (Yeong et al,1998) and incubated at 27^{0}c on a shaker incubator at 150 rpm for 5 days. Then the YMG medium was drained and the mycelium was blended for 15s at low level with blender. This blended culture was used as inoculum. For immobilization of P.chrysosporium with in loofa discs, mat of mycelia with inoculum size of 7 %(v/v) were added to four

pre-weighted loofa-sponge discs, as an immobilized matrix, in 250 Erlenmeyer flasks. After 2 days of incubating at 35^0c and 100 rpm, the growth media was drained and loofa sponge- immobilized biomass of P.chrysosporium (LIBPC) was washed with distilled water.

Dry weight of biomass was determined by weighting dried (70^0c, 24 hr) discs before and after fungal growth.

2.3. Metal solutions

Standard stock solutions of Pb (II) and Cd (II) (1000 ±2 mg l^{-1} Pb $(NO_3)_2$ and Cd $(Cl)_2$ salts from Merck Ltd.,) were used to prepare the appropriate required concentrations of each metal for biosorption studies.

2.4. Biosorption studies

Biosorption of Cd (II) and Pb (II) was carried out in batch experiments. The biosorption capacity of biosorbent was determined by shaking 100 ml solution of known concentration (100mgrl^{-1}) with 105 mgr of immobilized P.chrysosporium (LIBPC) and 286 mgr naked loofa-sponge as control in 250 ml flasks on a shaker incubator at 35^0c, 100 rpm. For determination the rate of biosorption and the biosorption equilibrium time the residual metal ions concentration in the solution was determined by allowing biosorbent - metal contact for different periods between 5 and 120 min and pH was adjusted to 6, using NaOH 0.1 N, HCl 0.1 N. Residual concentration of metal ions in single solution was determined using an atomic absorption spectrophotometer (AA-670/G V-7) .

2.4. Data analysis

The concentration of metal ions adsorbed per unit immobilized fungal biomass (mg metal g^{-1} dry biosorbent) was determined using the following expression:

$$q = V(C_i - C_{eq})/M \qquad (1)$$

Where q is the metal uptake (mg metal ions g^{-1} dry weight of fungal biomass entrapped within sponge discs), V is the volume of metal solution (ml), C_i is the initial concentration of metal ions in the solution (mg l^{-1}), C_{eq} is the final concentration of metal ions in the solution, and M is the dry weight of fungal biomass.

3. Results

3.1. Growth of Phanerochaete chrysosporium on loofa-sponge

Growth and immobilization was rapid in the first day and complete coverage of discs occurred at the end of the first day. The biomass of P.chrysosporium immobilized on loofa-sponge reached at stationary phase at day 2.

The mean amount of immobilized fungal biomass was 376 mgg^{-1} of dry loofa-sponge (Fig.1). This is about threefold higher than for the same fungi immobilized within

Ca-alginate beads (Kacar et al, 2002) and indicates the superiority of the open structured loofa sponge over the polymeric matrices previously used for immobilization.

Fig. 1: loofa sponge- immobilized biomass of P.chrysosporium (LIBPC)

The results show that LIBPC can simply be made by inoculating sponge discs with mat of mycelia in a suitable growth medium. In contrast, production of polymeric bead immobilized fungi is expensive, laborious and requires sophisticated equipment.

3.2. Effect of contact time on biosorption of Cd (II) and Pb (II) by loofa-sponge and immobilized P.chrysosporium

Immobilized P.chrysosporium has been successfully used as biosorbing agent for removal of Cd (II) and Pb (II). The kinetic profile of Pb (II) and Cd (II) biosorption by LIBPC and loofa sponge are shown in Fig.2. Metals' accumulation is rapid for LIBPC, reaching about 82% and 75% of sorption for Pb (II) and Cd (II) in the first 25 min. It is also relevant to point out that since active sorption sites in a system is a fixed number and each active site can adsorbed only one ion in a monolayer, the metal uptake by the sorbent surface will be rapid initially, slowing down as the competition for decreasing availability of active sites intensifies by the metal ions remaining in solution. (Saeed et al, 2005) Equilibrium was reached at 60 min for both metal ions. The maximum uptake obtained by naked loofa was 21.6mgg^{-1} for Pb (II) and 16.5mgg^{-1} for Cd (II). The maximum uptake of 88.9mgg^{-1} for Pb (II) and 63.1mgg^{-1} for Cd (II) by LIBPC was obtained .

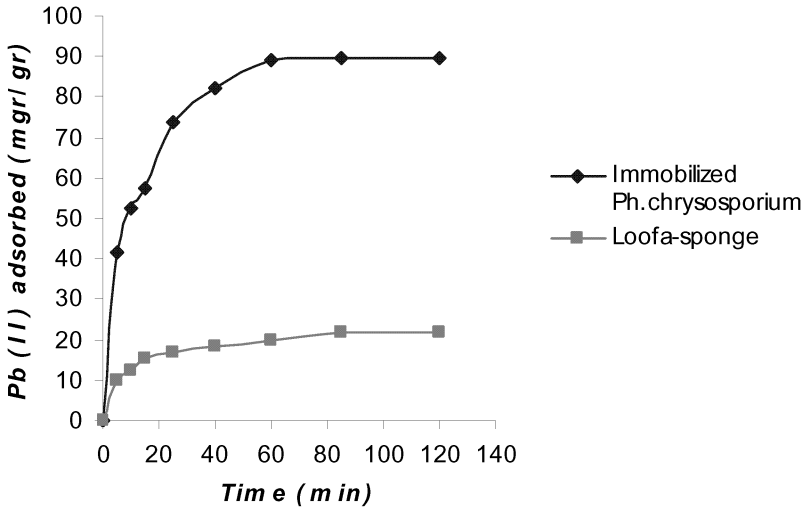

Fig. 2 (a): kinetic profile for Pb (II) biosorption

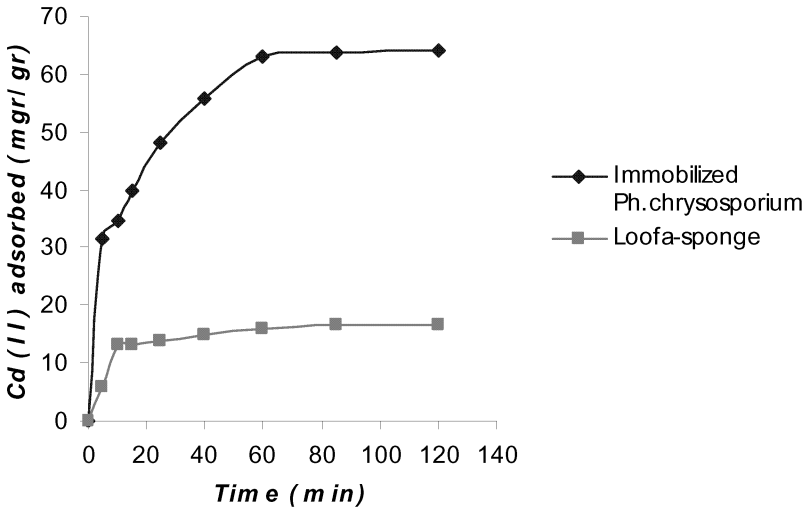

Fig. 2 (b): kinetic profile for Cd (II) biosorption

Loofa sponge discs with out fungal biomass adsorbed metals fourfold less than LIBPC, indicating little effect of the immobilized matrix on metals uptake.

This difference in the maximum level of uptake of these two metal ions has been explained in terms of difference in the ionic size of metals, the nature and distribution of active groups on the biosorbent, and the mode of interaction between the metal ions and the biosorbent .(Iqbal and Edvean,2004)

The biosorption kinetics were analyzed by applying the pseudo-first order (Lagergren equation) and pseudo-second order (Ho equation). Because LIBPC is our favorite biosorbent all the modelings are done for its data.

3.2.1. Pseudo-first order Lagergren model

The pseudo-first order model is generally express as follows:

$$\frac{dq_t}{dt} = K_l\left(q_e - q_t\right) \quad (1)$$

Where q_e and q_t have their usual meanings, and k_1 is the rate constant of first-order biosorption (min^{-1}). The integrated form of Eq. (1) is: (Wu and Yu, 2007)

$$Ln(q_e - q_t) = Ln\ q_e - t(K_l) \quad (2)$$

The first order rate constant k_1 and q_e values were determined from the slope and intercepts of the plot, presented in table 1.

Table 1. First order constants

Metal ion	First order model		
	r^2	$K_l(min^{-1})$	$q_e(mg/g)$
Pb (II)	0.9863	0.0574	67.08
Cd (II)	0.978	0.0414	39.4

3.2.2. Pseudo-second order Ho model

The pseudo-second order model is generally express as follows:

$$\frac{dq_t}{dt} = K_2\left(q_e - q_t\right)^2 \quad (3)$$

Where k_2 is the rate constant of second-order biosorption [g/(mg min)]. After integrating, the following equation is obtained: (Wu and Yu, 2007)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad (4)$$

The second order rate constant k_2 and q_e values were determined from the slope and intercepts of the plot, presented in table 2.

Table 2. Second order constants

Metal ion	Second order model		
	r^2	$K_2(mg/g\ min)*10^3$	$q_e(mg/g)$
Pb (II)	0.9987	1.352	96.15
Cd (II)	0.9967	1.48	69.9

The correlation regression coefficients indicate that the biosorption kinetic fits second order model better than lagergren model. Theoretical q_e values obtained from second order model were closer to the experimental q_e values than q_e values obtained from first order equation for both metal ions.

4. Conclusions

Loofa sponge is a suitable natural matrix for immobilization of P.chrysosporium. Immobilized P.chrysosporium has been successfully used as biosorbing agent for removal of Cd (II) and Pb (II). Biosorption was rapid and the equilibrium was obtained at 60 min for both metal ions and kinetics fitted second order model well.

5. Acknowledgement

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