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BIOSORPTION OF Cd^{2+} IONS BY IMMOBILIZED CELLS OF *SACCHAROMYCES CEREVISIAE*. ADSORPTION EQUILIBRIUM AND KINETIC STUDIES

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ABSTRACT. Biosorption of cadmium (II) ions from aqueous solution onto immobilized cells of *Saccharomyces cerevisiae* was investigated. Equilibrium and kinetic studies were conducted taking into consideration the effect of initial cadmium (II) concentration. The obtained results showed that the uptake of heavy metal increases with an increase of initial cadmium (II) concentration. Langmuir and Freundlich isotherm models were used to analyze the equilibrium data. Based on correlation coefficients, it has been concluded that the Langmuir isotherm is more suitable to describe the cadmium biosorption equilibrium data. First and pseudo-second order kinetic models were applied to describe the biosorption process. It was found that the kinetics data fitted well the pseudo second order model.

Keywords: *biosorption, cadmium, Saccharomyces cerevisiae cells, adsorption isotherm, kinetics*

INTRODUCTION

The presence of industrial effluent containing heavy metals into freshwater poses serious problems to the ecological system including humans as they are toxic even at low concentrations [1,2]. One of the most common toxic metals found in industrial effluents is cadmium. It may come from various industrial sources such as electroplating, fertilizers, mineral processing and battery manufacturing [3,4].

The removal of this metal from waters and industrial wastewaters has become a challenge for researchers. Manny studies confirm that various biological materials including fungi, algae, bacteria and yeast could be used in

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biosorption process to remove metal ions in wastewater [5,6.] The biosorption process is a passive uptake that utilizes cell wall of biomass to sequester the metal ions from aqueous solutions [7,8]. The presence of functional groups on biomass cell wall such as carboxyl, hydroxyl, ketones and amino groups will involve a physical-chemical interaction between the metal ions during the biosorption processes [9]. Metal uptake is dependent not only on the type of species of microorganism, but also on growth conditions. Growth conditions considerably influence the composition of all yeast and thereby the binding abilities of cells for metal ions also. Since cell wall structure and the metabolic state of the cell depend on substrate composition, the growth in different media should influence the capacity and selectivity of metal uptake by creating other binding sites or diverse enzymatic system within the cell [10,11].

Cell immobilization is one of the methods used to overcome the incorporating free suspended cell in industrial operations. It offers several advantages including minimal clogging in continuous systems, is easy to separate from the reaction system and can be regenerated and reused the immobilized cells for a few cycles [3]. Natural polymers mostly used, as the matrix for the immobilization of cells is the alginate.

This study was carried out in order to determine the potential of immobilized living cells of *Saccharomyces cerevisiae* (DSM 1333) to adsorb cadmium (II) ions. Langmuir and Freudlich adsorption isotherms were used to correlate the equilibrium adsorption data, while first and pseudo-second order kinetic models were applied to describe the biosorption process.

RESULTS AND DISCUSSION

Cadmium biosorption

The biosorption of cadmium ions on the pure *Saccharomyces cerevisiae* strain (DSM 1333) in immobilized form was investigated in biosorption equilibrium experiments. The effect of initial cadmium ions concentration on the biosorption capacity of Cd^{2+} onto immobilized cells was studied.

Initial cadmium concentration influence over the equilibrium adsorption capacities (maximum adsorption capacity for specific working conditions) obtained during Cd^{2+} adsorption experiments is presented in Figure 1. Equilibrium adsorption capacities increase from 0.2197 mg Cd^{2+}/g for the initial 4.82 mg Cd^{2+}/L to 3.7825 mg Cd^{2+}/g for the initial 99.75 mg Cd^{2+}/L. These results suggest that the *Saccharomyces cerevisiae* cells we used as biosorbent have high capacity for heavy metal biosorption.

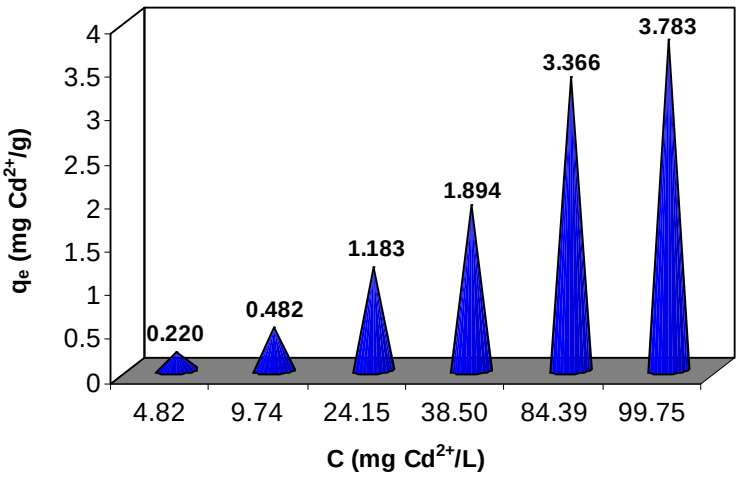

Figure 1. Initial cadmium concentration influence over the equilibrium adsorption capacities obtained during Cd^{2+} adsorption experiments.

Equilibrium isotherm models

Langmuir and Freundlich models were used to determine the sorption equilibrium between the biosorbent and metal ions.

The Langmuir model assumes that a monomolecular layer is formed when biosorption takes place without any interaction between the adsorbed molecules [12]. Freundlich isotherm is an empirical equation based on a heterogeneous adsorption due to the diversity of adsorption sites or diverse nature of the adsorbed metal ions, free or hydrolyzed species [13].

The Langmuir isotherm equation has a hyperbolic form:

$$q_e = \frac{q_{max} \cdot b \cdot C_e}{1 + b \cdot C_e} \qquad (2)$$

where, q_e is the solid-phase adsorbate concentration at equilibrium (mg/g),
q_{max} is the maximum adsorption capacity corresponding to the monolayer adsorption capacity (mg/g),
C_e is the concentration of Cd^{2+} solution at equilibrium (mg/L), and
b is related to the strenght of adsorbent-adsorbate affinity.

The linear form of the Langmuir isotherm, eq. (3), is expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{max} \cdot b} \cdot \frac{1}{C_e} + \frac{1}{q_{max}} \qquad (3)$$

From the $1/q_e$ vs. $1/C_e$ plot, Figure 2, q_{max} = 2.713 mg Cd^{2+}/g and b = 1.936 L/mg were calculated. Langmuir isotherm model describes well the experimental values (q_e and C_e), Figure 3.

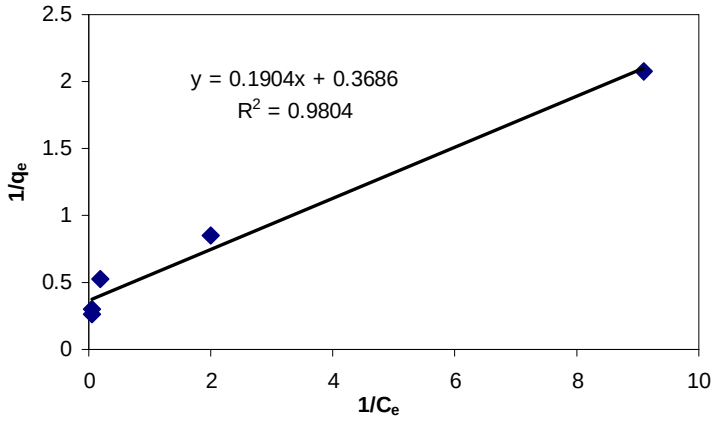

Figure 2. Langmuir adsorption model for cadmium biosorption on immobilized biomass.

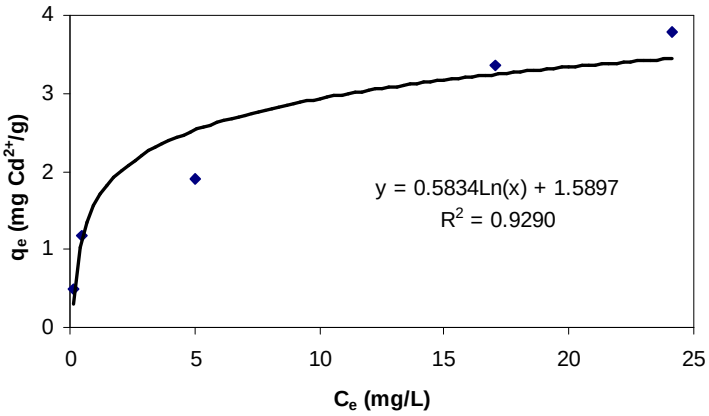

Figure 3. Langmuir adsorption isotherm for cadmium biosorption on immobilized biomass.

The empirical Freundlich isotherm equation given by eq. (4), while its logarithmic form (linear) is given by eq. (5):

$$q_e = k \cdot C_e^{(1/n)} \tag{4}$$

$$\log q_e = \log k + \frac{1}{n} \cdot \log C_e \tag{5}$$

where, k is related to adsorption capacity, and

n is related to intensity of adsorption.

From the $\log q_e$ vs. $\log C_e$ linear plot, (figure not shown), we determined a correlation coefficient of 0.9600, which is smaller then that obtained for the Langmuir model, 0.9804. Therefore we concluded that cadmium biosorption on immobilized biomass is better described by the Langmuir isotherm.

Kinetic models

The kinetic of heavy metal ions biosorption is usually described by two different kinetic models, i.e. the first- and second order [14,15].

The first-order rate equation may be represented as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

Integrating eq. (6) from the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

where q_e and q_t are the amounts of cadmium adsorbed (mg/g) at equilibrium and time t, respectively, and

k_1 is the rate constant of first order adsorption (1/min).

In order to determine the rate constant and equilibrium cadmium uptake, the straight line plots of $\ln(q_e-q_t)$ against t, eq. (7), were made at five different initial cadmium concentrations. Correlation coefficients obtained in this case were under 0.9 (figure not shown).

The pseudo second order kinetic model may be expresses as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

Integrating eq. (8) from the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{9}$$

where, q_e and q_t as above, and

k_2 is the rate constant of pseudo second order adsorption (g/mg·min).

Equation (9) can be rearranged in a linear form, as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

In order to determine the rate constant and equilibrium cadmium uptake, the straight line plots of t/q_t against t, eq. (10), were made at five different initial cadmium concentrations. Correlation coefficients between 0.9941 and 0.9998 were obtained (Figure 5 and Table 1).

If we compare correlation coefficient for the first and pseudo second order models, we can conclude that cadmium biosorption on immobilized biomass can be classified as pseudo second order, fact confirmed by the literature data [16].

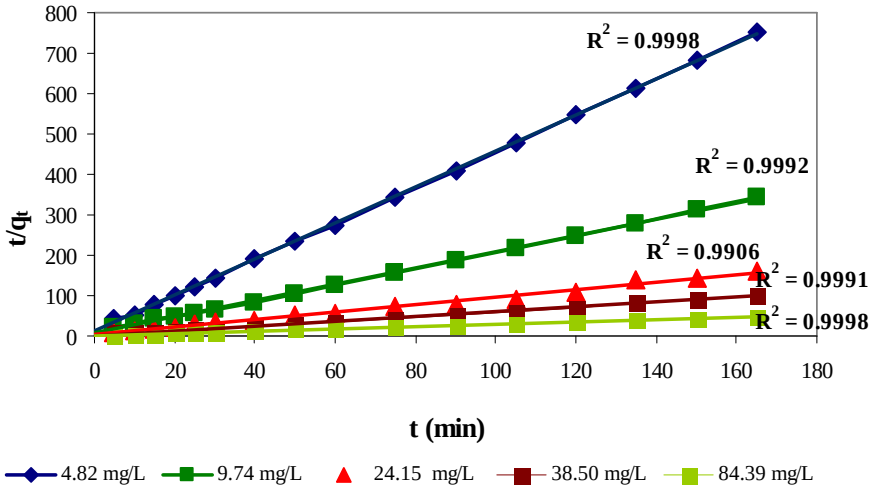

Figure 4. Correlation of the experimental data using the pseudo second order model for cadmium biosorption on immobilized biomass.

Table 1. Second order adsorption kinetic parameters.

C, (mg Cd^{2+}/L)	q_e (exp), (mg Cd^{2+}/g)	q_e (calc), (mg Cd^{2+}/g)	k_2, (g/mg·min)	R^2
4.82	0.220	0.224	1.80	0.9998
9.74	0.482	0.496	0.59	0.9992
24.15	1.183	1.084	0.23	0.9906
38.50	1.894	1.720	0.17	0.9991
84.39	3.366	3.433	0.11	0.9998

CONCLUSIONS

The ability of immobilized cells (DSM 1333) to adsorb cadmium (II) ions from aqueous solution was investigated. The obtained results showed that the uptake of heavy metal increases with an increase of initial cadmium (II) concentration. Cadmium adsorption capacity increases with an increase of the initial cadmium (II) concentration suggesting that the *Saccharomyces cerevisiae* cells we used have high capacity for heavy metal biosorption. The biosorption of metal ions studied is a rapid process and often reaches equilibrium within three hours; the maximum biosorption capacity was calculated to be 3.7825 mg Cd^{2+}/g yeast.

Langmuir and Freudlich adsorption isotherms were used to correlate the equilibrium adsorption data. The cadmium ions biosorption by immobilized *Saccharomyces cerevisiae* cells is well described by the Langmuir isotherm model.

Also, first and pseudo-second order kinetic models were applied to describe the biosorption process. Based on mathematical calculations carried out, it was found that the kinetics data fitted well the pseudo-second order model and the parameters for this kinetic were determined.

EXPERIMENTAL SECTION

Microorganism, media and culture conditions

Saccharomyces cerevisiae (DSM 1333) yeast was used in this study. The yeast was provided by University of Pécs Medical School, Department of Medical Microbiology and Immunology (Hungary), in the lyophilized form. The composition of growth medium was Müller-Hinton substrate (3% glucose, pepton, yeast-extra, NaCl, pH=7). The medium was sterilized by autoclaving at a pressure of 1.5 atm and temperture of 121°C for 20 minutes. The pure yeast culture grown in an incubator at 30°C, 200 rpm for 48 hours (New Brunswick Scientific). During the process the growth of yeast was controlled by measuring the absorbance of the culture. After completion of the yeast production the suspension was centrifuged 4500 rpm for 30 minutes, and two times washed with steril PBS (phosphate-buffer solution). Cells were then lyophilized and used in this form for all trials [17,18].

Biosorbent immobilization

The cross-linking procedure with calcium alginate that we used, is the current method for immobilization of biomass [19].

The immobilization of yeast was carried out as follows: 2 g of lyophilized biosorbent was suspended in 50 ml distilled water. This suspension was next blended with a mixture formed from 1g sodium-alginate and 2 ml ethanol. The mixture was then dropped with a peristaltic pump into a solution containing 0.2 M $CaCl_2$. During this process, the drops of alginate-biomass mixture were gelled into beads with a diameter of 4.0±0.2 mm. The Ca-alginate immobilized yeast beads were stored in 0.2 M $CaCl_2$ solution at 4°C for 1 hour to cure and to form the cross-linking bonds. The beads were rinsed with distilled water to remove the excess of calcium ions and stored at 4°C prior to use.

Cadmium solution preparation

The stock cadmium solution was prepared by dissolving $Cd(NO_3)_2 \times 4H_2O$ of analytical grade reagent in an appropriate amount of distilled water. Cadmium solutions of different concentration (4.82, 9.74, 24.15, 38.5, 84.39 and 99.75 mg/L) were obtained by diluting the stock solution. The concentration of Cd^{2+} ions from different samples was determined using a flame atomic absorption spectrophotometer (SensAA Dual GBS Scientific Equipment, Australia).

Biosorption studies

The immobilized pure yeast biomass was contacted with 100 ml of initial cadmium solution. The reaction mixture was agitated at 875 rpm on a magnetic stirrer at room temperature (20°C) in isothermal conditions, pH 6.8-7.2, for 3 hours.

Kinetics studies were performed using different concentrations of cadmium solutions (4.82, 9.74, 24.15, 38.50, 84.39, 99.75 mg/L).

In order to determine the exact concentration of cadmium ions and establish the evolution of the removal process, samples of 100 μL from the supernatant were collected at different time intervals.

The amount of cadmium (II) ions bound by biosorbent was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)}{w} \cdot \frac{V}{1000} \quad (1)$$

where, q_t is time t adsorption capacity (mg/g),

C_0 is the initial cadmium concentration (mg/L),

C_t is time t cadmium concentration (mg/L),

V = 100 ml, and

w is the quantity of the adsorbent (g).

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