Cadmium biosorption by baker's yeast in aqueous suspensions

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Abstract: The biosorption of cadmium from artificial aqueous solutions using native baker's yeast was investigated. The highest metal uptake value was 110 mg g^{-1} yeast in a suspension of 0.30 g L^{-1}. The effect of pH, initial cadmium concentration, adsorption time and biosorbent dosage on biosorption by baker's yeast was studied. The maximum biosorption capacity of yeast for cadmium was observed at pH 6.0. The adsorption equilibrium was reached within sixty minutes and the sorption process followed pseudo second-order kinetics. Cadmium biosorption isotherms were determined in the cadmium concentration range of 10–500 mg L^{-1} at pH 6 in a suspension of 0.30 g L^{-1}. For evaluation of biosorption equilibrium, Langmuir and Freundlich equations were applied to the experimental data.

Keywords: cadmium; baker's yeast; biosorption; pH; kinetics; isotherm; biosorbent dosage.

INTRODUCTION

Heavy metal pollution has become one of the most serious environmental problems today. Cadmium is a heavy metal that poses serious health hazards through entry into the food chain by anthropogenic pathways. In the last decade, biosorption using microbial biomasses as sorbent materials has emerged as a cost-effective removal technique for the treatment of high volume and low concentration complex wastewaters containing heavy metal(s) at concentrations in the order of 1 to 100 mg L^{-1} metal, compared to other processes such as chemical precipitation, evaporation, ion exchange and membrane separation. The conventional methods have disadvantages, including incomplete metal removal,

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requirements for expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal.[1–3] The utilization of microorganisms (bacteria, fungi, yeast and algae) as biosorbents (biosorption) offers a potential alternative for heavy metal detoxification and the recovery and reuse of toxic/precious metals.[4]

In the concept of biosorption, several physical or chemical processes may be involved, such as physical and/or chemical adsorption, ion exchange, coordination, chelation and microprecipitation. Biomass cell walls, consisting mainly of polysaccharides, proteins and lipids, offer many functional groups, such as carboxylate, hydroxyl, sulfate, phosphate and amino groups, which can bind metal ions.[2,5]

Some potential biomaterials with high metal-binding capacity have been identified in part. Algae, bacteria, fungi, yeast and waste microbial biomass from the fermentation and food industry are amongst them. For economic reasons, researchers have paid much attention to various by-products from the fermentation industry. The application of these waste microbes as biosorbents for the biosorption of heavy metals and radionuclides is to kill two birds with one stone because it uses waste to dispose of waste. The enterprises can sell their waste biomass and earn money, simultaneously, they can save the cost associated with disposing of the waste biomass they produced.[2,5–9] A biomass used as a biosorbent must be selective and inexpensive.[6,9] Among the promising biosorbents for heavy metal removal, *Saccharomyces cerevisiae* is still under consideration as a biomaterial due to its unique nature in spite of its mediocre capacity for metal uptake compared with other fungi. Yeast fungi are widely used for food and beverage production, are easily cultivated using cheap media, are also, as waste of the fermentation industry, a by-product produced in large quantities, and are easily manipulated at the molecular level.[2,6–8] Yeasts have been studied in various forms, for example living cell/dead cell, intact cell/deactivated cell, immobilized cell/free cell, raw material/pretreated cell by physicochemical process, wild type/mutant cells, flocculent/non-flocculent cells, engineered/ non-engineered cells, lab culture/waste industrial cell, and cells from different industries.[2,6–11]

However, little information exists on the use of commercial native baker's yeast as a biosorbent for metal removal. Yeast biosorption depends on several parameters, such as pH, the ratio of the initial metal ion and initial biomass concentrations, culture conditions, the presence of various ligands and competitive metal ions in solution, and on temperature to a limited extent.[2,9,12–15]

The objectives of this study were:
– to test the recycling of native commercial baker's yeast biomass as a sorbent material for the immobilization of cadmium in polluted water,

– to evaluate using batch technique the influences of different experimental parameters, such as pH, sorption time, cadmium concentration and biosorbent dosage, on biosorption,

– to model cadmium biosorption kinetics by yeast using a second-order kinetic equation and

– to determine adsorption isotherms using batch technique and analyze the adsorption equilibrium using the Freundlich and Langmuir isotherm equations.

EXPERIMENTAL

Fungal biomass

The biosorbent was fresh and compressed baker's yeast (commercial yeast, "Budafok" Yeast and Spirit Factory, Budapest, Hungary). The baker's yeast was used as the sorbent material in natural commercial form. Its water content was 70 %. The determination of the water content was performed according to the protocol of the yeast factory (data obtained from the factory).

Chemicals

Cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$) (purity > 99 %) was purchased from Fluka (Switzerland) and used without further purification. The stock solution was prepared by dissolving 1.3718 g $Cd(NO_3)_2 \cdot 4H_2O$ in 1.0 L of distilled water. The test solutions were prepared by diluting 500 mg L^{-1} of stock solution to the desired concentrations. The cadmium concentration of the prepared test solutions varied between 5–500 mg L^{-1} in the sorption experiments. The pH of the suspensions was adjusted to the required value with 0.10 M HCl or 0.10 M NaOH solutions (Merck, Germany).

Analyses of cadmium

The concentration of cadmium was determined by atomic absorption spectrophotometry (Perkin–Elmer 2380) at 228.8 nm. The calibration of cadmium was made with standard cadmium solution (Scharlau, Germany) in the concentration range of 0–2.5 mg L^{-1}.

Effect of pH on the biosorption

The effect of pH on cadmium adsorption by baker's yeast was investigated using a 0.3 g L^{-1} suspension of baker's yeast and an initial cadmium concentration of 50 mg L^{-1}. The initial pH of the yeast suspension was 5.6, which was adjusted to the desired value in the range 2–11.

Zeta potential measurements

The zeta potential of aqueous suspensions of baker's yeast was measured with Zetameter instrument (Malvern Zetasizer nano ZS, UK). The suspensions were made from baker's yeast and distilled water. The suspensions contained 0.3 g L^{-1} yeast. After pH adjustment, the suspensions were stirred on a magnetic stirrer for 30 minutes and then the zeta potential was measured.

Kinetics study of biosorption

In the kinetics study of cadmium biosorption by baker's yeast, the concentrations of the metal ions were 5, 10, 25 and 50 mg L^{-1} at a suspension concentration of 0.30 g L^{-1}. The experimental time was 180 min. During the first 30 min of agitation at 250 rpm, samples were taken every 5 min, in the following 30 min every 10 min and in the following 2 h every 15 min. The samples were centrifuged at 5500 rpm for 10 min and the supernatants diluted for analysis by atomic absorption spectrophotometry.

Determination of biosorption isotherms

Biosorption experiments were performed in the batch mode for the determination of the adsorption isotherms. The concentrations of baker's yeast in the suspensions were 0.3, 0.6, 1.5 and 3.0 g L^{-1}. The initial concentration of cadmium was varied between 10–500 mg L^{-1}. A defined mass of biosorbent and a defined volume of cadmium solution were placed in a test-tube. The tubes were agitated on a shaker at 150 rpm at a constant temperature (22.5±1 °C). Samples were taken after 24 h and then spin-dried at 5500 rpm for 10 min. The supernatants were used for analysis of the residual amount of cadmium. The adsorbed amount of cadmium at time t, q_t (mg g^{-1}), was obtained as follows:

$$q_t = \frac{(c_0 - c_t)V}{m} \tag{1}$$

where c_0 and c_t are the initial and at time t liquid phase cadmium concentrations (mg L^{-1}), V is the volume of the solution (L) and m is the mass of the dry biomass used (g).

Correspondingly, the adsorbed amount of cadmium at equilibrium, q_e (mg g^{-1}), is given by:

$$q_{eq} = \frac{(c_0 - c_{eq})V}{m} \tag{2}$$

where c_{eq} is the concentration of cadmium in the supernatant at equilibrium (mg L^{-1}).

RESULTS AND DISCUSSION

Effect of solution pH and zeta potential on the adsorption of cadmium

Previous studies on heavy metal biosorption showed that the pH value of the solution is an important factor in both the solution chemistry of the metal and the surface characteristics of the biosorbent.[2,5,9,13–18] The effect of the initial pH on cadmium biosorption by yeast biomass is presented in Fig. 1. The biomass concentration was 0.30 g L^{-1} and the initial metal concentration was 50.0 mg L^{-1}.
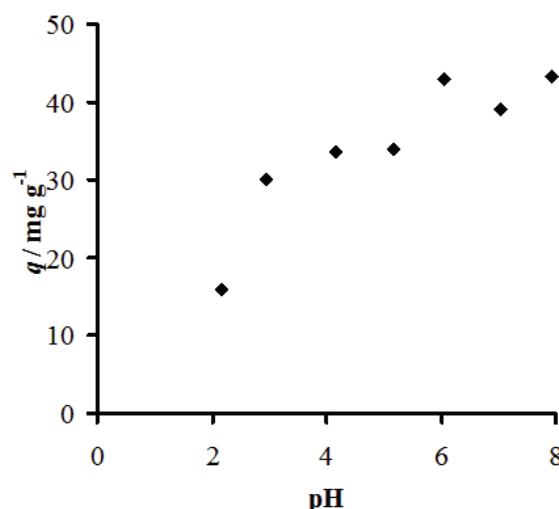

Fig. 1. The effect of pH on cadmium biosorption on baker's yeast. The biomass concentration was 0.30 g L^{-1} and the initial cadmium concentration was 50 mg L^{-1}.

The cadmium biosorption capacity of biosorbent increased with increasing pH from 2.0 to 6.0. The highest metal uptake value obtained for cadmium was 42.9 mg g^{-1}. At the pH values of greater than pH 8.0, the cadmium ions precipitated as Cd(OH)$_2$ due to the increasing concentration of OH$^-$ in the solution. For this reason, the experiments were not conducted at higher pH values. It is well known that at low pH values, cell wall ligands are closely associated with hydronium ions, which restrict the approach of positively charged metal ions because of the repulsive force. As the pH increases, more ligands carrying negative charges would be exposed, with the subsequent attraction of metal cations and biosorption onto the binding sites on the cell surface.[7] The values of the zeta potential of the biomass at different pH values are shown in Fig. 2. The zeta potential value of the biomass was –0.61 at pH 2.2 and the overall surface of the biomass was negatively charged at the pH values between 2.2 and 11.0. The zeta potential values varied from –0.61 mV at pH 2.2 to –35.8 mV at pH 11.
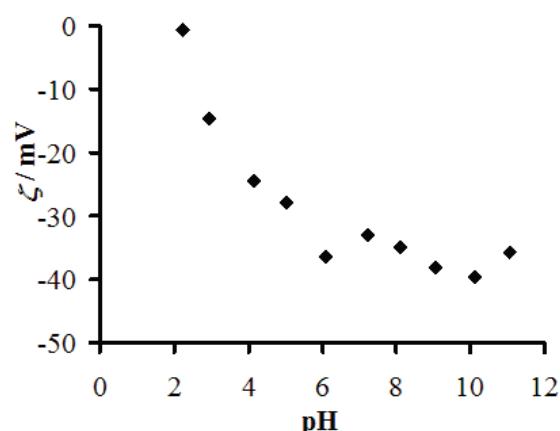

Fig. 2. Effect of pH on the zeta potential of baker's yeast cells in aqueous suspension. The biomass concentration was 0.30 g L^{-1}.

Several researchers have also investigated the effect of pH on the biosorption of cadmium by microbial biomass and similar results were reported. Shu-Juan *et al.* found that the adsorption rate of cadmium by *S. cerevisiae* from a brewery is low when the pH is lower than 4.0. Better adsorption results were obtained in the pH range of 4.0–7.0, and the percent adsorption reached 83.7 % when the pH was 6.0.[18] Vasudevan *et al.*[14] also reported that the cadmium ion adsorption capacity of a commercial yeast increased with increasing pH and it had a maximum at pH 6.5.[14] Experiments were not conducted beyond pH 7.0 to avoid possible hydroxide precipitation.[14] Göksungur *et al.*[5] studied cadmium and lead biosorption by ethanol-treated waste baker's yeast. The maximum biosorption of the heavy metal ions by the yeast were observed at pH 6.0 for cadmium and at pH 5.0 for lead.[2]

Effect of contact time and initial cadmium concentration on biosorption

Adsorption equilibrium studies are important to determine the efficiency of adsorption. With the purpose of investigating the mechanism of biosorption and its potential rate-controlling steps that include mass transport and chemical reaction processes, kinetic models have been exploited to test the experimental data.

Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate at the solid–solution interface.

The kinetics of cadmium adsorption was investigated using a concentration of baker's yeast in the suspension of 0.3 g L^{-1} at pH 6. The initial cadmium concentrations were 5.0, 12.5, 25.0 and 50.0 mg L^{-1}. The amounts of adsorbed cadmium against the adsorption time are presented in Fig. 3a. The biosorption

(a)

(b)
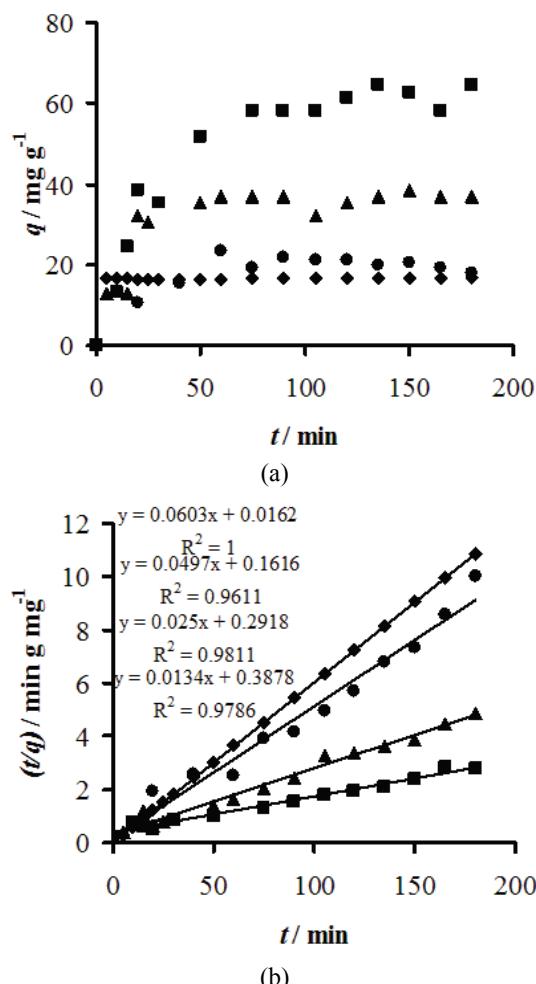
Figs. 3. a) The effect of the initial cadmium concentration on the kinetics of cadmium sorption by baker's yeast. b) Linearized pseudo second-order kinetic model for cadmium adsorption by baker's yeast at different initial cadmium concentrations. Initial concentrations: 5.0 (♦); 12.5 (●); 25.0 (▲); 50.0 mg L^{-1} (■), temperature: 22.5 °C, biomass concentration: 0.30 g L^{-1}.

process of heavy metal by *S. cerevisiae* usually occurs rapidly.[2,4,13,14] The adsorption rate was higher in the first thirty minutes and then decreased until equilibrium was reached. Similar trends were found by other workers.[2,14] By investigating the biosorption of Cr(VI) and Fe(III) on *Streptococcus equisimilis*, *S. cerevisiae* and *Aspergillus niger*, Goyal *et al.*[19] confirmed that metal uptake by the microorganisms proceeds in two stages: a passive uptake that occurs immediately and an active uptake that progresses slowly.[19] The first stage is thought to be physical adsorption or ion exchange at the cell surface, reaching the adsorption equilibrium within 30–40 min at the end of the rapid physical adsorption. Vasudevan *et al.* found that the process of cadmium biosorption by inactive and protonated cells of *S. cerevisiae* was dependent on the availability of metal ion in aqueous solution or the metal ion concentration.[14] However, the researchers suggested that the adsorption process occurred in four distinct steps and the rates for these steps decreased sequentially. The rate of cadmium (II) uptake in each case was pseudo second-order, with respect to the metal ion concentration. It should be noticed that the adsorption of cadmium increased with increasing sorption time.[4,12]

When the initial cadmium concentration was 5.0 mg L^{-1}, the adsorption equilibrium was attained within 5 minutes, while when it was 12.5, 25.0 or 50.0 mg L^{-1}, equilibrium was reached within 60 min.

In adsorption equilibrium, at an initial cadmium concentration of 5.0 mg L^{-1}, the maximal adsorbed cadmium amount $q_{eq,exp}$ was 16.5 mg g^{-1}, at an initial concentration of 12.5 mg L^{-1}, $q_{eq,exp}$ was 20.1 mg g^{-1}, at initial concentration of 25.0 mg L^{-1}, $q_{eq,exp}$ was 36.5 mg g^{-1} and at initial concentration of 50 mg L^{-1}, $q_{eq,exp}$ was 60.7 mg g^{-1}.

Kinetic modeling

The pseudo first- and second-order kinetic models are the most employed models to study the biosorption kinetics of heavy metals and to quantify the extent of uptake in biosorption kinetics.[9,12,16,21] For an evaluation of the cadmium bioadsorption kinetics, two kinetic models were used to fit the experimental data at 5.0, 12.5, 25.0 and 50.0 mg L^{-1} initial cadmium concentrations at pH 6. The pseudo first-order Lagergen model could not be applied to the experimental results of the kinetics of cadmium biosorption by baker's yeast, as the correlation coefficients for the pseudo first-order kinetics were lower than those for the pseudo second-order one. For this reason, the application of the pseudo second-order kinetic model will be pursued for an evaluation of the cadmium bioadsorption kinetics.

If the sorption rate is second-order, the pseudo second-order kinetic rate equation is expressed as:[22]

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_{2,\mathrm{ad}}\left(q_{\mathrm{eq}} - q\right)^2 \tag{2}$$

where $k_{2,\mathrm{ad}}$ is the rate constant of the second-order biosorption (g mg^{-1}·min^{-1}). After integration, the following equation is obtained:

$$\frac{t}{q} = \frac{1}{k_{2,\mathrm{ad}}q_{\mathrm{eq}}^2} + \frac{t}{q_{\mathrm{eq}}} \tag{3}$$

It should be noticed that for the utilization of this model, it is not necessary for the experimental value of q_{eq} to be pre-estimated. By plotting t/q against t for the initial concentrations (5.0, 12.5, 25.0, 50.0 mg L^{-1}), straight lines were obtained, as shown in Fig. 3b. The values of the second-order rate constants $k_{2,\mathrm{ad}}$ and q_{eq}, determined from the slopes and intercepts of the plots, respectively, are presented in Table I.

TABLE I. The second-order adsorption rate constants of cadmium adsorption for different initial concentrations, at pH 6.0, temperature: 22.5 °C, biomass concentration: 0.30 g L^{-1}

c_0 / mg L^{-1}	$k_{2,\mathrm{ad}}$ / g mg^{-1} min^{-1}	$q_{\mathrm{eq,cal}}$ / mg g^{-1}	R^2	$q_{\mathrm{eq,exp}}$ / mg g^{-1}
5.0	0.22	16.6	1.000	16.5
12.5	1.5×10^{-2}	20.1	0.961	20.1
25.0	2.1×10^{-3}	40	0.981	36.5
50.0	4.6×10^{-4}	74.6	0.979	60.7

The correlation coefficients for the second-order kinetic model were close to 1.0 for all cases, and the theoretical values of q_{eq} also agreed well with the experimental data (Table I). The values of second-order rate constant $k_{2,\mathrm{ad}}$ were in the range of 4.6×10^{-4}–0.22 g mg^{-1}·min^{-1}. This suggests that the sorption of cadmium by baker's yeast follows second-order kinetics. The second-order kinetic parameters can be used to determine the equilibrium sorption capacity, the percent removal of cadmium, the rate constants and the initial sorption rate to facilitate bioreactor design.

Adsorption isotherms

The adsorption isotherms of cadmium adsorption by baker's yeast were determined in aqueous suspension using the batch technique. The adsorption isotherms of the adsorption of cadmium ions by baker's yeast in the initial concentration range of 10–500 mg L^{-1} are displayed in Fig. 4a. The adsorption isotherms determined in the low concentration range of 5–25 mg L^{-1} are shown in Fig. 4b. The biomass concentration was 0.30 g L^{-1} in both cases.

It can be observed from Figs. 4a and 4b that the uptake of cadmium by the biomass almost linearly increases with increasing initial cadmium concentration in solution. At an equilibrated concentration of 136.9 mg L^{-1} ($c_0 = 214$ mg L^{-1}),

$q_{eq,exp} = 263.8$ mg g^{-1} and at ($c_0 = 52$ mg L^{-1}) an equilibrated concentration of 32.6 mg L^{-1} ($c_0 = 52$ mg L^{-1}), $q_{eq,exp} = 59.9$ mg g^{-1}.

Equilibrium modeling

The analysis of equilibrium is important for developing a model that can be used for the design of biosorption systems. Several isotherm equations have been used for equilibrium modeling of biosorption systems.[12] Two classical adsorption models, Langmuir and Freundlich isotherms, are the most frequently employed. In this work, the Freundlich and Langmuir models were used to describe the relationship between the amounts of cadmium adsorbed and its equilibrium concentration in solution.

Freundlich isotherm

The Freundlich isotherm is capable of describing the adsorption of organic and inorganic compounds onto a wide variety of adsorbents, including bio-sorbents. The Freundlich Equation based on sorption onto a heterogeneous surface is:

$$q_{eq} = K_F c_{eq}^{1/n} \tag{4}$$

where K_F and n are the Freundlich constants, which are indicators of the adsorption capacity and adsorption intensity of the sorbent. Eq. (4) can be linearized in logarithmic form as follows:

$$\log q_{eq} = \log K_F + \frac{1}{n}\,\log c_{eq} \tag{5}$$

A plot of $\log q_{eq}$ *vs.* $\log C_{eq}$ has a slope with the value of $1/n$ and an intercept of $\log K_F$. $\log K_F$ is equivalent to $\log q_{eq}$ when $1/n$ equals unity. However, in other case, when $1/n \neq 1$, the K_F value depends on the units in which q_{eq} and C_{eq} are expressed. The experimental cadmium adsorption and non-linearly fitted (using Gnuplot software) by Freundlich model isotherms can be seen in Fig 4a. The values of K_F and n calculated are 6.5 [(mg g^{-1}) (mg L^{-1})]^n and 1.4, respectively (Table II).[12,23]

Langmuir Isotherm

The Langmuir Isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. It is given as:

$$q_{eq} = \frac{Q^0 b c_{eq}}{1 + b c_{eq}} \tag{6}$$

where c_{eq} and q_{eq} are equilibrium concentration (mg L^{-1}) and the amount adsorbed at equilibrium time (mg g^{-1}), respectively. Q^0 and b are Langmuir

(a)

(b)

(c)
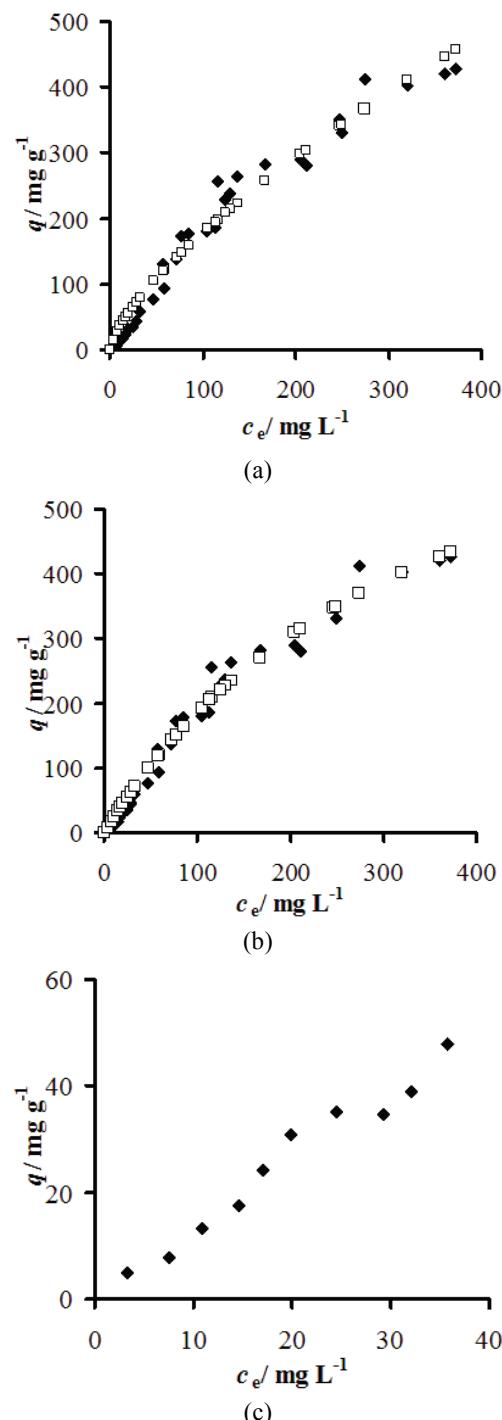
Figs. 4. Adsorption isotherms of cadmium by baker's yeast from aqueous solutions at a biomass concentration of 0.30 g L^{-1} and initial cadmium concentrations in the range a) 0–500 mg L^{-1} ♦ – experimental data, □ – non-linear fitted data using the Freundlich Equation; b) ♦ – experimental data, □ – non-linear fitted data using the Langmuir Equation; c) adsorption isotherm in the initial concentration range of 5–25 mg L^{-1}.

constants related to the capacity and energy of adsorption, respectively. The linearized form of the Langmuir Equation is:

$$\frac{c_{eq}}{q_{eq}} = \frac{1}{Q^0 b} + \frac{c_{eq}}{Q^0}$$ (7)

Q^0 and b can be determined from a linear plot of c_{eq}/q_{eq} vs. c_{eq}.[8]

The experimental cadmium adsorption and the non-linearly fitted (using Gnuplot software) by the Langmuir model isotherm can be seen in Fig. 4b. The calculated values of b and Q^0 are 2.8×10^{-3} L mg^{-1} and 852.6 mg g^{-1}, respectively (Table II). The calculated monomolecular adsorption capacity Q^0 is fits well to the experimental value.

TABLE II. Bioadsorption isotherm constants for the biosorption of cadmium onto baker's yeast

Isotherm	K_F / [(mg g^{-1})(mg L^{-1})]^n	n	b / L mg^{-1}	Q^0/ mg g^{-1}
Langmuir	–	–	2.8×10^{-3}	852.6
Freundlich	6.5	1.4	–	–

Biosorption yield

The biosorption yields are presented against the suspension concentrations at an initial cadmium concentration of 50.0 mg L^{-1} in Fig. 5. The biomass concentrations were 0.30, 0.60, 1.5 and 3.0 g L^{-1}. Increasing of biomass concentration from 0.30 to 3.0 g L^{-1} caused the biosorption yield to increase up to 38 %. Above a biomass concentration of 1.5 g L^{-1}, the biosorption yield did not change significantly.
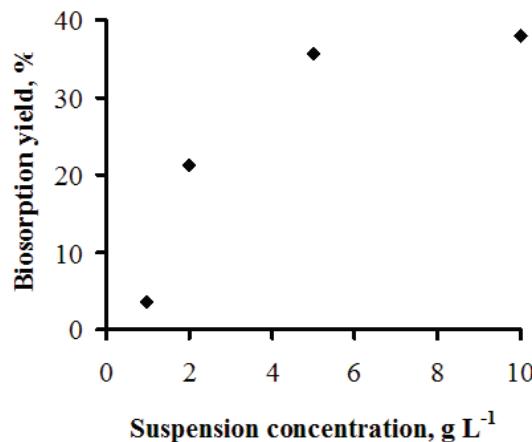

Fig. 5. Effect of the suspension concentration of biomass on cadmium biosorption onto baker's yeast. The initial cadmium concentration was 50.0 mg L^{-1}.

CONCLUSIONS

The biosorption properties of waste baker's yeast (*S. cerevisiae*) were studied for cadmium removal from aqueous suspension. The initial heavy metal concentration, pH of the solution and contact time were found to have an effect on the bioadsoption capacity of the biomass. The maximal biosorption capacity was determined at pH of 6.0. With increasing initial cadmium concentration and contact time, the amount of cadmium adsorbed increased as well. The biosorption kinetics followed pseudo second-order kinetics. The Freundlich Equation and the Langmuir adsorption model were used for a mathematical description of the biosorption of cadmium onto native baker's yeast. It was found that the adsorption equilibrium data fitted well to the Freundlich and Langmuir Models. With increasing biomass concentration, the adsorption efficiency increased significantly up to a biomass dosage of 1.5 g L^{-1}. It seems that the use of readily available waste baker's yeast from the fermentation industry offers an alternative in the removal of metals from contaminated waters.

ИЗВОД

БИОСОРПЦИЈА КАДМИЈУМА ПЕКАРСКИМ КВАСЦЕМ У ВОДЕНОЈ СУСПЕНЗИЈИ

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Испитана је биосорпција кадмијума из вештачких водених раствора помоћу изворног пекарског квасца. Највиша вредност преузете количине била је 110 mg g^{-1} у суспензији од 0,30 g L^{-1}. Истраживани су утицаји pH, почетне концентрације кадмијума, адсорпционог времена и дозе биосорбента на биосорпцију помоћу пекарског квасца. Максимални капацитет биосорпције кадмијума квасцем био је уочен на pH 6. Адсорпциона равнотежа је била достигнута након 60 min, а процес сорпције је пратио кинетику псеудо-другог реда. Изотерме биосорпције кадмијума одређене су у опсегу концентрација кадмијума од 10 до 500 mg L^{-1} при pH 6 у суспензији од 0,30 g L^{-1}. За процену равнотеже биосорпције, на експерименталне податке су примењене Лангмирове и Фроиндлихове једначине.

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