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Application of immobilized waste brewery yeast cells for Cd^{2+} removal. Equilibrium and kinetics

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Abstract: In this investigation, the removal of Cd^{2+} by a brewery waste biomass in immobilized (Ca alginate beads) form was studied. The removal process was conducted at room temperature under batch conditions (magnetic stirring) using different initial cadmium concentrations. The equilibrium of biosorption was reached in 150 min for all employed initial concentrations. The maximum biosorption capacity was calculated to be 5.96 mg Cd^{2+} g^{-1} yeast for an initial Cd^{2+} concentration of 169 mg L^{-1}. Langmuir and Freundlich adsorption isotherms were used to correlate the equilibrium adsorption data. Based on the correlation coefficients, it was concluded that the Langmuir isotherm is more suitable for describing the equilibrium data of cadmium biosorption. In addition, first and pseudo-second order kinetic models were applied to describe the biosorption process. The kinetic parameters for the pseudo-second order kinetics were determined.

Keywords: *Saccharomyces cerevisiae*; immobilization; cadmium biosorption; Freundlich and Langmuir models; kinetic models.

INTRODUCTION

Heavy metal ions, such as cadmium, lead and mercury, are highly toxic to living organisms. Cadmium is one of the three most toxic heavy metals, its toxicity being attributed in part to its ability to accumulate in living organisms. Cadmium tends to accumulate slowly over time in bones, liver and kidneys, where it can impair normal functions.

Adsorption of metals by microbial biomass and agricultural materials is a relatively recent method for the removal and recovery of metals. This method

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was used to remove toxic metals from industrial liquid waste products and, due to its high efficiency, it appears to be more attractive in comparison to other processes.[1] Various kinds of microbial biomasses (*e.g.*, yeast, algae and fungi)[2–4] and agricultural by-products (*e.g.*, rice straw, soybean hull, sugarcane bagasse, peanut shells, pecan and walnut shells, almond shells, olive stones and peach stones)[5,6] have been tested for this purpose. For example, Norris and Kelly[7] studied the adsorption of cadmium and cobalt ions by *Saccharomyces cerevisiae* yeast surface. Biosorption is considered a fast physical and/or chemical process depending on the yeast type and treatment. The biosorption rate depends on the type of the process. According to the literature, biosorption can be divided into two main processes: adsorption of the ions on the cell surface and bioaccumulation within the cell.[8]

The uptake capacity of biomasses is always affected by many factors, such as pH, temperature, initial concentrations of biomass and metal ions, culture condition and some others, such as the presence of various ligands and metal ions. If all other culture conditions are the same, the biosorption capacity of a biomass depends mainly on the type of biomass cells. To understand the interaction between metal ions and the biomass, the hard and soft principle of metal ions proposed by Nieboer and Richardson has been widely used.[9–12]

The commercial applications of biomass as biosorbents has been hindered by operational limitations associated with their physical characteristics, such as small particle size, low density, poor mechanical strength, low rigidity and solid/liquid separation problems.[13] These difficulties can be overcome by entrapment of microbial biomass in immobilized preparations. The efficiency of these preparations as potential metal biosorbents can be further enhanced by using plant waste material as the immobilizing matrix.[14] Immobilization techniques are one of the key elements for the practical application of biosorption, especially by dead biomass.[15] The most commonly used matrix materials for the immobilization of microbial cells *via* entrapment are carbohydrate polymers, such as alginate, chitosan, chitin and carboxymethyl-cellulose,[16] polysulphone, polyacrylamide, polyurethane and silica.[17] The selection of immobilization matrix is crucial in the application of immobilized biomass. The polymer matrix determines the mechanical strength, rigidity, and porosity characteristics and chemical resistance of the final biosorbent particles to be utilized for successive sorption–desorption cycles; thus, it is very important to choose the appropriate immobilization matrix in every case.[18] Natural polymers, such as Na alginate, have been used as the matrix for cell immobilization. Chang and co-workers found that the adsorption capacity of Ca alginate immobilized cells was greater than that of polyacrylamide-entrapped cells for the adsorption of Cd^{2+}.[19]

Other authors studied the removal of different heavy metals (Cd^{2+}, Cu^{2+}, Hg^{2+}, Zn^{2+}, *etc.*) onto diverse immobilized bacteria, fungi, algae, yeasts, *etc.*

(*Spirulina platensis*, *Laminaria digitata*, *Aspergillus niger*, *etc*.).[20–24] All proved to be very efficient in the removal of heavy metal ions from aqueous solutions.

Yeast biomass has been successfully used as a biosorbent for the removal of Ag, Au, Cd, Co, Cr, Cu, Ni, Pb, U, Th and Zn. A number of studies showed that *Saccharomyces cerevisiae* could remove toxic metals, recover precious metals and clean radionuclides from aqueous solutions to various extents. The advantages of *S. cerevisiae* for metal biosorption, the forms of *S. cerevisiae* in biosorption research, the biosorptive capacity of *S. cerevisiae*, and the selective and competitive biosorption by *S. cerevisiae* were depicted in detail by Wang and Chang.[25]

The same authors reviewed the metal uptake capacity of *S. cerevisiae*, in different forms (calculated for dry biomass), and found values ranging between 10 and 300 mg M^{n+} g^{-1}.[18] In case of cadmium, the uptake (adsorption) capacity was usually above 10 but less than 100 mg Cd^{2+} g^{-1} dry mass. It should be noted that comparing results from different studies involves standardizing the different ways the adsorption capacity may be expressed. Simultaneously, metal uptake should be compared in almost the same equilibrium concentration of metals in the solution when evaluating the performance of a biomaterial. In particular, there is no standard measurement of dry weight of biomass, *i.e*., no standard drying temperature and time when drying biomass.[18]

Various kinds of immobilized *S. cerevisiae* have been studied with different support materials suitable for use in practical applications.[15,26]

The objective of this work was to investigate the biosorption of Cd^{2+} by immobilized Romanian brewery waste biomass. The cadmium removal efficiency and adsorption capacity were determined. Adsorption equilibrium (Langmuir and Freundlich isotherms) and kinetic models (first and pseudo second order) were used to describe the biosorption process.

EXPERIMENTAL

Biosorbent

The biosorbent, brewery waste biomass, *S. cerevisiae*, was collected from the CIUC brewery (Miercurea-Ciuc, Romania) after use in fermentation processes and transported to the laboratory in plastic containers. The yeast was then washed with bi-distilled water, separated by vacuum filtration and dried in a hot air oven at 80 °C for 24 h.

Biosorbent immobilization

The employed cross-linking procedure with calcium alginate was an adapted version of the method for treatment of fungi biomass outlined by Schiewer and co-workers.[27,28]

For immobilization of yeast, 2 g of biosorbent (brewery waste biomass) was suspended in 50 mL distilled water. This suspension was then blended with a mixture formed from 1 g sodium alginate and 2 mL ethanol. The mixture was then dropped using a peristaltic pump into 200 ml of 0.2 M $CaCl_2$ solution. During this process, the drops of alginate-biomass mixture were gelled into beads of diameter of 4.0±0.2 mm. The Ca alginate immobilized yeast beads were left in the 0.2 M $CaCl_2$ solution at 4 °C for 1 h to cure and form 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

A stock metal ion solution, 1.0 g L^{-1}, was prepared by dissolving $Cd(NO_3)_2$ $4H_2O$ of analytical grade reagent into an appropriate amount of distilled water. Cadmium solutions of different concentrations (10, 24, 48, 100, 169 mg L^{-1}) were obtained by diluting the stock solution. The concentration of Cd^{2+} in the supernatant fluids was determined using a flame atomic absorption spectrophotometer (SensAA Dual GBS scientific equipment, Australia).

Metal biosorption studies

Experiments were realised under batch conditions with continuously magnetic stirring (875 rpm) at room temperature (20 °C), pH 6.5, for 3 h. The immobilized brewery yeast biomass was contacted with 100 mL of the initial cadmium solutions, as described. The kinetic studies were performed using different concentrations of cadmium solutions. In order to determine the exact concentration of cadmium ions and establish the evolution of the removal process, samples of 100 μL (dilution ratio in each case was 50) from the supernatant were collected at different time intervals (Fig. 1).

The amount of adsorbed cadmium was calculated using the following equation:

$$q_t = \frac{(c_0 - c_t)}{w} \frac{V}{1000} \quad (1)$$

where q_t is the adsorption capacity (mg g^{-1}) at time t, c_0 is the initial cadmium concentration (mg L^{-1}), c_t is the cadmium concentration (mg L^{-1}) at time t, V = 100 mL and w is the quantity of the adsorbent (g).

RESULTS AND DISCUSSION

Cadmium biosorption

The dynamics of cadmium uptake until equilibrium by the waste brewery biomass for various initial cadmium concentrations are represented in Fig. 1.

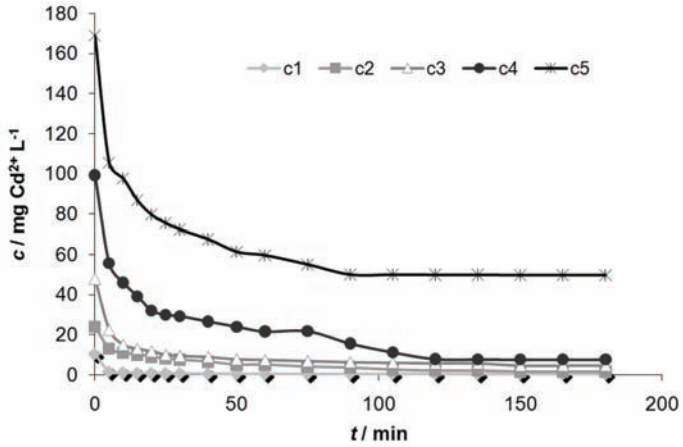

Fig. 1. Dynamics of cadmium uptake by waste brewery biomass for various initial cadmium concentrations; c_1 = 10 mg Cd^{2+} L^{-1}, c_2 = 24 mg Cd^{2+} L^{-1}, c_3 = 48 mg Cd^{2+} L^{-1}, c_4 = 100 mg Cd^{2+} L^{-1}, c_5 = 169 mg Cd^{2+} L^{-1}.

Following the decrease in concentrations with time, three distinct zones can be discerned, which represent:

a) a rapid decrease in the cadmium concentration during the first 5 min, corresponding to cell surface adsorption by interactions between the metal ions and functional groups, such as carboxyl, phosphate, hydroxyl, amino, sulphur, sulphide, thiol, *etc*., present in the cell walls;

b) a slow decrease in the cadmium concentration, corresponding to metal ions that penetrate the cell membrane and enter into the cells; this decrease of the adsorption rate could be associated with a diffusion limitation of the transport of heavy metal ions through the cell wall;

c) the attainment of adsorption equilibrium between metal ions from solution and the immobilized cell surface. Biosorption equilibrium was reached in 150 min for all the investigated initial cadmium concentrations.

The obtained results are in good agreement with those from the literature.[29–32]

Maximum adsorption capacities (Fig. 2) increased from 0.5003 mg Cd^{2+} g^{-1} for an initial cadmium concentration of 10 mg L^{-1} to 5.960 mg Cd^{2+} g^{-1} for an initial concentration of 169.0 mg Cd^{2+} L^{-1}.

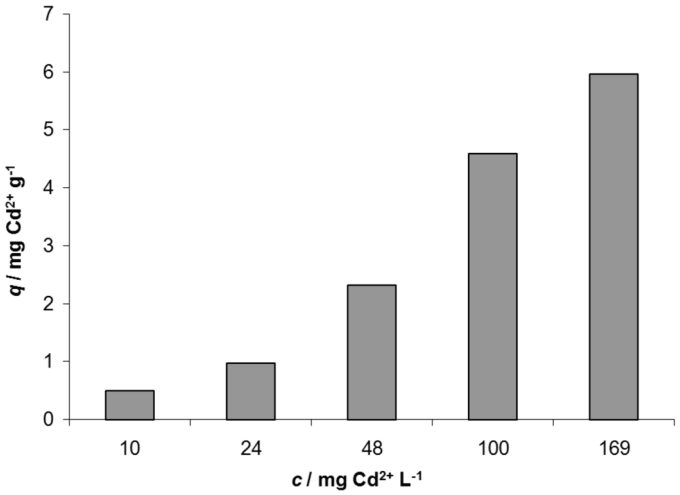

Fig. 2. Maximum adsorption capacities obtained during cadmium adsorption experiments: influence of the initial concentration.

Adsorption equilibrium models

The cadmium biosorption equilibrium was described using the Langmuir and Freundlich models, which are widely used to fit biosorption data.[26,33] The Langmuir model suggests a monolayer adsorption, with no lateral interaction between the adsorbed molecules. The Freundlich model assumes heterogeneous adsorp-

tion due to the diversity of the adsorption sites or diverse nature of the adsorbed metal ions, free or hydrolyzed species.[33]

The Langmuir isotherm can be expressed as follows:

$$q_e = \frac{q_{max} b c_e}{1 + b c_e} \tag{2}$$

where q_e is the solid-phase adsorbate concentration at equilibrium (mg g^{-1}), q_{max} is the maximum adsorption capacity corresponding to a monolayer adsorption capacity (mg g^{-1}), c_e is the concentration Cd^{2+} in solution at equilibrium (mg L^{-1}) and b is related to the strength of the adsorbent–adsorbate affinity.

The linear form of the Langmuir isotherm, Eq. (1), is expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{max} b} \frac{1}{c_e} + \frac{1}{q_{max}} \tag{3}$$

From the linear $1/q_e$ *vs.* $1/c_e$ plot, Fig. 3, the q_{max} and b values were calculated to be 17.4825 mg Cd^{2+} g^{-1} and 0.0660 L mg^{-1}. The experimental values of q_e and c_e, represented in Fig. 4, fitted well on a Langmuir type of isotherm.

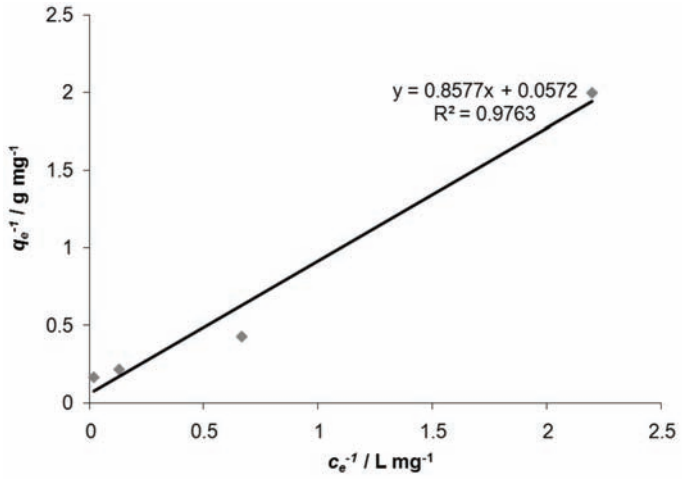

Fig. 3. Langmuir adsorption model of cadmium biosorption on immobilized brewery waste biomass.

The Freundlich isotherm can be expressed as:

$$q_e = k c_e^{1/n} \tag{4}$$

and in the logarithmic (linear) form:

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

where k is related to the adsorption capacity and n to the intensity of the adsorption.

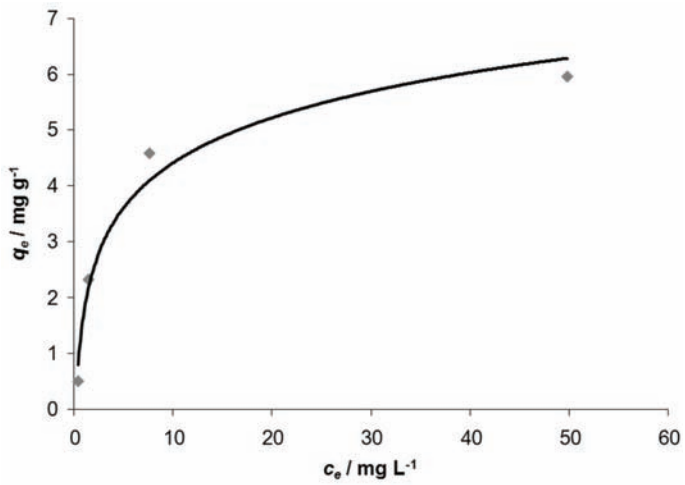

Fig. 4. Adsorption isotherm of cadmium biosorption on immobilized brewery waste biomass.

From the linear log q_e *vs.* log c_e plot, Fig. 5, a correlation coefficient of 0.9183 was determined, which is smaller than that obtained for the Langmuir model, 0.9763. Therefore, it was concluded that cadmium biosorption on immobilized brewery waste biomass followed a Langmuir isotherm.

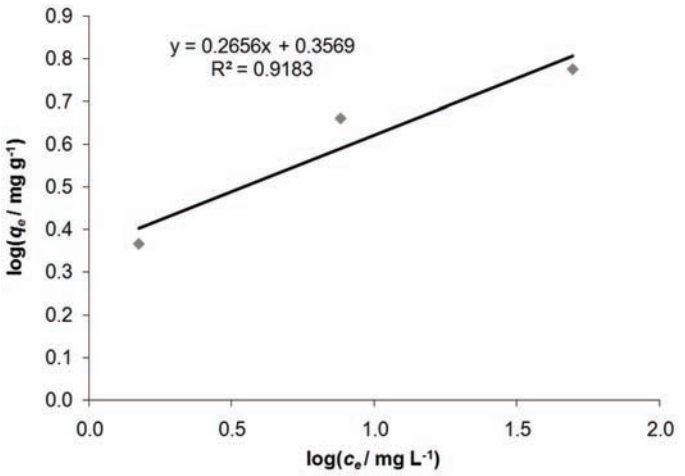

Fig. 5. Freundlich adsorption model of cadmium biosorption on immobilized brewery waste biomass.

Kinetic models

Kinetic data were analyzed using first and pseudo-second order models. Using these models it is possible to investigate the mechanism of adsorption and rate controlling steps.[19,33–35]

The first order equation for adsorption in a liquid/solid system based on capacity of the solid can be expressed as follows:

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

Integrating Eq. (2) from the boundary conditions $t = 0$ to t and $q_t = 0$ to q_t gives:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

where q_e and q_t are the amounts of cadmium adsorbed (mg g^{-1}) at equilibrium and time t, respectively, and k_1 is the rate constant of the first order adsorption (min^{-1}).

In order to determine the rate constant and equilibrium cadmium uptake, straight line plots of ln ($q_e - q_t$) against t, Eq. (7), were made at five different initial cadmium concentrations. Correlation coefficients between 0.8126 and 0.9513 were obtained (figure not shown).

The pseudo-second order kinetic model is derived based on the adsorption capacity of the solid phase, which assumes that the measured heavy metal ion concentrations are equal to the cell surface concentration, expressed as:

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

Integrating Eq. (8) over the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to q_t gives:

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

where k_2 is the rate constant of second order adsorption (g mg^{-1} min^{-1}).

Eq. (9) can be rearranged in linear form, as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

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 0.9966 and 1.0000 were obtained (Fig. 6 and Table I).

Compare the correlation coefficients for the first- and pseudo-second order models, it can be concluded that cadmium biosorption on immobilized brewery waste biomass can be classified as pseudo-second order.

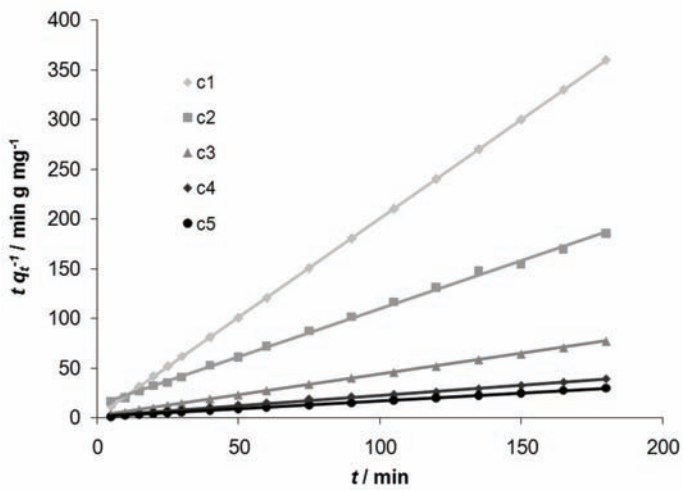

Fig. 6. Correlation of the experimental data using the pseudo-second order model for cadmium biosorption on immobilized brewery waste biomass; c_1 = 10 mg Cd^{2+} L^{-1}, c_2 = 24 mg Cd^{2+} L^{-1}, c_3 = 48 mg Cd^{2+} L^{-1}, c_4 = 100 mg Cd^{2+} L^{-1}, c_5 = 169 mg Cd^{2+} L^{-1}.

Table I. Second order adsorption kinetic parameter

c / mg Cd^{2+} L^{-1}	q_e(exp) / mg Cd^{2+} g^{-1}	q_e(calc) / mg Cd^{2+} g^{-1}	k_2 / g mg^{-1}·min^{-1}	R^2
10	0.5003	0.5033	2.2189	1.0000
24	0.9715	1.0331	0.0727	0.9986
48	2.3250	2.3958	0.0754	0.9998
100	4.5825	4.8614	0.0186	0.9966
169	5.9600	6.2657	0.0211	0.9994

CONCLUSIONS

In this study, an immobilized Ca alginate beads from waste brewery biomass (yeast cells), from Miercurea-Ciuc, Romania, was successfully used as a biosorbent for the removal of Cd^{2+} from aqueous solutions. Calcium alginate proved to be a suitable matrix for the immobilization of bakers' yeast cells.

The maximum biosorption capacity was calculated to be 5.9600 mg Cd^{2+} g^{-1} yeast for an initial concentration of Cd^{2+} of 169 mg L^{-1}.

Langmuir and Freundlich adsorption isotherms were used to correlate the equilibrium adsorption data. Based on the correlation coefficients, it was concluded that the Langmuir isotherm is more suitable to describe the equilibrium data of cadmium biosorption.

In addition, first- and pseudo-second order kinetic models were applied to describe the cadmium biosorption process. Based on the performed mathematical calculations, it was concluded that this process followed pseudo second order kinetics and the parameters for this kinetic model were determined.

The results presented in this paper proved that a biosorbent from the fermentation industry, *i.e.*, waste brewery biomass, which as a by-product of an industrial process is inexpensive and available in large quantities, could be successfully used to remove cadmium ions from aqueous solutions. Further investigations will be conducted in order to explain the adsorption mechanism and to establish the optimum parameters for the biosorption process.

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И З В О Д

ПРИМЕНА ИМОБИЛИЗОВАНИХ ЋЕЛИЈА ПИВСКОГ КВАСЦА ЗА УКЛАЊАЊЕ Cd^{2+}. РАВНОТЕЖА И КИНЕТИКА

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У раду је описан поступак укањања Cd^{2+} имобилисаном отпадном биомасом пивског квасца на честицама калцијум-алгината. Процес уклањања је изведен тзв. "batch" методом, на магнетној мешалици и собној температури, користећи различите почетне концентрације кадмијума. Равнотежа биосорпције је постигнута после 150 min без обзира на почетну концентрацију кадмијума. Максималан капацитет биосорпције је био 5,96 mg Cd^{2+} g^{-1} квасца за 169 mg Cd^{2+} L^{-1} почетне концентрације. Ленгмирове и Фројндлихове адсорпционе изотерме су коришћене за корелацију података. На основу израчунатих коефицијената корелације закључено је да Ленгмирова изотерма боље описује равнотежу биосорпције кадмијума. Тестирани су, такође, кинетички модели првог и псеудо-другог реда за описивање процеса биосорпције. Одређени су кинетички параметри за кинетику псеудо-другог реда.

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REFERENCES

1. L. Deng, X. Zhu, Y Su, H. Su, X. Wang, *Chin. J. Oceanol. Limnol.* **26** (2008) 45
2. P. Dostalek, M. Patzak, P. Matejka, *Int. Biodeter. Biodegrad.* **54** (2004) 203
3. A. Saeed, M. Iqbal, *J. Microbiol. Biotechnol.* **22** (2006) 775
4. M. G. Lee, J. H. Lim, S. K. Kam, *Korean J. Chem. Eng.* **19** (2002) 277
5. R. R. Bansode, J. N. Losso, W. E. Marshall, R. M. Rao, R. J. Portier, *Bioresour. Technol.* **89** (2003) 115
6. M. A. Ferro-Garcia. J. Rivera-Utilla, J. Rodriguez-Gordillo, I. Bautista-Toledo, *Carbon* **26** (1988) 363
7. P. R. Norris, D. P. Kelly, *J. General Microbiol.* **99** (1977) 317
8. C. Chen, J. L. Wang, *Appl. Microbiol. Biotechnol.* **74** (1980) 911
9. E. Neiboer, D. H. S. Richardson, *Environ. Pollut. Series B1* **1** (1980) 3
10. C. Chen, J. L. Wang, *J. Hazard. Mater.* **151** (2008) 65
11. J. M. Brady, J. M. Tobin, *Enzyme Microb. Technol.* **17** (1995) 791
12. A. Kogej, A. Parko, *World J. Microbiol. Biotechnol.* **17** (2001) 677

13. J. K. Park, Y. P Jim, H. N. Chang, *Biotechnol. Bioeng.* **63** (1999) 116
14. M. Gopal, K. Pakshirajan, T. Swaminathan, *Appl. Biochem. Biotechnol.* **102**–**103** (2002) 227
15. F. Veglio, F. Beolchini, *Hydrometallurgy* **44** (1997) 301
16. M. Yakup Arica, M. Bayramolu, G. Yılmaz, M. Bekta, G. Genc, *J. Hazard. Mater.* **109** (2004) 191
17. K. Vijayaraghavan, Y. S. Yun, *Biotechnol. Adv.* **26** (2008) 266
18. J. Wang, C. Chen, *Biotechnol. Adv*. **27** (2009) 195
19. J. Wu, H.-Q. Yu, *Bioresour. Technol*. **98** (2007) 253
20. Y. Lu, E. Wilkins, *J. Hazard. Mater.* **49** (1996) 165
21. T. Lebean, D. Bagot, K. Jezequel, B. Fabre, *Sci. Total Environ.* **291** (2002) 78
22. N. Rangsayatorn, P. Pokethitiyook, E. S. Upatham, G. R. Lanza, *Environ. Int.* **33** (2006) 57
23. M. Y Arica, G. Bayramoglu, M. Yilmaz, S. Bekta, Ö. Genc, *J. Hazard. Mater.* **109** (2004) 191
24. Y.-L. Lai, G. Annadurai, F.-C. Huang, J.-F. Lee, *Bioresour. Technol.* **99** (2008) 6480
25. J. L. Wang, C. Chen, *Biotechnol. Adv.* **24** (2006) 427
26. J. Park, S. B. Choi, *Korean J. Chem.* **19** (2002) 68
27. S. Schiewer, E. Fourest, K. H. Chong, B. Volesky, *Biohydrometall. Proc.* **2** (1995) 219
28. M. Zhao, J. R. Duncan, *Biotechnol. Lett.* **19** (1997) 953
29. Y. Göksungur, S. Üren, U. Güvenç, *Bioresour. Technol.* **96** (2005) 103
30. K. K. I. U. Arunakumara, Z. Xuecheng, *J. Ocean Univ. Chin.* **7** (2008) 60
31. P. Vasudevan, V. Padmavathy, S. C. Dhingra, *Bioresour. Technol.* **89** (2003) 281
32. P. Vasudevan, V. Padmavathy, S. C. Dhingra, *J. Sci. Ind. Res.* **65** (2006) 1013
33. C. Namasivayam, D. Sangeetha, *Adsorp. Sci. Technol.* **12** (2006) 103
34. J. Febrianto, A. N. Kosasih, J. Sunarsao, Y. Ja, N. Indraswati, S. Ismadji, *J. Hazard. Mater.* **162** (2009) 616
35. J. L. Wang, C. Chen, *Biotechnol. Adv.* **24** (2006) 427.