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SUSPENDED AND IMMOBILIZED BREWERY WASTE BIOMASS AND COMMERCIAL YEAST AS BIOSORBENTS FOR Cd(II) REMOVAL. A THERMODYNAMIC STUDY

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Bioremediation of heavy metals pollution remains a major challenge in environmental biotechnology. This paper presents the potential of yeast collected from two sources, used in two forms (commercial yeast and brewery waste biomass, in suspended and immobilized forms) for cadmium ions biosorption from synthetic monocomponent solution. Thermodynamic parameters, including Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption were calculated. The obtained results showed that the biosorption of Cd(II) onto *Saccharomyces cerevisiae* strain was a feasible, spontaneous and endothermic process in nature. Between the four tested biosorbents, the best efficiency and adsorption capacity was determined for the brewery waste biomass, which could be successfully used as an alternative low-cost biosorbent.

INTRODUCTION

Pollution by toxic heavy metals is a global environmental problem. Heavy metals are nonbiodegradable and can be accumulated in living organisms.[1] Cadmium is a dangerous pollutant originating from metal plating, metallurgical alloying, mining, ceramics and other industrial operations.[2] According to Romanian legislation, the maximum concentration limit for Cd(II) discharge into surface waters is 0.2 mg l^{-1} and in potable water is 5×10^{-3} mg l^{-1}.[3,4]

Heavy metals can be removed from wastewater using conventional (ion exchange, adsorption, solvent extraction, chemical precipitation, reverse osmosis, ultrafiltration) and advanced (biosorption and phytoremediation) methods.[5]

Biosorption utilizes the ability of certain materials to accumulate heavy metals from aqueous solutions by either metabolically mediated or physico-chemical pathways of uptake.[6] The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution (e.g., less than 100 mg heavy metal l^{-1}), minimization of chemical and/or biological sludge, reusability of biomaterial, short operation time and the possibility of metal recovery.[7,8] Various types of biomass including bacteria,[9] yeast,[10] fungi[11] and algae[12] have been investigated with the aim of

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finding more efficient and cost-effective metal removal biosorbent.

The word biomass usually refers to the material derived from the living beings after their death. The immobilization in alginate and the fermentation processes for brewery industry produce yeast biomass.[13]

Saccharomyces cerevisiae can be used to remove toxic metals, recover precious metals and clean radionuclides from aqueous solutions to various extents. *S. cerevisiae* is not only a by-product of some fermentation processes, but also can be easily obtained in substantial quantities at low costs.[10] Often, the economics of the process can be improved by using waste biosorbent instead of cultured biosorbent.[14] As a biosorbent, *S. cerevisiae* not only successfully removes metals from wastewaters but also eases the burden of disposal costs associated with the waste.[15]

Yeast cell walls, consisting mainly of polysaccharides, proteins and lipids, offer many functional groups that can bind ions such carboxylate, hydroxyl, sulphate, phosphate and amino groups, which can act as binding sites for metals.[13,16]

The purpose of this work was to investigate the biosorption capacities of suspended (SBW) and immobilized (IBW) brewery waste biomass for cadmium removal. The results were compared with suspended (SFY) and immobilized (IFY) commercial fresh yeast. Effect of contact time and thermodynamics were used to describe the biosorption process.

RESULTS AND DISCUSSION

Effects of contact time and temperature

Effect of contact time on Cd(II) concentration during the biosorption process for all four considered biosorbents, SBW, IBW, SFY, and IFY at constant temperature (295 K) is presented in figure 1. Following the evolution in time of cadmium ions concentration it was observed that in the first 5 minutes from the beginning of the experiment there is a significant decrease, while the equilibrium was reached after another 35 minutes. For all considered biosorbents, equilibrium was reached in approximately 40 minutes. Values of cadmium ions concentration determined at equilibrium were smaller in case of SBW and IBW (0.71 and 0.91 mg Cd^{2+} l^{-1}, respectively) by comparison with SFY and IFY (4.16 and 2.33 mg Cd^{2+} l^{-1}, respectively). The difference observed between SBW and IBW, could be attributed to the internal diffusion limitation that occur when adsorption takes place on immobilized form (beads). Regarding to the temperature effect over the biosorption process, presented in figure 2 for IFY biosorbent, an important decrease of cadmium ions concentration was observed with an increase in temperature from 295 to 323 K. Equilibrium concentrations decreased from 2.33 mg Cd^{2+} l^{-1} at 295 K to 0.93 mg Cd^{2+} l^{-1} at 323 K. This effect could be attributed to the intensification of the diffusion processes and to the fact that the biosorption process was endothermic. It can be seen that the adsorbed amount of Cd(II) increased with contact time up to 40 min, and on this point, it attained the maximum removal. Therefore, 40 minutes was selected as the optimum contact time for all further experiments.

Previous conclusions are also reflected by the maximum biosorption efficiency values and adsorption capacities at equilibrium, figures 3 and 4. Highest biosorption efficiencies were found for SBW, with the maximum value of 99.83% calculated at 323 K. This result could indicate also that cadmium biosorption process onto considered biosorbents was endothermic. Also, adsorption capacities have maximum values for SBW and IBW biosorbents, 0.5841 and 0.5531 mg Cd^{2+} g^{-1}, respectively (figure 4). In all cases when brewery waste biomass was used for biosorption, higher values for adsorption capacities were calculated, fact that can be attributed to the destruction of the yeast cell walls, which led to an increase of the surface available for biosorption. In order to exemplify the influence of the temperature over the adsorption capacity, in figure 5, we presented values obtained in case of SBW biosorbent. Adsorption capacities increase with temperature from 0.5133 mg Cd^{2+} g^{-1} at 295 K to 0.5852 mg Cd^{2+} g^{-1} at 323 K.

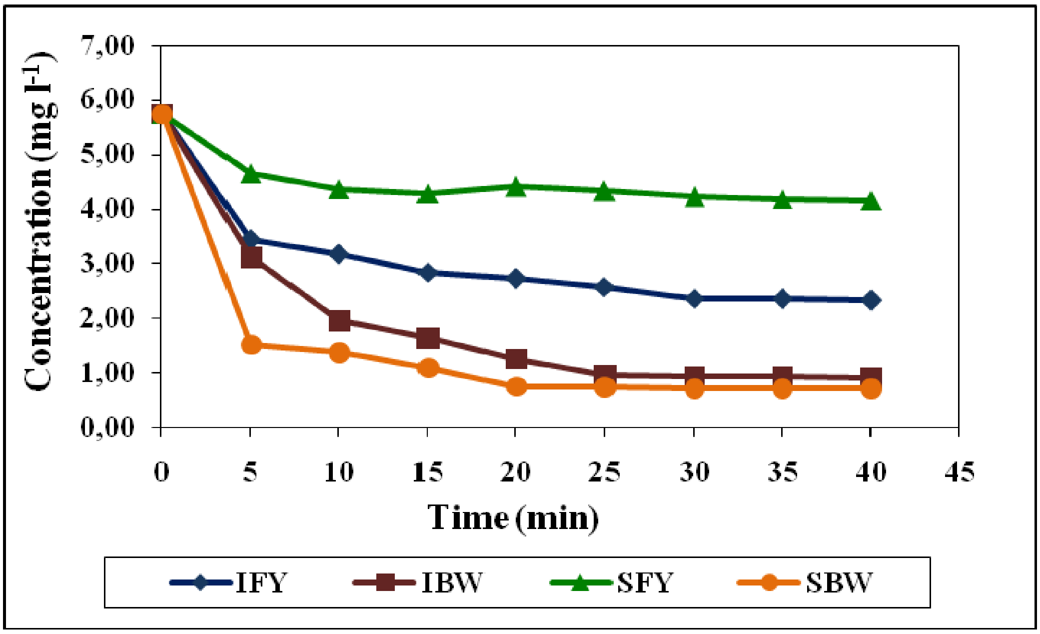

Fig. 1 – Effect of contact time on Cd^{2+} concentration during the biosorption process for SBW, IBW, SFY and IFY biosorbents at constant temperature (295 K).

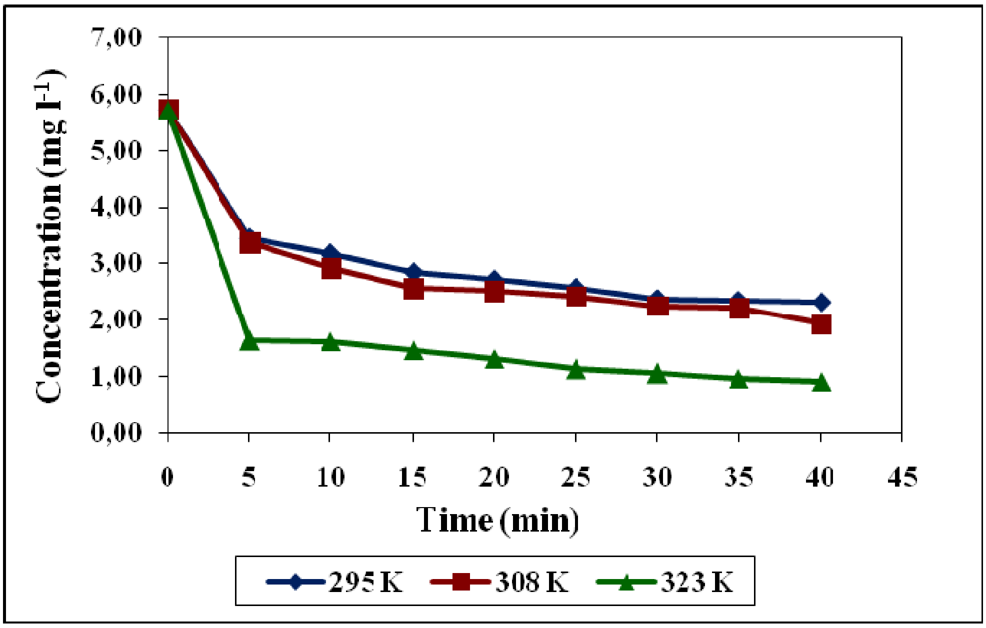

Fig. 2 – Effect of contact time and temperature (295, 308, 323 K) on Cd^{2+} concentration during the biosorption process for IFY biosorbent.

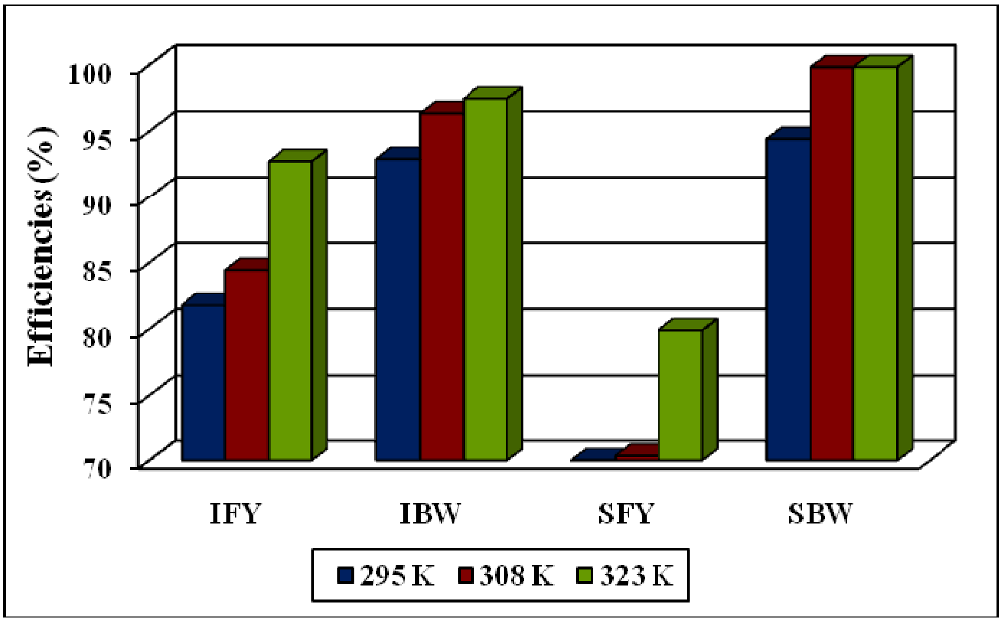

Fig. 3 – Effect of temperature on the maximum removal efficiencies (E,%) of Cd^{2+} onto SBW, IBW, SFY, and IFY biosorbents.

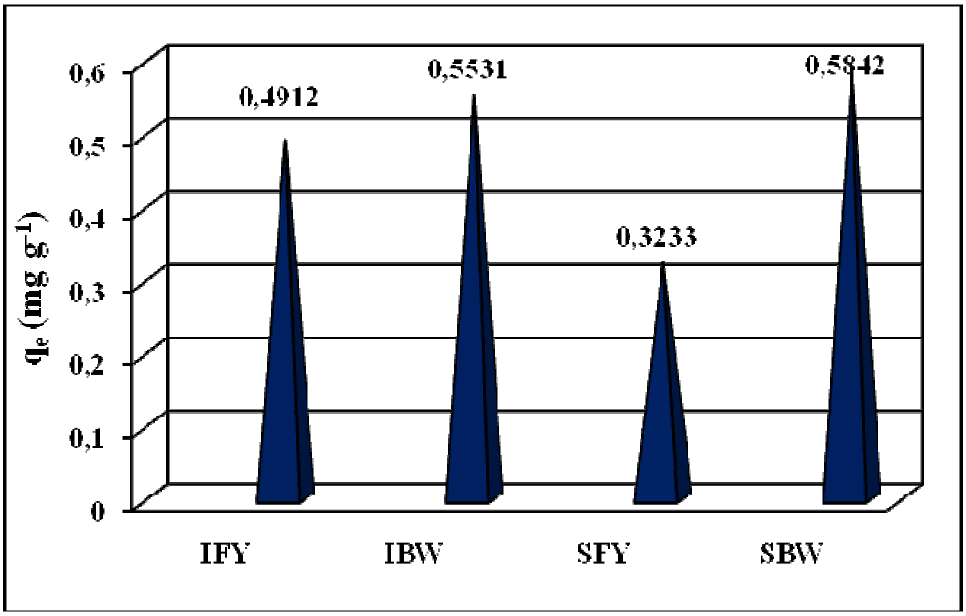

Fig. 4 – Effect of biosorbent type over the adsorption capacity values (q_e, mg Cd^{2+} g^{-1}) at constant temperature (323 K).

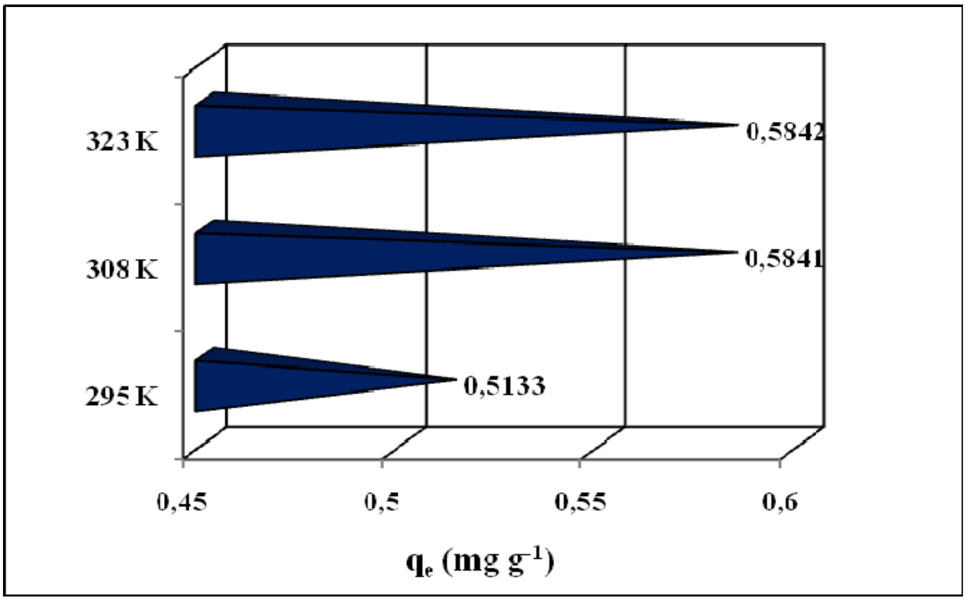

Fig. 5 – Effect of temperature on the adsorption capacity values (q_e, mg Cd^{2+} g^{-1}) for SBW biosorbent.

Biosorption thermodynamic parameters

The thermodynamic parameters for the biosorption process were computed from the $\ln K_d$ vs 1/T plots, figure 6, for a constant yeast quantity (0,978 g and 100 ml cadmium solution), in batch conditions, under magnetic stirring. K_d values calculated as (q_e/C_e) are presented in table 1.

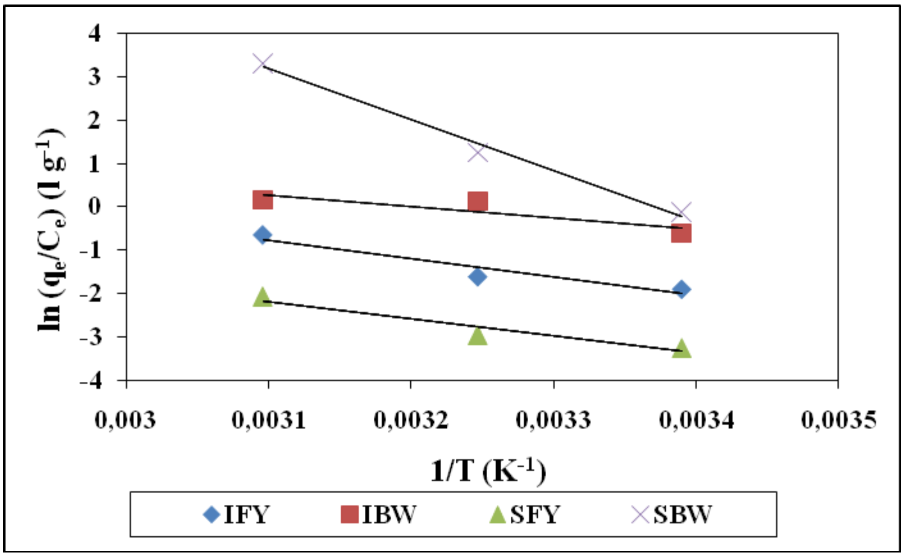

Fig. 6 – Plot of $\ln K_d$ vs 1/T for the estimation of the thermodynamic parameters for Cd(II) biosorption onto SBW, IBW, SFY, and IFY.

Table 1

Distribution coefficient, K_d (l g^{-1}), values calculated at different temperatures (295, 308 and 323 K) for SBW, IBW, SFY, and IFY biosorbents

T, [K]	**K_d, (l g^{-1})**			
	IFY	**IBW**	**SFY**	**SBW**
295	0.1494	0.5434	0.0388	0.7184
308	0.1995	1.1487	0.0522	25.8998
323	0.5276	1.1799	0.1256	27.9084

Cd(II)–biosorbent interactions, at 295-323 K, took place through sufficiently strong endothermic interactions accompanied by thermodynamically favorable entropy and Gibbs energy changes (ΔG°).[17,18]

The enthalpy values for IFY–Cd, IBW–Cd, SFY–Cd, and SBW–Cd interactions vary from 21.8200 to 102.9863 kJ mol^{-1} (table 2). The positive ΔH° values indicate the endothermic nature of the biosorption processes at temperatures between 295 and 323 K.

The corresponding adsorption entropy values are ranging between 0.0697 for IBW and 0.3514 kJ K^{-1} mol^{-1} for SBW, positive values suggesting a certain degree of randomness at the solid–solution interface during the biosorption process.[17] In case of SBW biosorbent the highest value of ΔS° confirms the best results discussed previously in terms of efficiency and adsorption capacity, by a highest randomness degree.

The negative values of Gibbs free energy calculated from experimental results, indicated the fact that the cadmium biosorption process is feasible and spontaneous for IBW at 323 K and for SBW at temperatures varying from 295 to 323 K (table 2). In case of all studied biosorbents the decrease in ΔG° values with increase in temperature shows that the biosorption process is endothermic and it is favored by an increase in temperature.[19]

Table 2

Thermodynamic parameters for Cd(II) biosorption onto SBW, IBW, SFY, and IFY biosorbents (0,978 g yeast, 100 ml cadmium solution, 40 minutes)

Biosorbent material	**ΔS°, (kJ mol^{-1} K^{-1})**	**ΔH°, (kJ mol^{-1})**	**ΔG°, (kJ mol^{-1})**		
			295 K	**308 K**	**323 K**
IFY	0.1047	35.9747	5.0715	3.7097	2.1384
IBW	0.0697	21.8200	1.2547	0.3484	-0.6972
SFY	0.0853	33.4307	8.2422	7.1322	5.8514
SBW	0.3514	102.9863	-0.6785	-5.2468	-10.5179

EXPERIMENTAL

Materials

In our experiments we used four types of biosorbents that contain the same strain, namely *Saccharomyces cerevisiae*, as described bellow: (a) suspended brewery yeast waste biomass (SBW) – the brewery waste biomass was collected from CIUC brewery (Miercurea-Ciuc, Romania) after being used in fermentation processes and transported to the laboratory in plastic containers. The yeast was then washed with bi-distilled water and separated by vacuum filtration, dried in a hot air oven at 80°C for 24 hours; (b) immobilized brewery yeast waste biomass (IBW) – the brewery waste biomass was immobilized using the cross-linking procedure with calcium alginate, an adapted version of the method for treatment of fungi biomass outlined by Schiewer and coworkers;[20,21] (c) suspended fresh yeast (SFY) – commercial baker's yeast produced by Pakmaya (wet); (d) immobilized fresh yeast (IFY) – commercial baker's yeast immobilized using the procedure described above.

For cadmium ions biosorption study we used synthetic monocomponent solutions containing Cd(II) ions (5.75 mg Cd^{2+} l^{-1}), prepared from $Cd(NO_3)_2 \cdot 4H_2O$ salt, analytically pure reagent. Effect of contact time and thermodynamic study of cadmium biosorption were conducted at 295, 308 and 323 K, and constant pH for the synthetic solutions (pH = 5.5). Cadmium ions in solution were determined using an ion-selective electrode pHoenix Electrode Co. and a Jenway 3330 pH meter. The cadmium ions biosorption process was carried out in a batch reactor under magnetic stirring (750 rpm), using 0,978 g *Saccharomyces cerevisae* suspension (SBW, SFY) and alginate immobilized beads (IBW, IFY) within 100 ml cadmium solution of the established concentration. In order to determine the concentration of cadmium ion, water samples were taken every 5 minutes until equilibrium was reached.

In order to establish the effectiveness of the biosorbent samples in the heavy metal ion removal process, removal efficiencies and adsorption capacities were calculated. Removal efficiencies of cadmium ions were calculated using equation (1), while adsorption capacities were calculated with equation (2):

$$E = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_t)}{w} \cdot \frac{V}{1000} \quad (2)$$

where: C_0 is the initial cadmium concentration (mg Cd^{2+} l^{-1}), C_t is time t cadmium concentration (mg Cd^{2+} l^{-}), V = 100 ml, and w is the quantity of yeast (g).

The calculated values of removal efficiencies and adsorption capacities should be considered with respect to the precision of the determination method used.

Biosorption thermodynamics

The thermodynamic parameters were determined using the equilibrium constant, K_d (q_e/C_e), which depends on temperature. The modification in free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) associated with the adsorption process were calculated using the following equations:[17,18]

$$\Delta G^\circ = -RT \ln K_d \quad (3)$$

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4)$$

where: R is the universal gas constant, T is temperature (K), and K_d is the distribution coefficient (l g^{-1}).

According to van't Hoff equation (4), enthalpy (ΔH°) and entropy (ΔS°) parameters can be calculated from the slope and intercept of the plot $\ln K_d$ versus 1/T.

CONCLUSIONS

Bioremediation of heavy metals pollution remains a major challenge in environmental biotechnology. Biosorption of heavy metals is one of the most promising technologies involved in the removal of heavy metals from wastewaters. *Saccharomyces Cerevisiae* was selected for studying biosorption in order to assess the possibility of utilizing a brewery yeast waste biomass (CIUC brewery) for Cd(II) removal from monocomponent synthetic solution.

Yeast collected from two sources, used in two forms (commercial yeast and brewery waste biomass, in suspended and immobilized forms) was investigated in cadmium ions biosorption process. Thermodynamic parameters, including Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption were calculated. The obtained results showed that the biosorption of Cd(II) onto *Saccharomyces Cerevisiae* strain was a feasible, spontaneous and endothermic process in nature. Between the four tested biosorbents, the best efficiency and adsorption capacity was determined for the brewery waste biomass, which could be successfully used as an alternative low-cost biosorbent.

REFERENCES

1. Y. Liu and H. Xu, *Biochem. Eng. J.*, **2007**, *35*, 174-182.
2. J.E.M. Ramiro, P. Rosana and A.R.B. Rui, *Water Res.,* **2004**, *38,* 693-699.
3. ***Romanian Government decisions, HG 188/2002 modified with HG 352/2005.
4. ***Romanian Law 458/2002 modified with Law 311/2004.
5. L. Huang, G. Zeng, D. Huang, L. Li, C. Du and L. Zhang, *Environ. Earth Sci.*, **2009**, DOI 10.1007/s12665-009-0309-3.
6. L. Deng, Y. Su, H. Su, X. Wang and X. Zhu, *Adsorption*, **2006**, *12*, 267-277.
7. F. Veglio, F. Beolchini and A. Gasbarro, *Process Biochem.*, **1997**, *32*, 99-105.
8. J. Choong and H.P. Kwang, *Water Res.,***2005**, *39*, 3938-3944.
9. A. Iyer, K. Mody and B. Jha, *Mar. Pollut. Bull.,* **2005**, *50*, 340-343.
10. Y. Göksungur, S. Üren and U. Güvenç, *Bioresour. Technol.*, **2005**, *96*, 103-109.
11. S. Tunali, T. Akar, A.S. Özcan, I. Kiran and A. Özcan, *Sep. Purif. Technol.*, **2006**, *47*, 105-112.
12. H.K. Hansen, A. Ribeiro, and E. Mateus, *Miner. Eng.*, **2006**, *19*, 486-490.
13. N. Lokeshwari and K. Joshi, *Global J. Envirom. Res.*, **2009**, *3*, 29-35.
14. P.A.S.S. Marques, M.F. Rosa and H.M. Pinheiro, *Bioprocess Biosyst. Eng.,* **2000**, *2*, 135-141.
15. Y-P. Ting and G. Sun, *J. Chem. Technol. Biotechnol.,* **2000**, *75*, 541-546.
16. Q. Yu, J.T. Matheickal and P. Kaewsarn, *Water Res.*, **1999**, *33*, 1534-1537.
17. A. Sari and M. Tuzen, *J. Hazard. Mater.*, **2009**, *164*, 1004-1011.
18. F.A.A. Al-Rub, *Sep. Sci. Technol.*, **2006**, *41*, 3499-3515.
19. N. Lokeshwari and K. Joshi, *Global J. Environ. Res.*, **2009**, *3*, 29-35.
20. S. Schiewer, E. Fourest, K.H. Chong and B. Volesky, *Biohydrometall. Process.: Proceedings of the International Biohydrometallurgy,* **1995**, *2*, 219-228.
21. M. Zhao and J.R. Duncan, *Biotechnol. Lett.*, **1997**, *19*, 953-955.