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Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*: determination of biosorption heats

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Abstract

In this study, the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto inactive *Saccharomyces cerevisiae* was investigated as a function of initial pH, initial metal ion concentration and temperature. The Langmuir model was applied to experimental equilibrium data of Pb(II), Ni(II) and Cr(VI) biosorption depending on temperature and the maximum metal ions uptake at optimum biosorption temperature of 25 °C, were found to be 270.3, 46.3 and 32.6 mg g^{-1}, respectively. Using the Langmuir constant, *b* values obtained at different temperatures, the biosorption heats of Pb(II), Ni(II) and Cr(VI) were determined as −1.125, −1.912 and −2.89 kcal mol^{-1}, respectively. The results indicated that the biosorption of Pb(II), Ni(II) and Cr(VI) ions to *S. cerevisiae* is by the physical adsorption and has an exothermic nature.

Keywords: Biosorption; Biosorption heat; *Saccharomyces cerevisiae*; Langmuir isotherm

1. Introduction

Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of freshwater and marine environment. According to the water standards used in most countries, levels of heavy metal ions in waste water must be controlled and reduced to a set value. Conventional physico-chemical methods for removing heavy metals from waste streams include chemical reduction, electrochemical treatment, ion exchange, precipitation and evaporative recovery. These processes are generally expensive when the initial heavy metal concentrations are in the range of 10–100 mg l^{-1} [1]. Recently,

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Nomenclature

b	a constant related to the energy or net enthalpy of adsorption ($l\,mg^{-1}$)
b_0	constant containing the entropy term
C_0	initial metal ion concentration ($mg\,l^{-1}$)
C_{eq}	residual metal concentration at equilibrium ($mg\,l^{-1}$)
ΔH	biosorption heat ($kcal\,mol^{-1}$)
q_{eq}	adsorbed metal amount per unit mass of dried yeast at equilibrium ($mg\,g^{-1}$)
Q^o	adsorption capacity ($mg\,g^{-1}$)
R	universal gas constant ($1.987\,cal\,mol^{-1}\,K^{-1}$)
R^2	correlation coefficient
T	absolute temperature (K)

Bailey et al. [2] reviewed a wide variety of low cost sorbents for the removal of heavy metals [2]. A low cost sorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry [3]. Biological wastes (microorganisms) obtained from certain industries (brewers, dairy products and pharmaceutical) may be employed as a potential alternative to remove the heavy metals from industrial solutions with remarkable economic advantages [4]. Many bacteria, yeast, algae and other fungi have been successfully used as adsorbing agents for heavy metals [5–13].

There are three general categories that describe the biological process of removing metal ions from solution: biosorption (adsorption) of metal ions onto the surface of a microorganism, intracellular uptake of metal ions and chemical transformation of metal ions by microorganisms. Because the biosorption has been reported as the more rapid mechanism, it has a more significant role in metal sorption from wastewater [14].

Biosorption refers to different modes of non-active metal uptake by microbial biomass, where metal sequestration by cells can take place through adsorption, ion exchange, coordination, complexation, etc. The diffusion of the metal ion from the bulk solution to the microorganism active sites, in non-living biomass, occurs predominantly by passive transport mechanisms. Initially, metal ions diffuse to the surface of the microbial cell where they bind to the active sites on the cell surface formed by the presence of various chemical groups such as carboxylate, hydroxyl, amino and phosphate which exhibit affinity for the metal ions [4]. In living cells, the ion exchange step may be followed by a metabolism-dependent uptake step in which the metal is transported into the cells [15]. The use of dead biomass is advantageous as the process is free from nutrient supply and moreover there are no toxicity constraints in the organism employed [16].

The interaction between the metal ions and the microbial cell functional groups depends not only on the nature of the biosorbent used but also on the solution chemistry of the metal to be removed. pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the heavy metals. The other environmental factor is temperature. Although the effects of pH on biosorption have been widely studied, processes which occur are not completely understood, for instance, the rate limiting step and the heat effect. The magnitude of the heat effect on the biosorption

process is the most important criterion to develop a relationship between thermodynamics and kinetics of the metal–microorganism interaction process.

Temperature changes will affect a number of important factors in heavy metal ion biosorption. Some of the factors include: (i) the stability of the metal ion species initially placed in a solution; (ii) the stability of the metal–microorganism complex depending on the biosorption sites; (iii) the wall configuration of the microorganism cell; (iv) the ionization of chemical moieties on the cell wall [9,12].

The magnitude of the heat effect for the biosorption process is the most important criterion to develop a thermodynamic and kinetic relationship for the metal–microorganism interaction process [9,17]. Various methods were used in the literature to calculate the adsorption heats of many heavy metal ion–adsorbent systems [9]. Singh and Tiwari [18] calculated the enthalpy change in two different ways (free energy changes and the Langmuir constants, b) for Cr(VI)–carbon slurry system and were found to be very close to each another. In another study, uranium biosorption by polyacrylamide-immobilized *S. viridochromogenes* and *C. regularis* was determined to be an overall endothermic process since increased binding occurs as the temperature is increased [19,20]. Biosorption of Cu(II) and Ni(II) ions by *Z. ramigera* and *R. arrhizus* was exothermic while biosorption of Fe(III), Cr(VI) and Pb(II) has endothermic nature [9]. The biosorption of the zinc by *C. crispata* was exothermic with an enthalpy change of $-2.905\,\text{kcal mol}^{-1}$ [21]. While cadmium(II) biosorption process by *C. vulgaris* was evaluated to be exothermic, nickel(II) biosorption to same algae was found as endothermic [10,17].

1.1. Modeling of the biosorption equilibrium

A rapid equilibrium is established between adsorbed metal ions on the microorganism (q_{eq}) and the residual metal ions in the solution (C_{eq}) during the surface adsorption. This equilibrium can be represented by the Langmuir or Freundlich adsorption isotherms, which are widely used to analyze data for water and wastewater treatment applications [22]. The most widely used isotherm equation for modeling equilibrium is the Langmuir equation, based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface, these binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules [22]. The mathematical description of this model is given below:

$$q_{eq} = \frac{Q^o b C_{eq}}{1 + bC_{eq}} \tag{1}$$

where q_{eq} is the adsorbate loading (mg g^{-1}) at equilibrium, C_{eq} the concentration in the fluid (mg l^{-1}), Q^o the adsorption capacity (mg g^{-1}) and b is a constant related to the energy or net enthalpy of adsorption (l mg^{-1}), respectively [23]. Q^o represents a practical limiting adsorption capacity when the surface is fully covered with heavy metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. Q^o and b can be determined from the linear plot of C_{eq}/q_{eq} versus C_{eq} according to Eq. (2):

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q^o b} + \frac{1}{Q^o} C_{eq} \tag{2}$$

1.2. The determination of the biosorption heats

The heat of adsorption can be evaluated from adsorption-equilibrium data. If b values are present at different temperatures, the slopes of $\ln b$ versus $1/T$ lines may be used to calculate the biosorption heats:

$$b = b_0 \exp\left[-\frac{\Delta H}{RT}\right] \tag{3}$$

where b_0 is a constant containing the entropy term, ΔH (kcal mol^{-1}) the heat of adsorption, R a universal gas constant (1.987 cal mol^{-1} K^{-1}) and T is the absolute temperature (K). The magnitude of adsorption heat may give an idea about the type of sorption. Two main types of adsorption may occur, physical and chemical. The adsorption heat for physical adsorption is usually no more than 1 kcal mol^{-1} (4.2 kJ mol^{-1}) since the forces involved in physical adsorption are weak. Chemical adsorption is specific and involves forces much stronger than in physical adsorption. So the adsorption heat for chemical adsorption is of the same magnitude as the heat of chemical reactions, 5–100 kcal mol^{-1} (21–420 kJ mol^{-1}) [24].

In this study, the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *Saccharomyces cerevisiae* was studied in a batch system with respect to the initial pH, initial metal ion concentration and temperature. The biosorption equilibrium was modeled by using the Langmuir isotherm model and isotherm constants were evaluated at different temperatures.

2. Materials and methods

2.1. Microorganism and preparation for biosorption

S. cerevisiae was grown in a shaker incubator at 30 °C and 150 rpm. The liquid medium used for growth contained 6.0 g yeast extract, 15.0 g sucrose, 0.52 g $MgSO_4{\cdot}7H_2O$, 3.0 g K_2HPO_4, 3.76 g NaH_2PO_4, 3.35 g $(NH_4)_2SO_4$, and 0.017 g $CaCl_2{\cdot}4H_2O$ per liter of distilled water. The pH of the medium was adjusted to 4.5 with 1 mol l^{-1} H_2SO_4 and NaOH.

After a growth period of 24 h, *S. cerevisiae* cells were separated from liquid medium by centrifuge. It was washed twice with double-distilled water and then dried at 100 °C for 24 h. For biosorption studies, the amount of dry yeast of 1 g was suspended in the double-distilled water of 100 ml and homogenized in a Waring mixer.

2.2. Chemicals

Lead(II), nickel(II) and chromium(VI) solutions were prepared by diluting 1 g l^{-1} of stock solutions of Pb(II), Ni(II) and Cr(VI) obtained by dissolving a weighed quantity of $Pb(NO_3)_2$, $NiCl_2$ and $K_2Cr_2O_7$ in the double-distilled and deionized water, respectively. The pH of each solution was adjusted to the required value with diluted or concentrated HNO_3 for Pb(II), HCl for Ni(II), H_2SO_4 for Cr(VI) and NaOH solutions before mixing the yeast solution.

2.3. Biosorption studies

The yeast solutions (10 ml) were mixed with 90 ml of the desired metal solutions in the erlenmayer flasks. The flasks were agitated on a shaker at constant temperature and agitating rate for 24 h, which was sufficiently long for adsorption-equilibrium. Samples (3 ml) of solution were taken before mixing the yeast solution and metal-bearing solution, then at 5 min intervals after reaching equilibrium, centrifuged at 7000 rpm (3500 g) for 3 min, then supernatant was used to analyze the metal ions studied. To determine the Langmuir isotherms at different temperature values, the initial metal ion concentrations were changed between 10 and 200 mg l^{-1} while the dry cell weight in each sample was held constant at 1 g l^{-1}.

2.4. Analysis of heavy metal ions

The concentrations of residual Pb(II) and Ni(II) in the biosorption media were determined by using an atomic absorption spectrophotometer, Perkin-Elmer 370 model. The concentration of unadsorbed Cr(VI) in the adsorption medium was determined spectrophotometrically. The colored complex of Cr(VI) ions with diphenly carbazide was read at 540 nm [25].

3. Results and discussion

The biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae* was investigated as a function of the initial pH, initial metal ion concentration and temperature. The results are given as units of adsorbed metal quantity per gram of dried biomass and unadsorbed metal ion concentration in solution at equilibrium, respectively (q_{eq} (mg g^{-1}); C_{eq} (mg l^{-1})).

3.1. The effect of initial pH

pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation are strongly influenced by pH and, on the other side, strongly influence the speciation and the biosorption availability of the heavy metals [26]. In this study, the effects of initial pH on biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae* are investigated in a batch system. The variations of equilibrium Pb(II), Ni(II) and Cr(VI) uptakes with initial pH are given in Fig. 1 for each metal ion at the initial concentration of 200 mg l^{-1}. The maximum equilibrium uptakes for Pb(II), Ni(II) and Cr(VI) ions were found to be 144, 23 and 44.4 mg g^{-1}, at the pH of 5.0, 5.0 and 1.0, respectively. Pb(II) and Ni(II) ions in solution at pH 5.0 appear as a divalent positive ion and are suitable to interact with negatively charged groups in biomass. On the other hand, the outer layer of the cell wall of *S. cerevisiae* consists on a coat protein, that can developed a charge by dissociation of ionizable side groups of the constituent amino acids. The ionic state of ligands such as carboxyl, phosphate, imidazole and amino groups will be to promote reaction with the positively charged metal ions. At low pH, cell wall ligands

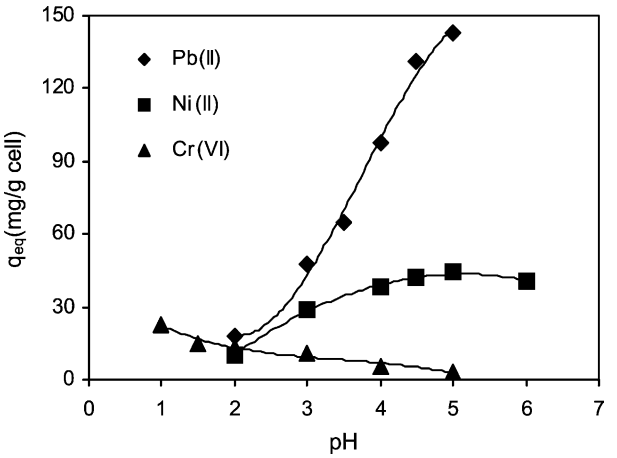

Fig. 1. The effect of initial pH ($C_0 = 200\,\text{mg}\,\text{l}^{-1}$, temperature = 25 °C, dry weight = $1.0\,\text{g}\,\text{l}^{-1}$).

were closely associated with the hydronium ions $[H_3O^+]$ and restricted the approach of metal cations as a result of the repulsive force.

Chromium exhibits different types of pH dependent equilibria in aqueous solutions [16]. At the low pH, the dominant species of Cr(VI) ions in the solution are $[HCrO_4]^-$, $[Cr_2O_7]^{2-}$, $[Cr_4O_{13}]^{2-}$ and $[Cr_3O_{10}]^{2-}$ [16,22,27]. These chromate ion species could be sorbed on the protonated active sites of the biosorbent primarily electrostatically in nature. At very low pH values, the surface of sorbent would also be surrounded by the hydronium ions which enhance the chromium(VI) interaction with binding sites of the biosorbent by greater attractive forces. As the pH increased, however, the overall surface charge on the cells became negative and biosorption decreased. Electrostatic interactions have also been demonstrated to be responsible for chromium biosorption by fungi *Gonaderma lucidum* and *Aspergillus niger* [28,29]. The effect of pH on biosorption of Cr(VI) has been investigated by various investigators using a variety of different biomass types. Optimum biosorptive removal of Cr(VI) at low pH (2.0) has been reported for *Rhizopus nigricans* [16], *Bacillus* sp. [11] and *Dunaliella* sp. [22].

3.2. The effect of temperature

The equilibrium uptakes of Pb(II), Ni(II) and Cr(VI) ions on the inactive yeast were affected by the temperature change (Fig. 2). As seen from Fig. 2, the maximum equilibrium uptakes were found to be at 25 °C. The results indicated that an increase of the temperature in the interval 15–25 °C deals with an increase in the equilibrium uptake capacity of *S. cerevisia* for Pb(II), Ni(II) and Cr(VI) ions. The decrease of the equilibrium uptake capacity in the temperature interval of 25–40 °C means that the biosorption processes of these metal ions by *S. cerevisia* are exothermic. This decrease at higher temperatures may be due to the damage of active binding sites in the biomass.

Previous studies related to biosorption of heavy metals indicated that the effects of temperature on phenomenon of sorption were disparate for different metal–biomaterials systems.

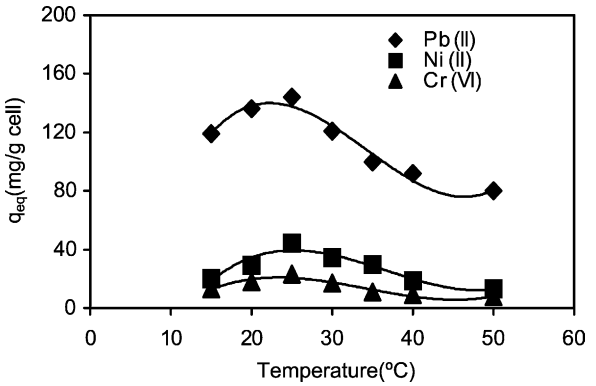

Fig. 2. The effect of temperature ($C_0 = 200\,\mathrm{mg\,l^{-1}}$, dry weight $= 1.0\,\mathrm{g\,l^{-1}}$, initial pH values $= 5.0$ for Pb(II), 5.0 for Ni(II), 1.0 for Cr(VI), respectively).

Similar results have been reported for the sorption of lindane and cadmium ion by chitin [30].

3.3. The Langmuir model

Analysis of the equilibrium data is important to develop an equation which accurately represents the results and which could be used for design purposes. Several isotherm models have been used for the equilibrium modeling of biosorption systems. One of these models is Langmuir model. The linearized Langmuir isotherms of Pb(II), Ni(II) and Cr(VI) ions obtained at the temperatures of 15, 25 and 35 °C and are given in Figs. 3–5, respectively. The experimental data were analyzed by linear regression analysis and then the Langmuir isotherm constants and correlation coefficients are given in Table 1. At all temperature

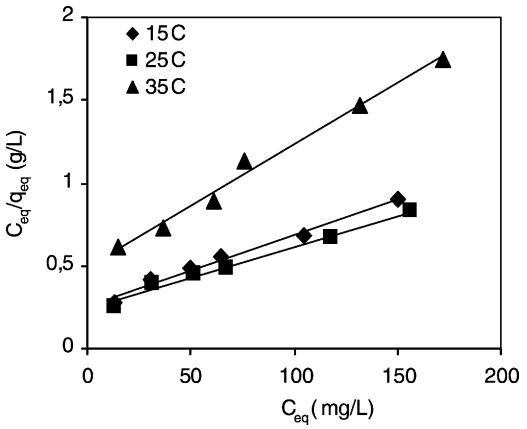

Fig. 3. The Langmuir isotherms for Pb(II) ions (dry weight $= 1.0\,\mathrm{g\,l^{-1}}$, initial pH value $= 5.0$).

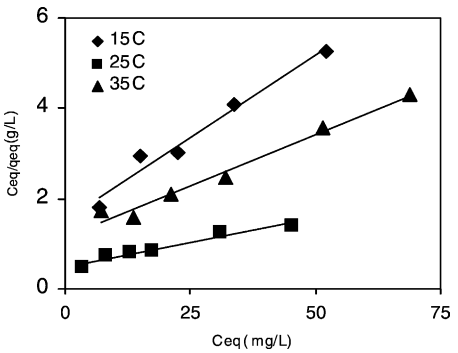

Fig. 4. The Langmuir isotherms for Ni(II) ions (dry weight = 1.0 g l^{-1}, initial pH value = 5.0).

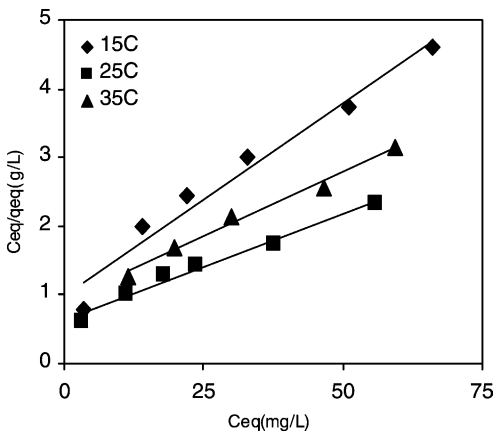

Fig. 5. The Langmuir isotherms for Cr(VI) ions (dry weight 1.0 g l^{-1}, initial pH value = 1.0).

Table 1
The Langmuir isotherm constants and the correlation coefficients at different temperatures

Metal ions	Temperature (°C)	Q^o (mg g^{-1} cell)	b (l mg^{-1})	R^2
Pb(II)	15	232.6	0.0168	0.96
	25	270.3	0.0155	0.98
	35	135.1	0.0149	0.99
Ni(II)	15	13.6	0.04808	0.97
	25	46.3	0.04360	0.96
	35	22.1	0.0389	0.98
Cr(VI)	15	17.9	0.0565	0.97
	25	32.6	0.0478	0.98
	35	26.7	0.04095	0.99

values, q_{eq} was found to be smaller than Q^o indicating that the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae* is occurred by a monolayer type adsorption in which the surface of microorganism is not fully covered.

As seen from Table 1, the maximum metal uptakes for Pb(II), Ni(II) and Cr(VI) ions were found at the temperature of 25 °C. The maximum uptake capacity for Pb(II) ions was significantly higher (270.3 mg g^{-1}) than the other metal ions evaluated: 46.3 mg g^{-1} for Ni(II) and 32.6 mg g^{-1} for Cr(VI) ions. The order of affinity based on a mg accumulation of metal per gram yeast by *S. cerevisiae* is determined as follows: Pb(II) > Ni(II) > Cr(VI). It is observed by comparison of the results that Pb(II) is removed more extensively than Ni(II) and Cr(VI) at the optimum temperature. Differences of metal uptake are due to the chemical structure of each metal and the properties of microorganism such as structure, functional groups and surface area. Holan and Volesky [6] also reported that metal sorption increased with increasing valence and atomic number [6]. The adsorption studies of Pb(II), Ni(II) and Cr(VI) ions have confirmed this report because the order of atomic number of studied metal ions is as follows: ^{82}Pb > ^{28}Ni > ^{24}Cr.

3.4. The biosorption heats for Pb(II), Ni(II) and Cr(VI)

The biosorption heat can be calculated by using the various methods. The biosorption heats of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae* have been calculated by using the Langmuir constants, *b*, related to the energy of adsorption. The biosorption heat has been obtained by calculating the slope of a plot of ln *b* versus 1/*T*, with large slope for large enthalpy change and with small slope for small enthalpy change [31]. The positive values of slope have been obtained (Fig. 6) for the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*. The values of the enthalpy change for Pb(II), Ni(II) and Cr(VI) ions and regression coefficients are summarized in Table 2. As seen from Table 2, very high regression correlation coefficients (>0.95) were found for the metal ions studied. The biosorption heats for Pb(II), Ni(II) and Cr(VI) were determined to be −1.125, −1.912

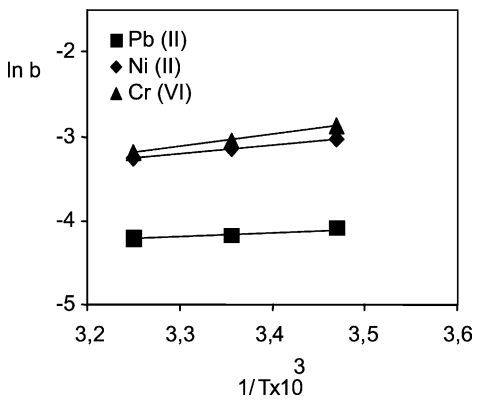

Fig. 6. The determination of biosorption heats (dry weight = 1.0 g l^{-1}, initial pH values = 5.0 for Pb(II), 5.0 for Ni(II), 1.0 for Cr(VI), respectively).

Table 2
The values of the enthalpy change for Pb(II), Ni(II) and Cr(VI) ions and regression coefficients

Metal ion	Adsorption heat (kcal mol^{-1})	R^2
Pb(II)	−1.124	0.9676
Ni(II)	−1.912	0.9958
Cr(VI)	−2.890	0.9998

and $-2.89\,\text{kcal mol}^{-1}$, respectively. These values are of the same magnitude as the heat of physical adsorption. These findings also show that Pb(II), Ni(II) and Cr(VI) biosorption processes by *S. cerevisiae* are exothermic. The biosorption heats of these heavy metal ions decreased in the following sequence: Cr(VI) > Ni(II) > Pb(II). The adsorption with high enthalpy changes are very temperature-sensitive such as the biosorption of Cr(VI) ions, the adsorption with low enthalpy changes are relatively temperature-insensitive such as the biosorption of Pb(II) ions. As also indicated by Smith [24], these results are typical in showing a decreasing the enthalpy change with increasing surface coverage (Tables 1 and 2).

4. Conclusion

The biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae* was studied in a batch system with respect to the initial pH, temperature and initial metal ion concentration. The initial pH and temperature of adsorption media affected the equilibrium uptake Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*. The Langmuir adsorption model was used to represent the experimental data and equilibrium data fitted very well to the Langmuir isotherm model. The maximum uptake capacity for Pb(II) ions was significantly higher ($270.3\,\text{mg g}^{-1}$) than the other metal ions evaluated: $46.3\,\text{mg g}^{-1}$ for Ni(II) and $32.6\,\text{mg g}^{-1}$ for Cr(VI) ions. These results suggested that Pb(II) has greater affinity to the binding sites presented on the surface of *S. cerevisiae*. It was observed that the maximum metal uptakes increased with atomic number to be follows: $^{82}\text{Pb} > {}^{28}\text{Ni} > {}^{24}\text{Cr}$. The biosorption heats were determined as $-1.125\,\text{kcal mol}^{-1}$ for Pb(II), $-1.912\,\text{kcal mol}^{-1}$ for Ni(II) and $-2.89\,\text{kcal mol}^{-1}$ for Cr(VI). The results indicated that the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae* is taken place by physical adsorption and exothermic nature. Consequently, dried *S. cerevisiae* is a good adsorbing agent for metals and especially has a high adsorption capacity for Pb(II) ions.

References

[1] Y.P. Ting, F. Lawson, I.G. Prince, Biotechnol. Bioeng. 34 (1989) 990–999.
[2] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, Water Res. 33 (1999) 2469–2479.
[3] K.S. Low, C.K. Lee, S.C. Liew, Process Biochem. 36 (2000) 59–64.
[4] M.C. Palmieri, O. Garcia Jr., P. Melnikov, Process Biochem. 36 (2000) 441–444.
[5] M. Tsezos, B. Volesky, Biotechnol. Bioeng. 24 (1982) 385–401.
[6] Z.R. Holan, B. Volesky, Biotechnol. Bioeng 43 (1994) 1001–1009.
[7] P. Chen, Y.P. Ting, Biotechnol. Lett. 17 (1995) 107–112.

[8] A. Özer, D. Özer, G. Dursun, S. Bulak, Waste Manage. 19 (1999) 233–240.
[9] Y. Sağ, T. Kutsal, Biochem. Eng. J. 6 (2000) 145–151.
[10] Z. Aksu, Sep. Purif. Technol. 21 (2001) 285–294.
[11] M.N. Nourbakhsh, S. Kılıçarslan, S. İlhan, H. Özdağ, Chem. Eng. J. 85 (2002) 351–355.
[12] G.W. Bedell, D.W. Darnall, Biosorption of Heavy Metals, CRC Press, Boca Raton, 1990, pp. 314–326.
[13] R.R. Karna, L.S. Sajan, P.M. Mohan, Biotechnol. Lett. 18 (1996) 1205–1208.
[14] N. Rangsayatorn, E.S. Upatham, M. Kruatrachue, P. Pokethitiyook, G.R. Lanza, Environ. Pollut. 119 (2002) 45–53.
[15] S.P.K. Sternberg, R.W. Dorn, Bioresource Technol. 81 (2002) 249–255.
[16] S.R. Sudha, T.E. Abraham, Bioresource Technol. 79 (2001) 73–81.
[17] Z. Aksu, Process Biochem. 38 (2002) 89–99.
[18] V.K. Singh, P.N. Tiwari, Chem. Technol. Biotechnol. 69 (1997) 376–382.
[19] A. Nakajima, T. Horikoshi, T. Sakaguchi, Eur. J. Appl. Microbiol. Biotechnol. 16 (1982) 88–94.
[20] L.E. Macaskie, A.C.R. Dean, Advances in Biotechnological Processes: Biolojical Waste Treatment, vol. 12, Alan R. Liss, New York, 1989, pp. 159–201.
[21] D. Özer, A. Özer, G. Dursun, J. Chem. Technol. Biotechnol. 75 (2000) 410–416.
[22] G. Dönmez, Z. Aksu, Process Biochem. 38 (2002) 751–762.
[23] J.R. Weber, Physicochemical Processes for Water Quality Control, Wiley/Interscience, New York, 1972, p. 200.
[24] J.M. Smith, Chemical Engineering Kinetic, third ed., McGraw-Hill, Singapore, 1981, pp. 314–320.
[25] F.D. Snell, C.T. Snell, Colorimetric Methods of Analysis, vol. 2, third ed., Wiley/Interscience, New York, 1961, pp. 400–422.
[26] A. Esposito, F. Pagnanelli, F. Veglio, Chem. Eng. Sci. 57 (2002) 307–313.
[27] J. Lakatos, S.D. Brown, C.E. Snape, Fuel 81 (2002) 691–698.
[28] F. Veglio, F. Beolchini, Hydrometallurgy 44 (1977) 301–316.
[29] C. Venkobachar, Water Sci. Technol. 22 (1990) 319–320.
[30] B. Benguella, H. Benaissa, Water Res. 36 (2002) 2463–2474.
[31] O. Levenspiel, Chemical Reaction Engineering, second ed., Wiley, New York, USA, 1972, pp. 21–29.