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Equilibrium, thermodynamic and kinetic studies on biosorption of Mn(II) from aqueous solution by *Pseudomonas* sp., *Staphylococcus xylosus* and *Blakeslea trispora* cells

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ABSTRACT

Biosorption of Mn(II) from aqueous solutions using *Pseudomonas* sp., *Staphylococcus xylosus* and *Blakeslea trispora* cells was investigated under various experimental conditions of pH, biomass concentration, contact time and temperature. The optimum pH value was determined to 6.0 and the optimum biomass concentration to 1.0 g L^{-1} for all types of cells. Mn(II) biosorption was found to fit better to the Langmuir model for *Pseudomonas* sp. and *B. trispora* and to Freundlich model for *S. xylosus*. Langmuir model gave maximum Mn(II) uptake capacity 109 mg g^{-1} for *Pseudomonas* sp. and much lower, 59 mg g^{-1} and 40 mg g^{-1} for *S. xylosus* and *B. trispora*, respectively. Pseudo-second-order kinetic model was also found to be in good agreement with the experimental results. Thermodynamic parameters of the adsorption confirmed the endothermic nature of sorption process with positive heat of enthalpy, accompanied by a positive value of entropy change. Interestingly, desorption experiments by treating biomass with 0.1 M HNO_3 solution resulted to more than 88% recovery of the adsorbed Mn(II) from *Pseudomonas* sp. and almost 95% and 99% from *S. xylosus* and *B. trispora* cells respectively, thus indicating that Mn(II) can be easily and quantitatively recovered from biomass.

1. Introduction

The majority of toxic metal pollutants are waste products of industrial and metallurgical processes. Their concentrations have to be reduced to meet ever increasing legislative standards. According to the World Health Organization [1], the metals of most concern are cadmium, chromium, cobalt, copper, lead, nickel, mercury and zinc. The effluent from metal finishing processes may contain up to 10 mg L^{-1} of copper, chromium, nickel and zinc. Usually, methods such as chemical precipitation and reverse osmosis are used for the removal of these metal ions from dilute aqueous stream, resulting in incomplete metal removal. Furthermore, these processes have high reagent or energy requirements and generate toxic sludge that requires careful disposal [2].

The biological removal of metals through biosorption has distinct advantages over conventional methods as it rarely produces undesirable chemical by-products, it is highly selective, efficient, easy to operate and cost effective in the treatment of large volumes of wastewater containing toxic heavy metals [3,4]. Algae, fungi, yeast, and bacteria can remove heavy metals from aqueous solutions by binding the cationic metals onto negatively charged functional groups distributed on their cell walls, such as carboxyl and phosphoryl groups [5,6].

The evaluation of bacterial metal-sorbing properties has arisen some controversy. Most of the experiments performed with metals and bacteria really concern metabolically mediated bioaccumulation, while the basic principle of biosorption is the use of dead biomass. According to Volesky and Holan [7], who presented an extensive review on biosorption, the strong biosorbent behavior of certain types of microbial biomass towards metallic ions is a function of the chemical makeup of microbial cells. In fact, the biomass is dead and all cells are metabolically inactive. On the other hand, Beveridge [8] reported that bacteria are excellent biosorbents due to their high surface-to-volume ratios and high content of potentially active chemisorption sites such as teichoic acid in their cell walls.

Other kinds of high metal-sorbing biomass such as yeast have been also used. However, the most common yeast biomass (*Saccharomyces cerevisiae*) is not usually a waste, but a commercial commodity (feed-lot uses). Some chemical compounds of yeast cells can also act as ion exchangers with rapid reversible binding of cations [9].

When choosing biomass for biosorption experiments, its origin has to be taken into consideration. Biomass from industrial wastes should be free of charge, easily available in large amounts in nature and organisms of quick

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growth, specifically cultivated or propagated for biosorption purposes [10].

In the present study, adsorption of Mn(II) ions onto *Pseudomonas* sp., *Staphylococcus xylosus* and *Blakeslea trispora* cells was investigated systematically under various conditions of pH, biomass dosage, contact time and temperature. The kinetics of adsorption, the relative thermodynamic parameters were examined and Langmuir and Freundlich isotherms were used to analyze the equilibrium data.

2. Methods

2.1. Bacteria, fungi and media

As in previous work was referred [11], *Pseudomonas* sp. and *S. xylosus* were cultivated in Luria–Bertani broth containing 1% tryptone, 0.5% yeast extract and 0.5% NaCl (Scharlau Chemie, Barcelona, Spain) at 301 K, using shake flasks in a water bath at 100 rpm (Clifton SWB-NE5-28). Cells were harvested by centrifugation (4500 rpm; 20 min), at the static phase of growth, after 24 h of incubation. Biomass washed with 9‰ NaCl solution for the removal of impurities was used in batch experiment studies. Moisture content was determined by drying a pre-weighted amount of cells in an oven at 373 K for 10 h.

B. trispora cells were grown separately in Petri dishes with PDA (Potato Dextrose Agar) for 3 days at 299 K as reported [12]. The batch cultivation experiments were carried out in 0.5 L Erlenmeyer flasks, with media composition (g/l): corn steep liquor 80.0 (Tyte & Lyle, Thessaloniki, Greece), casein hydrolysate 2.0, yeast extract 1.0, KH_2PO_4 1.5, $MgSO_4{\cdot}7H_2O$ 0.5 (Scharlau Chemie, Barcelona, Spain), L-asparagine 2.0 (Fluka Chemicals, Buchs, Switzerland), BHT 0.02, Span 20 10.0, Tween 80 1.0, thiamine–HCl 0.005 (Sigma Chemicals Co., St. Louis, MO, USA), starch 50.0 (Mallinckrodt J.T. Baker, Phillipsburg, New Jersey, USA) and 0.67% (v/v) from each oil (olive, soybean and sunflower). The initial pH for all cultures was adjusted to 7.5. The flasks were placed into shaker at 200 rpm at 299 K for 12 days [12]. After cultivation, moisture was removed by placing the cells in an oven at 333 K for 24 h.

2.2. Preparation of metal solutions

Test solutions containing single Mn(II) were prepared from $MnSO_4{\cdot}H_2O$ (Merck Chemicals Co., Darmstadt, Germany) at concentrations ranging from 50 to 500 mg L^{-1}. The pH of each test solution was adjusted to the appropriate value by using 0.01 M HCl or 0.01 M NaOH solutions after the addition of biomass. During the process pH values were recorded and noticeable changes had not been found.

2.3. Biosorption experiments

To determine optimum pH range, biomass concentration, contact time and temperature, Mn(II) solutions of 100 mg L^{-1} were used. The effect of pH was investigated in the range of 3.0–7.0, biomass in the range of 1.0–4.0 g as dry biomass L^{-1} of solution and the optimum values were used in the batch experiments. In all experiments biomass was used in slurry form meaning that moisture had been previously estimated. The effect of temperature was also investigated in the range of 288–318 K. Cell suspensions were mixed with the metal solutions and agitated on a shaking bath at 150 rpm for 180 min. Samples were taken, the biomass was separated from metal solutions by centrifugation at 4500 rpm for 5 min and the metal content in the supernatant was determined. The metal uptake was calculated according to the equation:

$$q = \frac{V(C_o - C_{eq})}{M} \quad (1)$$

where q is the metal uptake (mg g^{-1}); C_o and C_{eq} are the initial and equilibrium metal concentrations in the solution (mg L^{-1}) respectively; V is the volume of solution (L); and M is the mass of biosorbent (g). All experiments were performed in duplicates.

2.4. Kinetic and equilibrium studies

Zero order, first order, pseudo-first-order, pseudo-second-order, Elovich model and intraparticle diffusion model rate equations have been used for modeling the kinetics of Mn(II) biosorption. To examine the relationship between sorbed and aqueous concentration at equilibrium, two-parameter sorption isotherm models as Langmuir and Freundlich were used for fitting the data.

2.5. Thermodynamics

ΔG^o is the fundamental criterion of spontaneity. Reaction occurs spontaneously at given temperature if the value of ΔG^o is negative. ΔG^o can be determined from the following equation:

$$\Delta G^o = -RT \ln b \quad (2)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), b the Langmuir constant and T is the absolute temperature.

The relation between ΔG^o, ΔH^o and ΔS^o is given by the following equations:

$$\Delta G^o = \Delta H^o - T\ \Delta S^o \quad (3)$$

Eq. (3) can also be written as

$$-RT \ln b = \Delta H^o - T\ \Delta S^o \quad (4)$$

or

$$\ln b = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (5)$$

where ΔH^o and ΔS^o values can be obtained from the slope and the intercept of the plot $\ln b$ versus $1/T$ [13].

2.6. Metal desorption

Sorption experiments were conducted at optimum pH values by mixing 50 mg L^{-1} of Mn(II) solutions with 1.0 g L^{-1} of the sorbent. Then the samples were collected, centrifuged and analyzed for Mn(II). For desorption experiments, the Mn(II) loaded biomass was taken and treated with 50 mL of 0.1 M HNO_3 solution for 180 min. The HNO_3 extract was then collected and analyzed for Mn(II).

2.7. Analysis

Mn(II) concentration was determined using a flame atomic adsorption spectrophotometer Perkin–Elmer, model AAnalyst 800.

3. Results and discussion

3.1. pH effect

For biosorption of heavy metal ions, pH is one of the most important environmental factors. The pH value of solution strongly influences not only the site dissociation of the biomass' surface, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions,

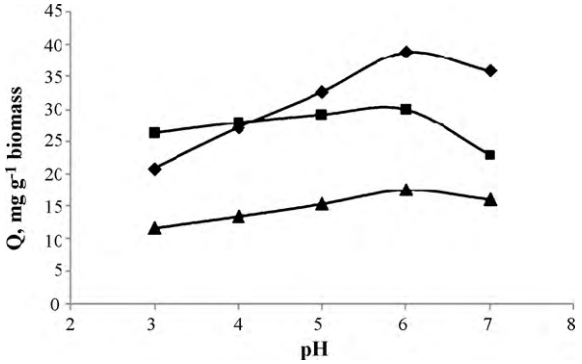

Fig. 1. Effect of pH on Mn(II) biosorption using *Pseudomonas* sp. (♦), *Staphylococcus xylosus* (■) and *Blakeslea trispora* (▲) cells. Initial Mn(II) concentration 100 mg L^{-1}, contact time 180 min and biomass concentration 1.0 g L^{-1}.

precipitation, the speciation and the biosorption availability of the heavy metals [14].

Cell wall contains several functional groups such as amines, amides, and carboxyl that are protonated or deprotonated, depending on the pH of the aqueous medium [15]. At low pH values, several functional groups of the cell's wall such as amine, phosphonate, sulphonate, carboxyl, and hydroxyl groups are probably associated with the hydrogen ions, and the overall surface charge on the microorganisms becomes positive [16]. Rise of pH increases the negative charge at the surface of the cells until all relevant functional groups are deprotonated, which favors electrochemical attraction and adsorption of cations.

Metal uptake by the biomass in all cases was increased with increasing pH and reached a maximum value after which it began to decrease. As it can be seen from Fig. 1, the optimal pH value for Mn(II) biosorption was 6.0 for all types of cells suggesting that the adsorption of metals onto the biomass could be ruled by ionic attraction. Most specifically, at low pH values the inactivated cell surface becomes more positively charged, reducing the attraction between metal ions and functional groups on the cell wall whereas, at higher pH values cell surface is becoming more negatively charged and the process of retention is favored. However, at pH values higher than the optimal, a decrease on metals biosorption was found, indicating that the hydrolysis of cations probably reverses the charge of cell's surface according to the following general equation:

$$M^{2+} \xrightarrow{[OH^-]} MOH^{+} \xrightarrow{[OH^-]} M(OH)_2 \xrightarrow{[OH^-]} M(OH)_3^{-} \xrightarrow{[OH^-]} M(OH)_4^{2-}$$

This charge reversal occurs in the pH range where the divalent (M^{2+}) changes to the monovalent hydroxylated cation (MOH^{+}) [17]. Therefore, pH = 6.0 was selected for all further studies.

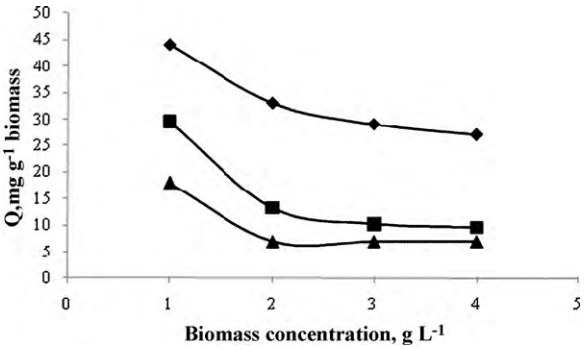

Fig. 2. Effect of biomass concentration on Mn(II) biosorption using *Pseudomonas* sp. (♦), *Staphylococcus xylosus* (■) and *Blakeslea trispora* (▲) cells. Initial Mn(II) concentration 100 mg L^{-1}, contact time 180 min, pH = 6.0.

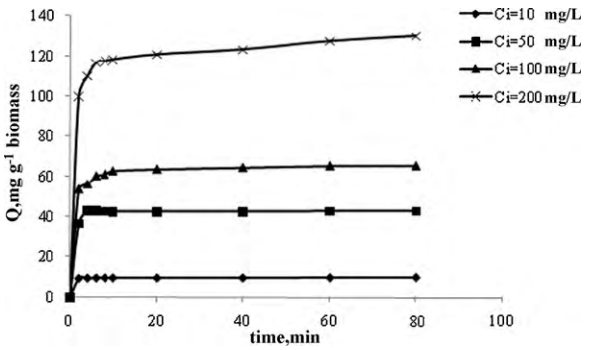

Fig. 3. Effect of contact time on Mn(II) biosorption using *Pseudomonas* sp. cells. Biomass concentration 1.0 g L^{-1}, pH = 6.0.

3.2. Effect of biomass concentration

Mn(II) removal at constant initial concentration of 100 mg L^{-1}, at different adsorbent doses (1.0–4.0 g L^{-1}) was studied at 298 K and pH = 6.0. Fig. 2 shows that the biosorption capacity of metal ions is inversely proportional to biomass concentration, when the initial concentration of metal ions is kept constant, and tends to a constant value for biomass concentrations over 4.0 g L^{-1}. This observation has also been reported by other authors [18]. However, increase of the biomass concentration results in reducing the equilibrium concentration of metal solution due to the fact that there are more available sites for interaction on biomass. The increase of the sorbent dose to 4.0 g L^{-1} reduced the equilibrium concentration in all types of cells around 18–25 mg L^{-1}, with better results for *Pseudomonas* sp. cells.

3.3. Effect of contact time

Experimental studies for investigating the effect of contact time were carried out at constant temperature (299 K) with varying initial metal ion concentrations of Mn(II) (10, 50, 100, 200 mg L^{-1}) using 1.0 g L^{-1} adsorbent dosage at pH = 6.0. In Figs. 3–5 is illustrated the effect of contact time on Mn(II) biosorption for the above initial metal concentrations. The equilibrium time of Mn(II) biosorption onto *Pseudomonas* sp. cells seems to be independent from the initial Mn(II) concentration due to the fact that in all cases the equilibrium is reached within 10 min (Fig. 3). The same conclusion can be taken out for the case of *S. xylosus* cells (Fig. 4). In both cases the biosorption capacity increased with contact time rapidly and thereafter it proceeded at a lower rate and finally attained equilibrium. This result is important because equilibrium time is one of the parameters for economical wastewater treatment plant application [19]. This behavior suggests that at the initial stage,

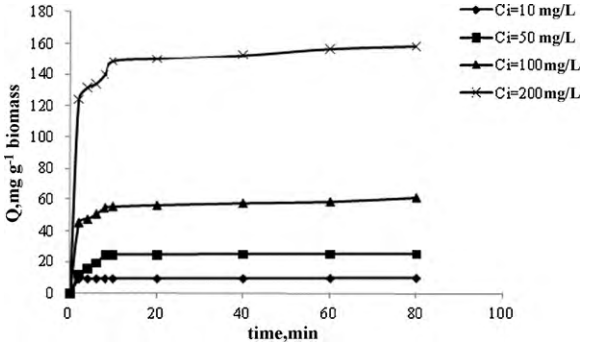

Fig. 4. Effect of contact time on Mn(II) biosorption using *S. xylosus* cells. Biomass concentration 1.0 g L^{-1}, pH = 6.0.

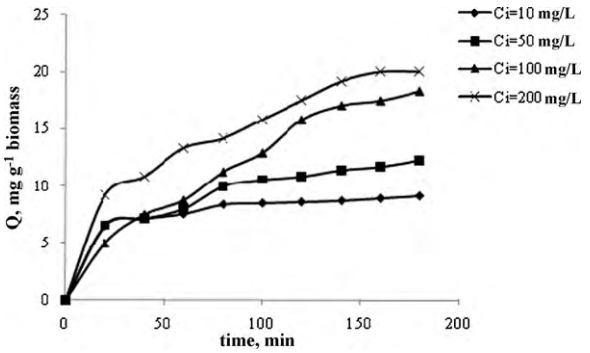

Fig. 5. Effect of contact time on Mn(II) biosorption using *B. trispora* cells. Biomass concentration 1.0 g L^{-1}, pH = 6.0.

adsorption takes place rapidly on the external surface of the adsorbent followed by a slower internal diffusion process, which may be the rate-determining step.

In the case of *B. trispora* cells, the equilibrium time of biosorption depends from the initial Mn(II) concentration. From Fig. 5, it is evident that when the initial concentration increases, the equilibrium time is longer. While at low initial concentrations the equilibrium time is around 50 min, at higher concentrations the equilibrium time seems to be prolonged to 150 min.

3.4. Kinetic studies

In order to examine the mechanism of biosorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to describe the data.The linear pseudo-first-order equation [20] is given as follows:

$$\log(q_{e,1} - q_t) = \log q_{e,1} - \frac{k_1}{2.303} t \quad (6)$$

where q_t and $q_{e,1}$ are the amounts of Mn(II) adsorbed at time t and equilibrium (mg g^{-1}), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). The values of pseudo-first-order rate constants, k_1, and equilibrium biosorption capacities, $q_{e,1}$, for each initial copper concentration and for any type of cell were calculated from slopes and intercepts of straight lines. Fig. 6 presents the plots for *Pseudomonas* sp. at all initial Mn(II) concentrations. The values of pseudo-first-order equation parameters together with correlation coefficients are given in Tables 1–3 for *Pseudomonas* sp., *S. xylosus* and *B. trispora* cells, respectively. The correlation coefficients for the pseudo-first-order equation obtained at all the studied concentrations were low. Also the theoretical $q_{e,1}$ values found from the pseudo-first-order equation did

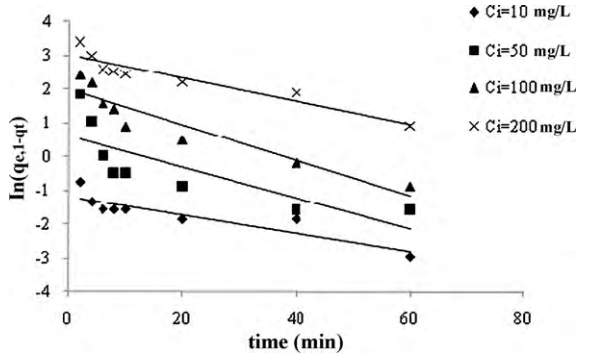

Fig. 6. Plot of the pseudo-first-order equation for the biosorption kinetics of Mn(II) on *Pseudomonas* sp. cells at different initial concentrations. Biomass concentration 1.0 g L^{-1}, pH = 6.0.

Table 1
First- and second-order equations, the intraparticle diffusion model and the Elovich equation rate constants, calculated and experimental q_e values for different initial copper concentrations for the case of *Pseudomonas* sp. cells.

C_o (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order equation			Pseudo-second-order equation			Elovich equation			Intraparticle diffusion equation	
		k_1 (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	α (mg g^{-1} min^{-1})	β (g min^{-1})	R^2	k_{int} (mg g^{-1} $min^{-1/2}$)	R^2
10	9.68	0.06	3.25	0.8	0.49	9.68	1	$3.7\ 10^{40}$	10.36	0.85	0.04	0.75
50	42.70	0.71	10.06	0.91	0.1	43.1	1	$21.9\ 10^{8}$	0.56	0.83	0.7	0.71
100	65.42	0.12	7.31	0.88	0.03	65.79	1	$6.63\ 10^{23}$	0.34	0.85	1.24	0.68
200	130	0.08	20.28	0.88	0.008	129.87	1	$17.16\ 10^{6}$	0.15	0.9	2.97	0.78

Table 2
First- and second-order equations, the intraparticle diffusion model and the Elovich equation rate constants, calculated and experimental q_e values for different initial copper concentrations for the case of *S. xylosus* cells.

C_o (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order equation			Pseudo-second-order equation			Elovich equation			Intraparticle diffusion equation	
		k_1 (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	α (mg g^{-1} min^{-1})	β (g min^{-1})	R^2	k_{int} (mg g^{-1} min$^{-1/2}$)	R^2
10	8.75	0.24	2.83	0.83	0.09	8.84	0.99	$3.4\ 10^3$	1.43	0.88	0.3	0.73
50	24.5	0.75	31.88	0.89	0.02	25.97	0.99	62.53	0.25	0.78	1.73	0.53
100	60.83	0.06	10.63	0.76	0.01	60.60	0.99	$3.7\ 10^5$	0.26	0.9	1.67	0.77
200	158.33	0.1	27.48	0.91	0.006	158.73	0.99	$4.72\ 10^6$	0.11	0.93	4.02	0.81

Table 3
First- and second-order equations, the intraparticle diffusion model and the Elovich equation rate constants, calculated and experimental q_e values for different initial copper concentrations for the case of *B. trispora* cells.

C_o (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order equation			Pseudo-second-order equation			Elovich equation			Intraparticle diffusion equation	
		k_1 (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	α (mg g^{-1} min^{-1})	β (g min^{-1})	R^2	k_{int} (mg g^{-1} min$^{-1/2}$)	R^2
10	9.06	0.04	3.8	0.95	0.008	9.58	0.99	11.69	0.82	0.97	0.29	0.95
50	12.25	0.04	9.05	0.93	0.002	14.38	0.98	2.80	2.81	0.94	0.68	0.96
100	18.33	0.05	27.88	0.93	0.0002	31.74	0.93	78.15	0.15	0.94	1.60	0.98
200	20	0.04	22.02	0.92	0.0007	26.31	0.97	27.46	0.18	0.95	1.36	0.99

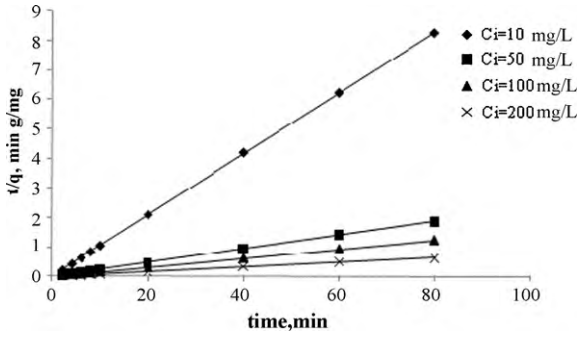

Fig. 7. Plot of the pseudo-second-order equation for the biosorption kinetics of Mn(II) on *Pseudomonas* sp. cells at different initial concentrations. Biomass concentration 1.0 g L^{-1}, pH = 6.0.

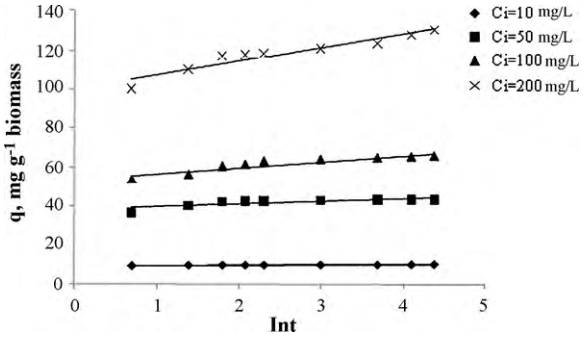

Fig. 8. Plot of the Elovich equation for the biosorption kinetics of Mn(II) on *Pseudomonas* sp. cells at different initial concentrations. Biomass concentration 1.0 g L^{-1}, pH = 6.0.

not give reasonable values. This suggests that this biosorption system is not a first-order reaction.

The linear pseudo-second-order equation [20] is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{1}{q_{e,2}} t \quad (7)$$

where k_2 is the equilibrium rate constant of pseudo-second-order biosorption (g mg^{-1} min^{-1}). From the values of pseudo-second-order equation parameters and the correlation coefficients, it is observed that there is agreement between them and the experimental data. The correlation coefficients were 1 and 0.99 for the *Pseudomonas* sp. and *S. xylosus* cells, respectively, at all initial concentrations. In the case of *B. trispora* cells, the correlation coefficients were lower than in the case of the other two types of cells and the calculated values of $q_{e,2}$ presented small deviation from the experimental data (Table 3), especially at high initial concentrations. These results strongly suggest that the biosorption of Mn(II) onto *Pseudomonas* sp. and *S. xylosus* cells is most appropriately represented by a pseudo-second-order rate process (Fig. 7).

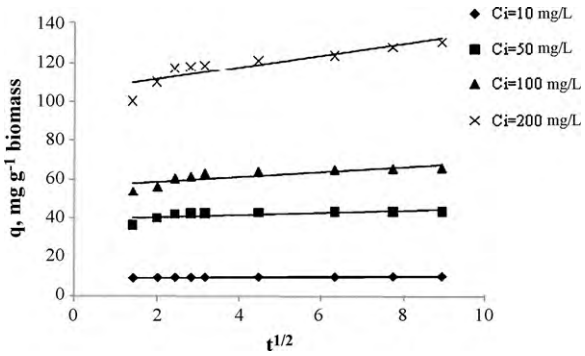

Fig. 9. Plot of the intraparticle diffusion equation for the biosorption kinetics of Mn(II) on *Pseudomonas* sp. cells at different initial concentrations. Biomass concentration 1.0 g L^{-1}, pH = 6.0.

The adsorption data may also be analyzed using the Elovich equation [21], which has the linear form:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (8)$$

where α is the initial sorption rate constant (mg g^{-1} min^{-1}), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}). Fig. 8 shows the plots of the linear form of Elovich equation for *Pseudomonas* sp. and Tables 1–3 present the parameters of this equation and the correlation coefficients, which vary between 0.78 and 0.97. These values are much lower than these for the pseudo-second-order equation and as a result the Elovich equation cannot be used to describe the kinetics of Mn(II) biosorption onto the three types of cells.

Due to the fact that Eqs. (6) and (7) cannot interpret the diffusion mechanism, the intraparticle diffusion model [22] was also tested. The initial rate of the intraparticle diffusion is the following:

$$q_t = k_{int} t^{1/2} \quad (9)$$

where k_{int} is the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$). Such plots may present a multilinearity [23] indicating that two or more steps take place. The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution.

Fig. 9 shows that the first step of external surface adsorption is absent. The external surface adsorption is completed very rapidly and then the stage of intraparticle diffusion control (stage 2) is attained and continues up to 5 min for *Pseudomonas* sp. Then Mn ions are slowly transported via intraparticle diffusion into the particles and are finally retained in the micropores. Same conclusions were extracted also in the case of *S. xylosus* and *B. trispora* cells. The correlation coefficients obtained for these two types of cells are low in contrast to *B. trispora* cells which are higher (Tables 1–3). However, as shown in Fig. 9, the plot does not pass through the origin, showing that the intraparticle diffusion is not the rate-determining step.

3.5. Thermodynamics

For the thermodynamic studies, the pH of the biosorption media was kept constant at the optimum pH value for each metal ion–microorganism system. The reason for that was the insignificant changes of pH during adsorption process. The adsorption experiments were then developed for different temperatures ranging from 288 to 318 K. The q values for different temperatures, at the optimum pH value, are presented in Fig. 10. As it can be seen, all systems present an increase in biosorption capacities as the temperature increases up to 308 K, suggesting an endothermic process for the systems. Interestingly, a noticeable decrease in biosorption capacity was observed above that temperature, possibly due to the destruction of binding sites on cell's surface at these temperatures.

The thermodynamic parameters such as the enthalpy change (ΔH^o), the entropy change (ΔS^o) and the free energy change of the sorption (ΔG^o) were calculated and presented in Table 4. As it can be seen, the values of ΔH^o calculated are positive in all cases, which enhances the previous assumption that biosorption in these cases is an endothermic process. One possible explanation of endothermicity of the enthalpy of adsorption is that Mn(II) are well solvated in water. In order for these ions to adsorb, they are to some

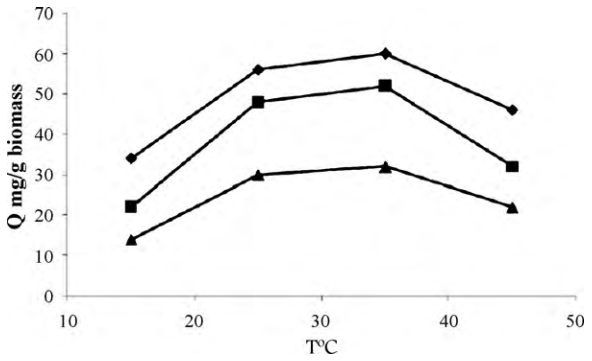

Fig. 10. Biosorption capacity values for Mn(II) biosorption on *Pseudomonas* sp. (♦), *Staphylococcus xylosus* (■) and *Blakeslea trispora* (▲) cells in different temperatures. Biomass concentration 1.0 g L^{-1}, pH = 6.0, contact time 180 min.

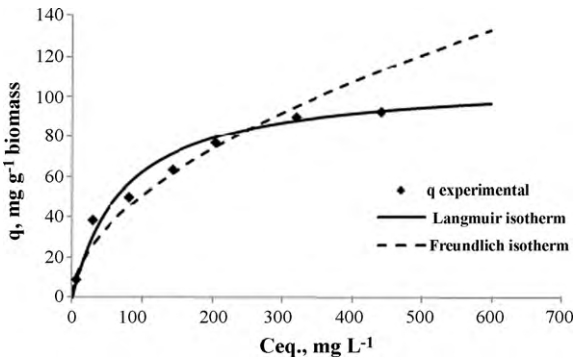

Fig. 11. Biosorption capacity values for Mn(II) biosorption on *Pseudomonas* sp. cells in different equilibrium concentrations. Comparison with Langmuir and Freundlich model. Biomass concentration 1.0 g L^{-1}, pH = 6.0, contact time 180 min.

extent denuded of their hydration sheath and this dehydration process requires energy. It is assumed that this energy of dehydration exceeds the exothermicity of the ions attaching to the surface. The implicit assumption here is that after adsorption the environment of the metal ions is less aqueous than it was in the solution state. The removal of water from ions is essentially an endothermic process, and it appears that endothermicity of the desolvation process exceeds that of enthalpy of adsorption considerably [20].

Comparing the heats of biosorption presented in this study with the heats of physical and chemical adsorption, the following can be concluded. The heat evolved during the physical adsorption process of 10 kJ mol^{-1} [24] is in the range of the heat of condensation (2.1–20.9 kJ mol^{-1}). Equilibrium between the cell surface and the metal ions is usually rapidly attained and easily reversible, because the energy requirements are small. In this study, the heats of biosorption of Mn(II) on *Pseudomonas* sp. and *S. xylosus* cells were found to be of the same order as the heat of chemisorption whereas the heat of biosorption on *B. trispora* cells is lower and in the range of physical adsorption (Table 4).

ΔS^o can also be calculated from the intercept of the plot ln b versus $1/T$. The positive values of ΔS^o suggest increased randomness at the solid/solution interface during the adsorption of metal ions onto adsorbent in all cases.

ΔG^o was calculated from Eq. (2) and the results are presented in Table 4. In all cases, ΔG^o values observed were positive, further enhancing that biosorption process is not spontaneous and the temperature rising gives the energy needed.

3.6. Adsorption isotherms

The Langmuir adsorption isotherm has been traditionally used to quantify the performance of different biosorbents. Its use was further extended to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase [25]. The Langmuir model isotherm is given by Eq. (10):

$$q = \frac{q_{max} b_L C_e}{1 + b_L C_e} \quad (10)$$

where q_{max} is the maximum metal uptake (mg g^{-1}) and b_L the Langmuir equilibrium constant (L mg^{-1}) that represents the affinity between the sorbent and sorbate. High b_L values are reflected in the steep initial slope of a sorption isotherm, indicating high affinity. Thus, a good biosorbent, is characterized by high q_{max} value and a steep initial isotherm slope [25].

The Freundlich isotherm is originally empirical in nature and is given by Eq. (11):

$$q = K_F C_e^{1/n} \quad (11)$$

where K_F is the Freundlich constant (L g^{-1}) and n is the Freundlich exponent [26]. The intercept K_F is an indication of the adsorption capacity of the adsorbent; the slope $1/n$ indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity. The forces within the surface layer are attractive if n is less than unity and repulsive if n is greater than unity [7,26].

Mn(II) sorption performance of *Pseudomonas* sp., *S. xylosus* and *B. trispora* cells was ascertained by the biosorption isotherms at concentrations of 10–500 mg L^{-1}. For *Pseudomonas* sp., Mn(II) sorption was linearly increased with the equilibrium concentration up to 200 mg Mn(II) L^{-1}, corresponding to uptake of 80 mg Mn g^{-1} (Fig. 11). Afterwards, Mn(II) uptake was linearly increased up to q = 90 mg Mn g^{-1} at the equilibrium concentration of 450 mg L^{-1} (Fig. 11). The Langmuir and Freundlich adsorption constants, calculated from linearization of the corresponding isotherms, and the correlation coefficients are presented in Table 5. From these values and Fig. 11 it is obvious that the experimental data fit better to Langmuir isotherm model. The q_{max} value calculated was 109 mg Mn(II) g^{-1}, which is much higher than other reported for Mn(II) biosorption: 19.34 and 18.95 mg g^{-1} for *Aspergillus niger* and *S. cerevisiae*, respectively [27], 66 mg g^{-1} for a thermally decomposed leaf [28], 5.83 mg g^{-1} for *Pseudomonas aeruginosa* [29]. Some species of *Pseudomonas* have been used in biosorption of heavy metals such as, *P. aeruginosa* PU21 for Cu(II), Cd(II) and Pb(II) biosorption [30] and *Pseudomonas putida* for Cu(II), Cd(II), Pb(II) and Zn(II) biosorption [31]. In all these cases the biosorption capacity was lower than that calculated in *Pseudomonas* sp.–Mn(II) system. Taking into consideration all these data, it seems that *Pseudomonas* sp. constitutes a very good biosorbent material for manganese removal.

In *S. xylosus* case, the experimental data seem to fit better in Freundlich isotherm equation (Table 5). The correlation coefficient is very high (R^2 = 0.99) for Freundlich model and the K_F constant shows high affinity between Mn(II) and *S. xylosus*. However,

Table 4
Differences of enthalpy (ΔH^o), entropy (ΔS^o) and Gibb's free energy (ΔG^o) for the biosorption of Ni(II) and Mn(II) on the examined cells.

	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1} K^{-1})	ΔG^o (298 K) (kJ mol^{-1})	ΔG^o (308 K) (kJ mol^{-1})	ΔG^o (318 K) (kJ mol^{-1})	ΔG^o (328 K) (kJ mol^{-1})
Pseudomonas sp.–Mn(II)	31.7	79.9	7.77	9.25	7.3	5.6
S. xylosus–Mn(II)	28.34	69	7.18	9.23	8.2	5
B. trispora–Mn(II)	15.28	20	9.57	8.89	9.49	8.7

Table 5
Langmuir and Freundlich constants for Mn(II) biosorption.

	Langmuir constants			Freundlich constants		
	q_{max} (mg g^{-1})	b ($\times 10^{-3}$ L mg^{-1})	R^2	K_F (L g^{-1})	$1/n$	R^2
Pseudomonas sp.	109	13	0.99	4.30	0.536	0.93
S. xylosus	59	26	0.97	3.22	0.533	0.99
B. trispora	40	16	0.98	1.75	0.539	0.96

Table 6
Desorption and re-adsorption efficiencies of Mn(II) on *Pseudomonas* sp., *Staphylococcus xylosus* and *Blakeslea trispora* cells in four cycles. Initial concentration 50 mg L^{-1}, biomass concentrations 1.0 g L^{-1}, pH = 6.0, contact time 180 min.

Number of cycles	Cells								
	Pseudomonas sp.			*S. xylosus*			*B. trispora*		
	Sorption (mg Mn g^{-1})	Desorption (mg Mn g^{-1})	Desorption (%)	Sorption (mg Mn g^{-1})	Desorption (mg Mn g^{-1})	Desorption (%)	Sorption (mg Mn g^{-1})	Desorption (mg Mn g^{-1})	Desorption (%)
I	43.3	38.3	88.5	36.2	34.3	94.8	15	14.9	99.7
II	12.5	10	83.3	10.4	11.2	91.5	13.9	12.5	89.2
III	11.6	11	82.4	8.8	9.2	95.7	12.9	11.7	80.9
IV	9.8	9.6	80	7.9	8.8	98	11.6	10.6	73.7

the maximum biosorption capacity calculated from the Langmuir model is lower in *S. xylosus* (q_{max} = 59 mg g^{-1}) than in *Pseudomonas* sp. *S. xylosus* has also been used in Cr(VI), Cd(II) [32] and Ni(II) [11] biosorption with very good results.

B. trispora has shown the lower affinity with Mn(II). As it can be seen from Table 5 the maximum biosorption capacity for *B. trispora* is 40 mg g^{-1}. The correlation coefficients for the two models show that the experimental data fit better to Langmuir model (Table 5). The K_F constant of Freundlich model was lower than the respective constant of the other two types of cells (Table 5). *B. trispora* was used for the first time for biosorption of heavy metals.

3.7. Desorption experiments

Recovery of metals sorbed onto the biomass is one of the important aspects of any successful biosorption process development [33]. In an attempt to determine the percentage of Mn(II) recovery from *Pseudomonas* sp., *S. xylosus* and *B. trispora* cells, biomass was treated with 0.1 M HNO_3 solution. As it is shown in Table 6, more than 88% of Mn(II) adsorbed by *Pseudomonas* sp. was released into the HNO_3 solution at the first cycle. These results are of interest since the removal of Mn(II) from aqueous solution and its recovery can be accomplished in two fast steps. Another series of experiments was conducted with the resultant biomass, which was used again for sorption and desorption experiments in three more cycles. As it is indicated in Table 6, after the first cycle *Pseudomonas* sp. presented a gradual reduction of its biosorption ability may be due to the fact that HNO_3 solution modifies the cell wall while the desorption ability remains to high levels. Similar results were obtained with *S. xylosus*, as shown in Table 6. The desorption experiments for *B. trispora* showed that HNO_3 solution recovers almost all the adsorbed Mn(II) and that biosorption capacity is reduced about 30% after the four cycles.

4. Conclusions

Pseudomonas sp., *S. xylosus* and *B. trispora* cells were investigated as possible sorbents for Mn(II) removal from aqueous solutions. Adsorption at pH = 6.0 enhanced the efficiency of adsorption process. Adsorption equilibrium data were correlated with the Langmuir and Freundlich isotherms and Langmiur model were found to provide the best fit of the experimental data in the cases of *Pseudomonas* sp. and *B. trispora*. Freundlich model was better for Mn(II) biosorption on *S. xylosus* cells. According to the Langmuir model, *Pseudomonas* sp. showed the higher efficiency for Mn(II) and the maximum capacity (109 mg g^{-1}) was higher than in the other two types of cells, indicating that *Pseudomonas* sp. is more suitable for Mn(II) removal.

From the various kinetic models investigated, including pseudo-first-order, pseudo-second-order, Elovich and particle-diffusion, only pseudo-second-order kinetic model was found to be in good agreement with the experimental results.

Thermodynamic parameters (positive heat of enthalpy and positive entropy change) of the adsorption confirmed the endothermic nature of sorption process. The standard Gibb's free energy change during adsorption process which was negative only in the case of *Pseudomonas* sp. shows a feasible and spontaneous adsorption.

Desorption experiments showed that a reduction of biosorption capacity is noticed after the first cycle but the recovery of Mn(II) remained at high levels in all four cycles.

Results obtained from this study showed that *Pseudomonas* sp. can be a very good adsorbent for the removal of Mn(II) from aqueous solutions in a static batch system.

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