

## Comparison of the fixation of several metal ions onto a low-cost biopolymer

Z. Reddad, C. Gérente, Y. Andrès and P. Le Cloirec

Ecole des Mines de Nantes, GEPEA, 4, rue A. Kastler, BP 20722, 44307 Nantes cedex 3, France  
(E-mail: [Claire.Gerente@emn.fr](mailto:Claire.Gerente@emn.fr); [Pierre.Le-Cloirec@emn.fr](mailto:Pierre.Le-Cloirec@emn.fr))

**Abstract** In the present work, sugar beet pulp, a common waste from the sugar refining industry, was studied in the removal of metal ions from aqueous solutions. The ability of this cheap biopolymer to sorb several metals namely  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  in aqueous solutions was investigated. The metal fixation capacities of the sorbent were determined according to operating conditions and the fixation mechanisms were identified. The biopolymer has shown high elimination rates and interesting metal fixation capacities. A pseudo-second-order kinetic model was tested to investigate the adsorption mechanisms. The kinetic parameters of the model were calculated and discussed. For  $8 \times 10^{-4}$  M initial metal concentration, the initial sorption rates ( $v_0$ ) ranged from  $0.063 \text{ mmol.g}^{-1}.\text{min}^{-1}$  for  $\text{Pb}^{2+}$  to  $0.275 \text{ mmol.g}^{-1}.\text{min}^{-1}$  for  $\text{Ni}^{2+}$  ions, with the order:  $\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+}$ . The equilibrium data fitted well with the Langmuir model and showed the following affinity order of the material:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$ . Then, the kinetic and equilibrium parameters calculated  $q_m$  and  $v_0$  were tentatively correlated to the properties of the metals.

Finally, equilibrium experiments in multimetallic systems were performed to study the competition of the fixation of  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  cations. In all cases, the metal fixation onto the biopolymer was found to be favourable in multicomponent systems. Based on these results, it is demonstrated that this biosorbent represents a low-cost solution for the treatment of metal-polluted wastewaters.

**Keywords** Adsorption; biopolymer; ion-exchange; metal ions

### Introduction

Mining and metallurgical activities produce wastewaters that can be considered as the major sources of heavy metal contamination of the environment. The main techniques that have been used to reduce the heavy metal content of effluents include chemical precipitation, ion exchange, membranes processes and electrolytic methods. These technologies have been found to be limited, since they often involve high operational costs or may also be insufficient to satisfy strict regulatory requirements for chemical precipitation. Therefore, economic and alternative treatment methods have been investigated, involving the sorption of metal ions onto wastes or natural materials. A number of solid wastes such as moss peat (Ho and McKay, 2000), rice hull (Low *et al.*, 2000), hazelnut shell (Cimino *et al.*, 2000), corncob (Vaughan *et al.*, 2001) and pine bark (Al-Asheh *et al.*, 2000) have been reported to be efficient in removing toxic metals from aqueous solutions.

Another cheap and unconventional adsorbent particularly suited to biosorption is sugar beet pulp (Dronnet *et al.*, 1997; Gérente *et al.*, 2000). Owing to the numerous carboxyl functions of the galacturonic acid in the pectins, this natural adsorbent is able to strongly bind metal cations in aqueous solution. Actually, about  $14 \times 10^6$  tones of sugar beet pulp are produced every year in Western Europe, where it is mainly used as animal feed.

In this study, a simple and economic preparation of the adsorbent was performed. Then, adsorption kinetics and equilibria of several divalent metal ions, namely  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  were investigated to determine the fixation mechanisms onto the biopolymer. Some classical models were used to describe the experimental kinetics and

isotherms. Equilibrium experiments in multimetallic systems were also conducted to study the competition of the fixation of  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  cations.

## Materials and methods

### Biosorbent

Sugar beet pulp was commercially supplied by Lyven (Cagny, France) and crushed in a hammer mill. These milled particles were sieved so that only particle sizes of 0.25–0.50 mm were used for the metal adsorption experiments. This fraction was washed with deionised water ( $20 \text{ g.L}^{-1}$ ) for 16 hours, filtered off and air-dried at  $40^\circ\text{C}$ .

As a preliminary step, a complete characterisation of the polysaccharide was performed. The main characteristics are reported in Table 1. This biosorbent is mainly composed of cellulose (20%) and pectic substances (40%). The results have shown that sugar beet pulp contained about 20% galacturonic acid and  $466 \mu\text{eq.g}^{-1}$  as carboxylic groups. The total cation exchange capacity ( $575 \mu\text{eq.g}^{-1}$ ) suggests good metal binding capacities.

### Metal adsorption study in batch reactor

*Kinetic studies.* Kinetic experiments were performed at  $20.0 \pm 0.5^\circ\text{C}$ . First, 2 g of beet pulp were introduced in 800 mL of deionised water. Prior to the introduction of the metal ions, the flasks were vigorously stirred for 1.5 h to hydrate the beet pulp, which naturally buffered the solution pH at 5.5. The initial concentrations of metal ions were  $8 \times 10^{-4} \text{ M}$  for the tests. Under these experimental conditions, it was verified that no chemical precipitation occurred and all the metal ions studied were in their divalent ionic form. After the introduction of the metal ions, samples were collected at suitable time intervals, filtered through a  $0.45 \mu\text{m}$  cellulose acetate membrane filter and then analysed for metal and calcium elements with an atomic absorption spectrophotometer (Perkin Elmer 2280). Indeed, the ionic surface functional groups of the biosorbent are mainly neutralised by  $\text{Ca}^{2+}$  ions, which may be endogenous but may also arise from the pressing stage during the sugar recovery process (Gieringer *et al.*, 1995).

The heterogeneous nature of the active sites onto the biosorbent suggest that a metal fixation mechanism with an order greater than one may occur in solution. Then, the kinetic data were modelled with a pseudo-second-order rate equation. The kinetic rate equation is (Ho and McKay, 2000):

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (1)$$

where  $k$  ( $\text{g.mmol}^{-1}.\text{min}^{-1}$ ) is the rate constant of pseudo-second order adsorption. Taking into account the initial sorption rate  $v_0$  ( $\text{mmol.g}^{-1}.\text{min}^{-1}$ ):

**Table 1** Main characteristics of the material

Elementary composition	(%-wt)	48% O, 43% C, 6% H, 1% N, 1% Ca
Sugar composition	(%-wt)	
	Neutral sugars	51.9
	Galacturonic acid	20.6
Functional groups	( $\mu\text{eq.g}^{-1}$ dry weight)	
	Carboxylic groups	$466 \pm 8$
	Phenolic groups	$109 \pm 5$
	Total cation exchange capacity	$575 \pm 13$
Point of zero net proton charge		5.0
Moisture	(%-wt)	9.5
Ash content	(%-wt)	3.9
Equilibrium pH (at $20^\circ\text{C}$ )		5.5

$$v_0 = k q_e^2 \quad (2)$$

Eq. (1) can be rearranged to obtain:

$$\frac{t}{q_t} = \frac{1}{v_0} + \frac{1}{q_e} t \quad (3)$$

The values of  $v_0$  and  $q_e$  can be determined experimentally by plotting  $t/q_t$  versus  $t$ .

### Equilibrium studies

*Adsorption in monometallic system.* The sorption experiments were carried out in 500 mL bottle flasks at  $20.0 \pm 0.5^\circ\text{C}$ . 1 g of beet pulp was thoroughly mixed with 400 mL deionised water for 1.5 h to hydrate the material and until the solution pH reached equilibrium (around 5.5). The initial concentrations of metals ranged from 0.2 to  $2.5 \times 10^{-3}$  M. Equilibrium times were deduced from the kinetic experiments and fixed at 2 h. The final pH was measured and the reaction mixtures were filtered through a  $0.45 \mu\text{m}$  cellulose acetate membrane. The filtrate was analysed for the concentration of metals and for the  $\text{Ca}^{2+}$  ions released by the polysaccharide. The equilibrium data were analysed in accordance with the Langmuir sorption isotherm as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

where  $q_m$  ( $\text{mmol.g}^{-1}$  of dry weight) is the maximum sorption capacity corresponding to complete monolayer coverage,  $C_e$  ( $\text{mmol.L}^{-1}$ ) the equilibrium solute concentration and  $b$  the equilibrium constant related to the energy of sorption ( $\text{L.mmol}^{-1}$ ).

*Adsorption in multimetallic system.* The same experimental procedure was used to perform adsorption isotherms in multimetallic systems. These experiments were conducted at initial equimolar metal concentrations for the pairs  $\text{Pb}^{2+}/\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}/\text{Zn}^{2+}$ ,  $\text{Zn}^{2+}/\text{Ni}^{2+}$  and the mixed solution  $\text{Pb}^{2+}/\text{Zn}^{2+}/\text{Ni}^{2+}$ . The metallic ion concentrations in each sample were measured with Oxford 2000 X-Ray fluorescence.

A model for competitive sorption based on the Langmuir equation and first developed by Butler and Ockrent (1930) was used to describe the data in multicomponent systems. This extended Langmuir isotherm can be used when each single component obeys Langmuir isotherm in monometallic system:

$$q_{e_i} = \frac{q_{m_i} b_i C_{e_i}}{1 + \sum_{j=1}^N b_j C_{e_j}} \quad (5)$$

where  $q_{m_i}$  and  $b_i$  are the Langmuir constants of component  $i$  determined in single solute system.

## Results

### Adsorption kinetics of $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Cd}^{2+}$ and $\text{Ni}^{2+}$ cations

Figure 1(a) shows the kinetics of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  adsorption onto the polysaccharide obtained by batch contact time studies. The plots represent the amounts of metal adsorbed  $q_t$  onto the polysaccharide versus time, for an initial metal concentration of  $8 \times 10^{-4}$  M. For all metal ions, it is shown that the fixation was very fast with an equilibrium state reached within 1 h. However, the equilibrium times were slightly different among the metal cations. For  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  ions, the equilibrium states were reached after 20 min contact time whereas it was about 1 h for  $\text{Pb}^{2+}$  ions. From Figure 1(a), large differences

between the kinetic rates of sorption were suggested. These differences were highlighted by using the pseudo-second-order equation. The lines in Figure 1(a) represent the modeled results using the kinetic equation. The values of  $v_0$  and  $q_e$  calculated are given in Table 2 for all the metals investigated. As shown in Table 2, the regression coefficients for the plots were good.

Based on the  $v_0$  values, the following affinity order was obtained:  $\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+}$ . Relating to the equilibrium fixation capacity  $q_e$ , a reverse order was observed, i.e.  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} \sim \text{Zn}^{2+} > \text{Ni}^{2+}$  despite the same experimental conditions used. The biosorbent showed a strong affinity for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  cations. The concentration of  $\text{Ca}^{2+}$  ions in solution was also measured during the adsorption kinetics. Figure 1(b) shows, for example, the respective concentration-decay curve for  $\text{Zn}^{2+}$  ions for an initial concentration of  $8 \times 10^{-4}$  M. The release of  $\text{Ca}^{2+}$  from the adsorbent was simultaneously so fast that the metal adsorption kinetic and revealed an ionic exchange mechanism for all the metal ions studied.

The very fast sorption kinetics observed with the sugar beet pulp represent an advantageous aspect when designing water treatment systems. It implies that the material could be suitable for continuous flow system.

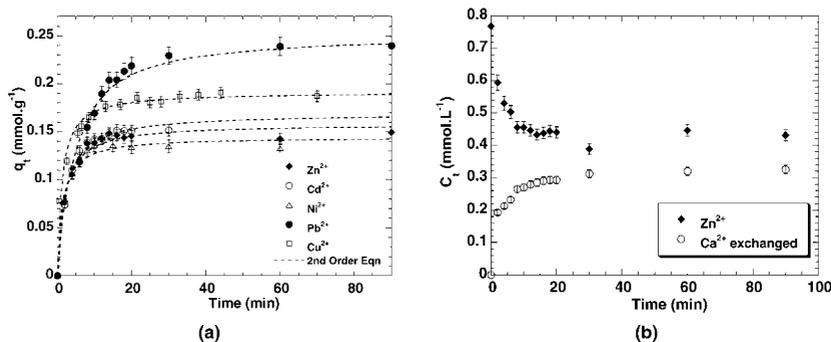
#### Adsorption isotherms of $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Cd}^{2+}$ and $\text{Ni}^{2+}$ Cations

*Adsorption in monometallic system.* The equilibrium sorption experiments were performed to provide the metal fixation capacities of the biopolymer. Figure 2(a) represents the experimental isotherms of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  ions with those given by the Langmuir equation.

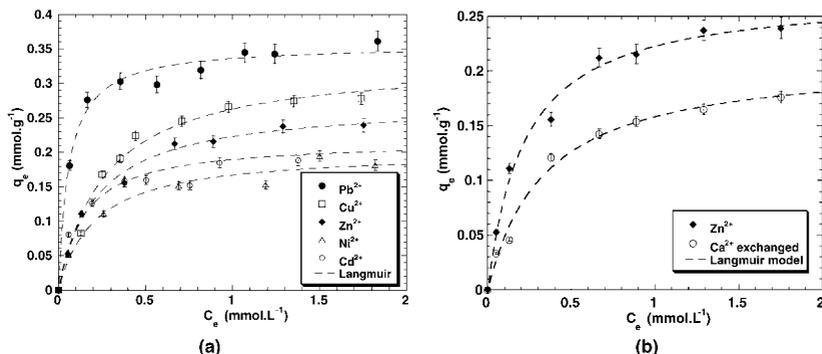
The Langmuir isotherm was found to provide an excellent description of the metal sorption. The  $q_m$  and  $b$  parameters calculated with the respective correlation coefficients  $R^2$  are

**Table 2** Kinetic parameters for metal adsorption onto the biopolymer

Metal	Pseudo-second order model				$R^2$
	$C_0$ ( $\text{mol.L}^{-1}$ )	$v_0$ ( $\text{mmol.g}^{-1}.\text{min}^{-1}$ )	$k$ ( $\text{g.mmol}^{-1}.\text{min}^{-1}$ )	$q_e$ ( $\text{mmol.g}^{-1}$ )	
$\text{Pb}^{2+}$	$8 \times 10^{-4}$	0.063	0.99	0.252	0.998
$\text{Cu}^{2+}$	$8 \times 10^{-4}$	0.104	2.73	0.195	0.999
$\text{Zn}^{2+}$	$8 \times 10^{-4}$	0.148	6.66	0.149	0.999
$\text{Cd}^{2+}$	$8 \times 10^{-4}$	0.262	11.19	0.153	0.987
$\text{Ni}^{2+}$	$8 \times 10^{-4}$	0.275	15.09	0.135	0.999



**Figure 1** The kinetics of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  adsorption (a) onto the polysaccharide for an initial pH 5.5 and metal concentration of  $8 \times 10^{-4}$  M. Figure 1(b) represents  $\text{Zn}^{2+}$  adsorption kinetic onto the polysaccharide and the respective  $\text{Ca}^{2+}$  desorption kinetic



**Figure 2** The adsorption isotherms of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  (a) onto the biosorbent for an initial pH 5.5. Figure 2(b) represents the desorption isotherm of  $\text{Ca}^{2+}$  corresponding to the  $\text{Zn}^{2+}$  fixation isotherm

reported in Table 3. The sugar beet pulp showed the strongest affinity for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ , then  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$  cations. For all metal ions, the concentration of  $\text{Ca}^{2+}$  exchanged from the material during the experiments was also followed. In all cases, this concentration was always correlated with the quantity of metal fixed on the material. However, the amounts  $q_m$  in  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  fixed at equilibrium were greater than the  $\text{Ca}^{2+}$  exchanged (see Figure 2(b)). This indicates that another mechanism, probably complexation with other chemical moieties than carboxylic groups of the polysaccharide, contributed to the fixation of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions. The less easily hydrolysable metal cations  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  seemed to be exclusively involved in an ion exchange mechanism with  $\text{Ca}^{2+}$  ions from the biopolymer.

**Adsorption parameters analysis.** The binding strength of a metal ion to a given biopolymer is dependent upon its properties. Many linear relationships can be discovered between the free energies or rates of complex formation and a variety of properties of the metals like the ionic radius  $r$  or the first hydrolysis constant  $\log K_1(\text{OH}^-)$  (Martell and Hancock, 1996). These correlations provide insights into the factors governing the complex formation with the biosorbent functional groups, and in addition may allow for prediction of unknown formation or rate constants. In our case, the ionic radius did not appear to reflect the adsorption capacities  $q_m$  neither the initial sorption rates  $v_0$ . The  $q_m$  and  $v_0$  values did not correlate with  $Z^2/r$  ( $Z$  = cationic charge), indicating that the bonding to the biosorbent was governed by more complex factors than simple electrostatic considerations.

However, relating to the first hydrolysis constant, linear relationships could be drawn with the initial sorption rate  $v_0$  and with the maximum adsorption capacities  $q_m$ , as shown in Figure 3(a) and 3(b) respectively. The regression equations are:

**Table 3** Langmuir parameters for metal adsorption onto the biopolymer

Metal	Langmuir model		$R^2$
	$q_m$ ( $\text{mmol.g}^{-1}$ )	$b$ ( $\text{L.mmol}^{-1}$ )	
$\text{Pb}^{2+}$	0.356	16.92	0.987
$\text{Cu}^{2+}$	0.333	3.73	0.984
$\text{Zn}^{2+}$	0.272	4.55	0.992
$\text{Cd}^{2+}$	0.217	6.92	0.936
$\text{Ni}^{2+}$	0.202	4.74	0.979

$$q_m = -0.0215 (\pm 0.0328) + 0.0581 (\pm 0.0063) \log K_1 (\text{OH}^-) \quad (6)$$

$$n = 5 ; r^2 = 0.966 ; s = 0.0145$$

and

$$v_0 = 0.575 (\pm 0.0658) - 0.0790 (\pm 0.0126) \log K_1 (\text{OH}^-) \quad (7)$$

$$n = 5 ; r^2 = 0.929 ; s = 0.0291$$

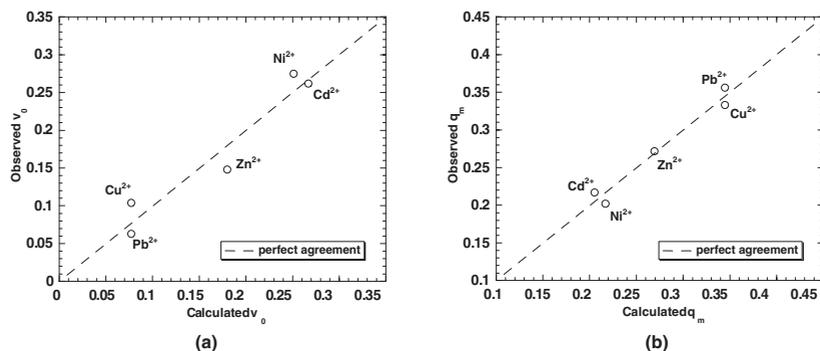
where  $n$  is the sample size,  $r^2$  the determination coefficient and  $s$  the standard deviation of the regression.

The numbers in brackets beside the independent variable coefficients represent the standard deviation associated with each coefficient. The statistical quality of both regressions seemed good. This indicates a significant relation between the  $\log K_1 (\text{OH}^-)$  parameter and  $v_0$  and  $q_m$  values. Indeed, the preference of several solids for metals has been related to the equilibrium constant of the first metal hydrolysis reaction. It has been stated that higher hydrolysis constant  $\log K_1 (\text{OH}^-)$  lowered the degree of solvation of metal ions (Burns *et al.*, 1999), thus enabling them to better approach the solid surface and exhibiting significant adsorption as for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  elements.

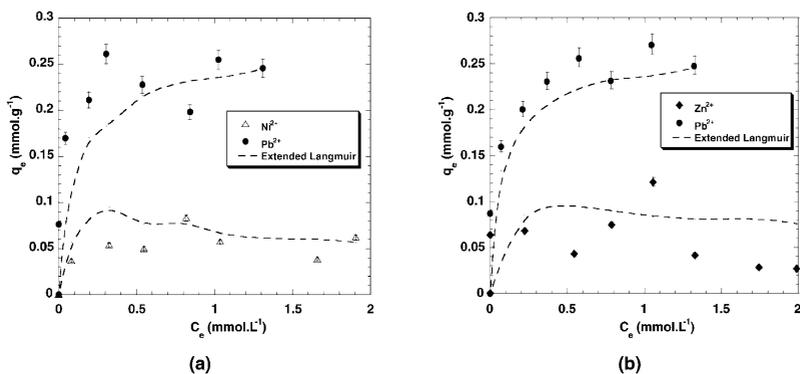
In fact, the affinity sequence  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$  based on  $q_m$  values separate the most readily hydrolysable metal ions ( $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ ) from those which are less easily hydrolysable ( $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ).

**Adsorption in multimetallic system.** Competitive adsorption experiments at equimolar metal concentrations were conducted to evaluate the selectivity of the polysaccharide for  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  ions. Considering the greatest equilibrium fixation capacity  $q_e$ ,  $\text{Ni}^{2+}$  sorption was strongly affected by the presence of  $\text{Zn}^{2+}$  ( $-50\%$ ) and  $\text{Pb}^{2+}$  ( $-67\%$ ) and more markedly when all metals were coexisting in solution ( $-72\%$ ). The decrease in  $\text{Zn}^{2+}$  uptake was about  $48\%$  in the presence of  $\text{Ni}^{2+}$  and  $65\%$  with  $\text{Pb}^{2+}$ . Among all metals studied,  $\text{Pb}^{2+}$  sorption was less affected. Its fixation decreased only by  $30\%$  with the presence of  $\text{Zn}^{2+}$  or  $\text{Ni}^{2+}$  and by  $43\%$  when all metals were mixed in solution. From these experiments, the following sequence of preferential fixation was confirmed:  $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ . Figures 4(a) and 4(b) show the competitive adsorption isotherms of  $\text{Pb}^{2+}/\text{Ni}^{2+}$  and  $\text{Pb}^{2+}/\text{Zn}^{2+}$  in mixed solutions, respectively.

The lines in Figures 4(a) and 4(b) represent the calculated isotherms using the extended Langmuir model. The calculation was based on the Langmuir parameters  $q_m$  and  $b$  obtained for single metal system and given in Table 3. Although the application of the model did not provide a completely satisfactory description of the data, the shapes of the isotherms were



**Figure 3** Comparison between the calculated initial sorption rates  $v_0$  (a) and maximum adsorption capacities  $q_m$  (b) and the observed values



**Figure 4** Adsorption isotherms of  $\text{Pb}^{2+}/\text{Ni}^{2+}$  (a) and  $\text{Pb}^{2+}/\text{Zn}^{2+}$  (b) in mixed solutions at initial equimolar ionic concentrations and pH 5.5

quite correctly simulated. In the case of the  $\text{Zn}^{2+}/\text{Ni}^{2+}$  and  $\text{Pb}^{2+}/\text{Zn}^{2+}/\text{Ni}^{2+}$  mixed solution, the extended Langmuir isotherm showed more limited success at describing these data. First, it is well known that this model is limited in the case of identical or close fixation capacities of the solutes as for  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  investigated in the present study. Many other reasons could explain the discrepancies observed like the non-ideality of the system induced by chemical interactions in the adsorbed phase. These difficulties in deriving competitive isotherms exclusively from single component data have been already reported by Ho and McKay (1999).

In all cases, the metal fixation onto the biopolymer was found to be favourable in multi-component systems even if the metal ions seem to compete for the same fixation sites.

## Conclusions

This study concerning the adsorption capacities of the native sugar beet pulp indicate a great potential for the removal of heavy metals from aqueous solutions, with the affinity order  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$ . The maximum adsorption capacity ( $q_m$ ) ranged from  $0.202 \text{ mmol.g}^{-1}$  for  $\text{Ni}^{2+}$  to  $0.356 \text{ mmol.g}^{-1}$  for  $\text{Pb}^{2+}$  ions. The predominant ion-exchange mechanism involving carboxyl groups of the galacturonic acid residues was evidenced. The main advantages in using sugar beet pulp are the substantially lower cost of the material (100 € per metric tone) and its economic feasibility. These preliminary results warrant further investigations using continuous flow processes.

## Acknowledgements

Gratitude is expressed to Dr Jean-François Thibault, President of the INRA Institute of Nantes (France) for valuable discussions. Partial financial support provided by GIS VANAM in Nantes (Groupement d'Intérêt Scientifique de Valorisation Alimentaire et Non Alimentaire des Macromolécules) is also gratefully acknowledged.

## References

- Al-Asheh, S., Banat, F., Al-Omari, R. and Duvnjak, Z. (2000). Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data. *Chemosphere*, **41**, 659–665.
- Burns, C.A., Cass, P.J., Harding, I.H. and Crawford, R.J. (1999). Adsorption of aqueous heavy metals onto carbonaceous substrates. *Colloids Surfaces A: Physicochem. Eng. Aspects*, **155**, 63–68.
- Butler, J.A.V. and Ockrent, C. (1930). Studies in Electrocapillarity. Part III The surface tensions of solutions containing two surface-active solutes. *J. Phys. Chem.*, **34**, 2841–2859.
- Cimino, G., Passerini, A. and Toscano, G. (2000). Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell. *Water Research*, **34**(11), 2955–2962.

- Dronnet, V.M., Renard, C.M.G.C., Axelos, M.A.V. and Thibault, J.-F. (1997). Binding of divalent metal cations by sugar-beet pulp. *Carbohydrate Polymers*, **34**, 73–82.
- Gérente, C., Couespel, Du Mesnil, P., Andrès, Y., Thibault, J.-F. and Le Cloirec, P. (2000). Removal of metal ions from aqueous solution on low cost natural polysaccharides: sorption mechanism approach. *Reactive and Functional Polymers*, **46**(2), 135–144.
- Gieringer, R., Steinert, P., Buttersack, C. and Buchholz, K. (1995). Anisotropic swelling of cell walls of sugar beet tissue: influence of ion-exchange and sucrose. *J. Sci. Food Agric.*, **68**, 439–449.
- Ho, Y.S. and McKay, G. (1999). Competitive sorption of copper and nickel ions from aqueous solution using peat. *Adsorption*, **5**, 409–417.
- Ho, Y.S. and McKay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Research*, **34**(3), 735–742.
- Low, K.S., Lee, C.K., Wong, S.Y. and Tang, P.L. (2000). Metal sorption enhancement of rice hull through chemical modification. *Environ. Technol.*, **21**, 1239–1244.
- Martell, A.E. and Hancock, R.D. (1996). *Metal Complexes in Aqueous Solutions*, ed.; Plenum: New York.
- Vaughan, T., Seo, C.W. and Marshall, W.E. (2001). Removal of selected metal ions from aqueous solution using modified corncobs. *Bioresource Technol.*, **78**, 133–139.