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Lead removal by a natural polysaccharide in membrane reactors

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Abstract Industrial wastewaters often contain heavy metal ions that are toxic to many living species. Therefore, economic treatment methods are investigated, involving the sorption of metal ions onto wastes or natural materials. In the present work, the ability of sugar beet pulp, a common waste of the sugar industry, to remove Pb^{2+} polluted waters is investigated. The kinetic and equilibrium experiments were performed in batch reactor in order to determine the Pb^{2+} adsorption mechanisms onto the polysaccharide. The dynamic studies of Pb^{2+} fixation onto the natural polysaccharide involve an adsorption reactor coupled with microfiltration membrane in order to confine the adsorbent particles. A mass balance model based on the Langmuir equilibrium isotherm was used to describe the Pb^{2+} breakthrough curves. This model successfully simulated the entire breakthrough curves whatever the operating conditions used. It provides a useful tool for process simulation and optimisation.

Keywords Adsorption; metal ions; microfiltration; modelling; polysaccharides

Introduction

Industrial activities produce wastewaters that can be considered to be the major sources of heavy metal contamination of the environment. The main techniques which have been used to reduce the heavy metal content of effluents include chemical precipitation, ion exchange, membranes processes and electrolytic systems. These methods have been found to be limited, since they often involve high operational costs or may also be insufficient to meet strict regulatory requirements for chemical precipitation. Therefore, economic and alternative treatment methods have been investigated, involving the sorption of metal ions onto waste materials. A number of solid wastes such as rice hull (Low *et al.*, 2000), hazelnut shell (Cimino *et al.*, 2000), corn cob (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). Actually, about 14×10^6 tonnes of sugar beet pulp are produced every year in western Europe, where it is mainly used as animal feed.

In the present study, a simple and economic preparation of the biosorbent was performed. Then, adsorption kinetics and equilibria of Pb^{2+} ions were investigated to determine the fixation mechanisms onto the biopolymer. Some models were used to describe the experimental kinetic and isotherm data. A continuous flow process, which includes a stirred semi-batch reactor for the adsorption step and a microfiltration membrane, was developed and tested for its performance in Pb^{2+} ions removal. The effects of biosorbent concentration and influent metal concentration on the breakthrough curves were investigated. A modelling study of the dynamic adsorption process was performed by using a mass balance model which included the Langmuir equilibrium isotherm.

Methods

Adsorbent

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 (10 g L⁻¹) for 16 h, filtered off and air-dried at 40°C. In a previous study (Reddad *et al.*, 2002a), a complete characterisation of the material revealed that the polysaccharides accounted for 72.5 % of the dry matter including 20% as galacturonic acid.

Pb²⁺ adsorption study in batch reactor

Kinetic studies. Kinetic experiments were performed at 20.0 ± 0.5°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 Pb²⁺ ions were 8 × 10⁻⁴ and 4.2 × 10⁻⁴ M for the tests. Under these experimental conditions, it was verified that no chemical precipitation occurred and Pb²⁺ ions were in their divalent ionic form. After the introduction of the Pb²⁺ ions, samples were collected at suitable time intervals, filtered through a 0.45 µm cellulose acetate membrane filter and then analysed for Pb²⁺ and Ca²⁺ elements with an atomic absorption spectrophotometer (Perkin Elmer 2280). Indeed, the ionic surface functional groups of the biosorbent are mainly neutralised by Ca²⁺ ions, which may be endogenous or 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 (Reddad *et al.*, 2002a). Then, the kinetic data were modelled with a pseudosecond-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 (g.mmol⁻¹.min⁻¹) is the rate constant of pseudosecond-order adsorption and q_e the equilibrium adsorption capacity (mmol.g⁻¹ of dry weight). Taking into account the initial sorption rate v_0 (mmol.g⁻¹.min⁻¹):

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

After integration, 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. The sorption experiments were carried out in 500 mL flasks at 20.0 ± 0.5°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 Pb²⁺ concentrations ranged from 0.2 to 3 × 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 µm cellulose acetate membrane. The filtrate was analysed for the concentration of Pb²⁺ and for the Ca²⁺ ions released by the polysaccharide. The equilibrium data were modelled in accordance with the Langmuir isotherm equation as:

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

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

Pb²⁺ adsorption study in membrane reactor

Experimental set-up. Figure 1 represents schematically the experimental system. It consists of a continuous stirred tank reactor (CSTR) coupled with a microfiltration cell. The sorption tests were performed as follows: the natural adsorbent was introduced into the glass reactor (8 L deionised water at 18 ± 1°C) and hydrated for 90 min. The solution was fed through a tubular membrane module by a centrifuge pump (tangential velocity 2.05 m.s⁻¹; transmembrane pressure 250 kPa). A ceramic membrane (ZrO₂/TiO₂) was used with 0.14 µm cut off and a total area of 94 cm². The mixing in the reactor was ensured by the recirculation flow of the retentate stream. The pH was continuously monitored. Lead element was taken as the metal pollutant. The lead solution (containing about 100 or 200 mg.L⁻¹ Pb²⁺ as PbCl₂) at pH 5 was fed to the bioreactor by a peristaltic pump. Its flow rate was always equal to the permeate flux thanks to the equilibrium of the solution levels at atmospheric pressure (Figure 1). By this method, the bioreactor worked at constant volume. The flux decrease was monitored during time. Lastly a blank test was performed, i.e. lead was introduced in the system without biosorbent.

Modelling. A mass balance model has been used in order to predict time courses of Pb²⁺ ions concentration in the permeate (Beolchini *et al.*, 2001).

Because metal biosorption onto sugar beet pulp was demonstrated to be very fast (Reddad *et al.*, 2002a, b), the equilibrium state was assumed in the reactor at any time t . Then, the Langmuir equation was included for equilibrium in the mass balance of the membrane reactor, which has been used to simulate metal concentration in the permeate. Considering the continuous stirred tank reactor shown in Figure 1, the model of sorption process (Eq. (6)) was obtained by coupling the mass balance of the metal ions in a transitory regime (Eq. (5)) and the Langmuir equilibrium equation (Eq. (4)):

$$V \frac{dC}{dt} = QC_0 - Q_p C - \frac{dq}{dC} \frac{dC}{dt} X V \quad (5)$$

since $Q = Q_p$,

$$\frac{dC}{dt} = \frac{Q_p (C_0 - C)}{V \left(1 + \frac{q_m b X}{(1 + bC)^2} \right)} \quad (6)$$

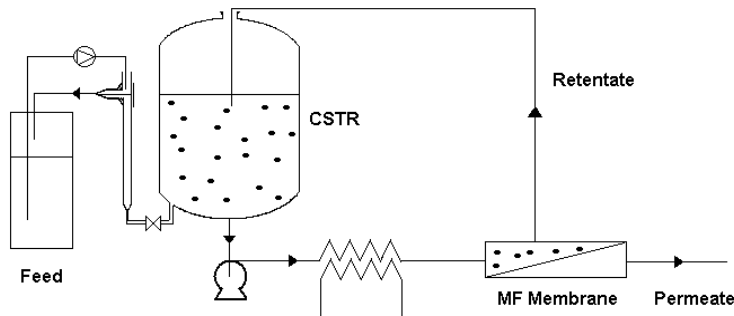


Figure 1 Scheme of the experimental set-up: CSTR coupled with a tubular microfiltration (MF) system

where C (mmol.L^{-1}) is the instantaneous lead concentration in the reactor and in the permeate at time t (min); C_0 (mmol.L^{-1}) is the lead concentration in the feeding stream; Q is the feed flow rate (L.min^{-1}); Q_p is the permeate flow rate (L.min^{-1}); V is the reactor volume (L) and X (g.L^{-1}) the biosorbent concentration in the reactor.

The inlet flow rate Q , which was always kept equal to the permeate flow rate Q_p , was a function of time due to permeate flux decline. $Q_p(t)$ was then fitted by the following relation:

$$Q_p(t) = l + m \exp(-nt) \quad (7)$$

$Q_p(t)$ then was included in Eq. (6) which was integrated numerically. The constants l , m and n were calculated by regression analysis for each experiment. The integration of Eq. (6) was performed by the Runge–Kutta algorithm with MATLAB software, by considering the following initial conditions: at $t = 0$ the initial metal concentration in the reactor was $C = 0$ M. After integration of the equation, the experimental and simulated results were compared.

Results and discussion

Pb²⁺ adsorption in batch reactor

Adsorption kinetics of Pb²⁺ cations. Figure 2(a) represents the kinetic of Pb²⁺ adsorption and the parallel release of Ca²⁺ cations from the polysaccharide for an initial metal concentration of 8×10^{-4} M. The desorption of Ca²⁺ from the beet pulp, which was faster than the Pb²⁺ adsorption kinetic, revealed an ionic exchange mechanism. For both metal ions, the times to reach equilibrium were very close, about 60 min. However, a large difference between the amounts of Pb²⁺ adsorbed and Ca²⁺ exchanged at equilibrium state were suggested from Figure 2(a). This difference could be explained by the existence of another mechanism, probably complexation completing the ion-exchange one (Reddad *et al.*, 2002b).

Figure 2(b) represents the amounts q_t of Pb²⁺ adsorbed onto the polysaccharide versus time, for an initial metal concentration of 8×10^{-4} and 4.2×10^{-4} M. The decrease in initial lead concentration slightly influenced the contact time to reach equilibrium but strongly decreased the sorption capacity.

The differences in the adsorption kinetic rates and the metal recoveries were highlighted by using the pseudosecond-order equation. The lines in Figures 2(a) and 2(b) represent the

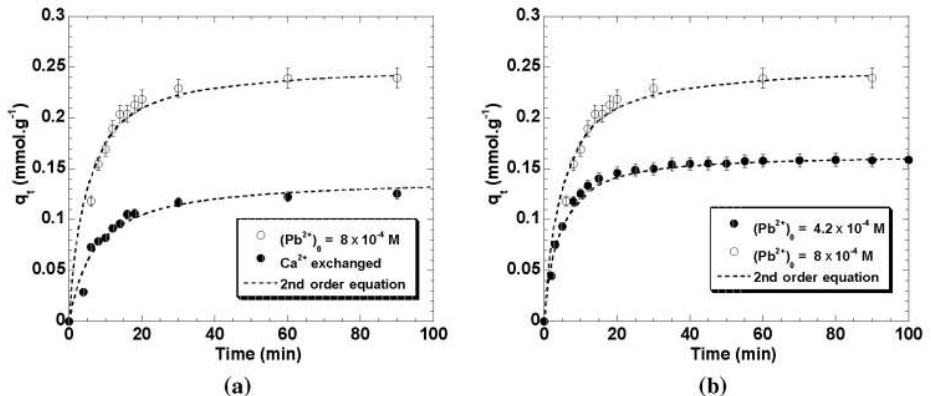


Figure 2 (a) The kinetics of Pb²⁺ adsorption (a) and Ca²⁺ desorption from the polysaccharide for 8×10^{-4} M initial Pb²⁺ concentration. (b) Pb²⁺ adsorption kinetics for 8×10^{-4} and 4.2×10^{-4} M initial metal concentration and modelled results using the pseudosecond-order equation

modeled results using the kinetic equation. The values of the initial sorption rate v_0 , the constant rate k and the equilibrium capacity q_e calculated are given in Table 1 for both kinetic experiments. As shown in Table 1, the regression coefficients for the plots were good.

The 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 isotherm of Pb^{2+} cations. Equilibrium sorption studies were performed to provide the maximum Pb^{2+} adsorption capacities of the polysaccharide. For the greatest initial metal concentration (3×10^{-3} M), the lowest final pH value was 4.7. The biosorbent was found to strongly buffer the solution pH. Then, no effort was made to control the solution pH during the experiments. The adsorption isotherm of Pb^{2+} cations is represented in Figure 3 with the respective Ca^{2+} desorption isotherm. The Langmuir plots are also represented and the good agreement with the experimental data suggest that the metal ions sorbed form a monolayer coverage on the adsorbent surface.

The values q_m and b obtained from these plots are listed in Table 2. In a previous work, it has been observed that the application of Langmuir model to the metal adsorption isotherms was more appropriate than that of Freundlich model (Reddad *et al.*, 2002b). As a consequence, we decided to apply the Langmuir isotherm in the dynamic mass balance model since it allows an accurate fit of the experimental data.

Pb^{2+} adsorption in membrane reactor

Feed Pb^{2+} concentration effect. The effect of the initial feed metal concentration was studied with the Pb^{2+} breakthrough for $C_0 = 0.491$ mmol.L⁻¹ or 0.973 mmol.L⁻¹ Pb^{2+} and 10 g.L⁻¹ beet pulp concentration. The change of the initial metal ion concentration has a

Table 1 Kinetic parameters for Pb^{2+} adsorption onto the biopolymer

	C_0 (mol.L ⁻¹)	v_0 (mmol.g ⁻¹ .min ⁻¹)	k (g.mmol ⁻¹ .min ⁻¹)	q_e (mmol.g ⁻¹)	R^2
Pb^{2+}	8×10^{-4}	0.063	0.99	0.252	0.998
Ca^{2+} exchanged		0.020	1.08	0.136	0.988
Pb^{2+}	4.2×10^{-4}	0.052	1.93	0.165	0.999

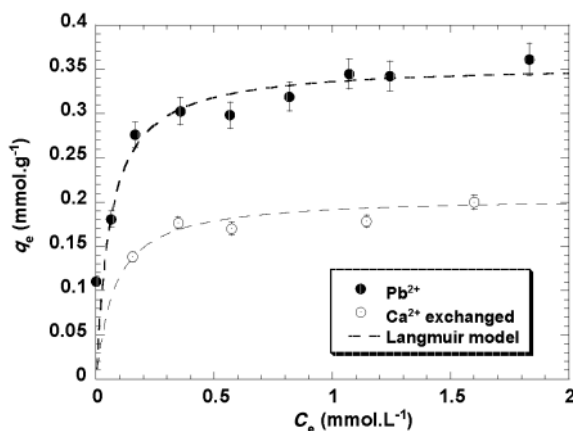


Figure 3 The adsorption isotherm of Pb^{2+} cations onto the biosorbent and the respective Ca^{2+} desorption isotherm modelled with Langmuir equation (2.5 g.L⁻¹ beet pulp, pH_i = 5.5)

Table 2 Langmuir parameters for Pb^{2+} adsorption onto the biopolymer

Metal	q_m (mmol.g ⁻¹)	b (L.mmol ⁻¹)	R^2
Pb^{2+}	0.356	16.92	0.987
Ca^{2+} released	0.206	12.85	0.852

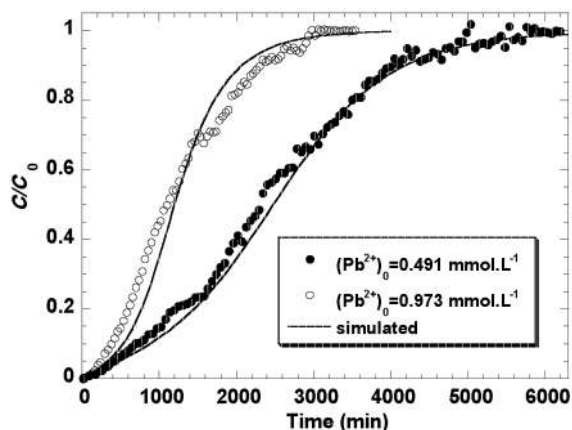
significant effect on the breakthrough curves as illustrated in Figure 4. As expected, the larger the initial metal concentration, the faster the breakthrough of the metal. For the experiment with $C_0 = 0.973 \text{ mmol.L}^{-1} \text{ Pb}^{2+}$, the pH was found to decrease from 5.5 to 4.6 during the first 200 min and restarted to increase until the final value 5.0. Relating to the experiment with $C_0 = 0.491 \text{ mmol.L}^{-1} \text{ Pb}^{2+}$, the pH decreased from 5.4 to 5.0 and finally remained constant at 5.2.

Biosorbent concentration effect. Numerous experimental trials were carried out by varying the beet pulp concentration inside the reactor for one fixed inlet Pb^{2+} concentration equal to $0.491 \text{ mmol.L}^{-1}$. A blank test without biosorbent was also performed under the same experimental conditions. Figure 5 represents the Pb^{2+} breakthrough curves for 0, 2.5, 5 and 10 g.L^{-1} biosorbent concentration.

The analysis of the breakthrough curves in Figure 5 indicates the evident effect of the biosorbent on the Pb^{2+} concentration in the permeate, since this concentration at a fixed time value was always lower when the beet pulp concentration inside the membrane reactor was increased.

Modelling of the Pb^{2+} breakthrough curves. Mathematical modelling is essential for process design and optimisation because it may avoid time consuming and costly experiments. Consequently, we assessed the ability of the mass balance model to predict the permeate lead concentration under the various experimental conditions used in the study.

The mass balance model was implemented separately under the same operating conditions used for each experiment. Indeed, the inlet flow rate profiles were different for each test, depending on operating conditions. All the model parameters were kept constant for the calculations including q_m and b Langmuir parameters. Then, the experimental metal concentration profiles in the permeate were compared with the theoretical curves obtained from the mathematical model. A first validation of the model was obtained for the blank test

**Figure 4** Experimental and calculated breakthrough curves of Pb^{2+} cations for 10 g.L^{-1} adsorbent and 0.491 or $0.973 \text{ mmol.L}^{-1}$ initial metal concentration

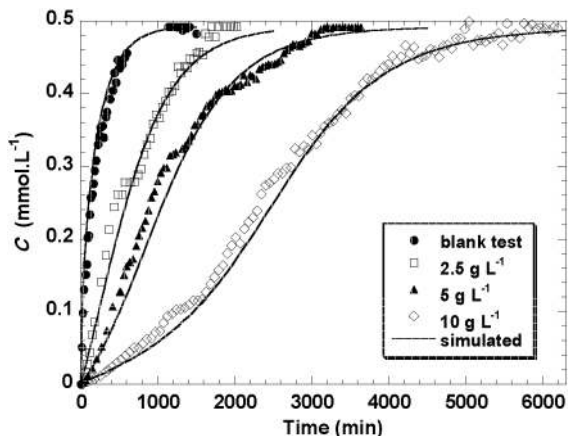


Figure 5 Experimental and calculated breakthrough curves for $C_0 = 0.491 \text{ mmol.L}^{-1} \text{ Pb}^{2+}$ and for 2.5, 5 and 10 g.L^{-1} adsorbent concentration

under the following operating conditions: no biosorbent inside the reactor and inlet lead concentration $C_0 = 0.491 \text{ mmol.L}^{-1} \text{ Pb}^{2+}$. An excellent agreement between the experimental and calculated results was observed in Figure 5. This result validates the previous CSTR assumption for the adsorption system.

More generally, the lines in Figures 4 and 5 represent the simulated breakthrough curves after integration of Eq. (6) under different operating conditions. The model always provides a good prediction of the experimental Pb^{2+} breakthrough curves. Then, it is demonstrated that the biosorbent adsorption capacity based on the batch equilibrium isotherms can be successfully used to simulate the adsorption performance of the present membrane reactor. Furthermore, these good simulation results have to be linked to the fact that pH varied very slightly during the adsorption experiments thanks to the significant buffering behaviour of the sugar beet pulp. Then, the Langmuir parameters always remained valid under the experimental conditions used for the membrane reactor.

These results confirmed the possibility of using sugar beet pulp in such a membrane system to remove toxic metal ions from polluted waters. The potential technical feasibility of the process has been also demonstrated.

Conclusions

In this study, the waste pulp of sugar beet remaining from industrial extraction of sugar has been considered as a metal adsorbent.

The sugar beet pulp developed fast Pb^{2+} sorption kinetics which involved ionic exchange with Ca^{2+} neutralising the carboxylic moieties and complexation mechanisms. The biosorbent is able to bind efficiently Pb^{2+} ions with a maximum adsorption capacity of $0.356 \text{ mmol.g}^{-1}$ in the batch system.

Then, a detailed experimental and theoretical analysis of Pb^{2+} adsorption onto the polysaccharide in dynamic membrane reactor was performed. The applied mass balance model was very effective in the description of the breakthrough curves of Pb^{2+} under different operating conditions. The biosorbent adsorption capacity based on the batch equilibrium isotherm was successfully used to simulate the adsorption performance of the membrane reactor. These results confirmed the possibility of using sugar beet pulp in such a membrane system, in order to remove toxic metal ions from polluted waters. The main advantages in using sugar beet pulp are the substantially lower cost of the material (€100 per metric tonne) and its economic feasibility. These preliminary results warrant further investigations on the continuous flow process proposed, including other toxic metal ions.

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