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Preliminary study of lead sorption by selected sorbents

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Lead sorption was investigated using several biosorbents, including five fungi (*Aspergillus niger*, *Mucor miehei*, *Penicillium chrysogenum*, *Rhizopus arrhizus* and *Rhizopus conhii*), two algae (*Ascophyllum nodosum*, *Lessonia trabeculata*), one yeast (*Saccharomyces cerevisiae*), alginate and chitosan. Experiments were performed with non-living microorganisms. In the present work alginate was tested as a powder. Preliminary experiments have been performed investigating the influence of the pH on lead sorption (between pH 3 and pH 6). Complementary experiments were carried out using 3 of the most efficient sorbents: alginate, *A. niger* and *A. nodosum*. Sorption properties were determined through isotherms and kinetics at pH 4. Maximum sorption capacities were comparable for *A. niger* and *A. nodosum*, tending to 130-150 mg Pb g⁻¹. Sorption kinetics was slightly faster for *A. nodosum* than for *A. niger*.

Keywords: lead, biosorption, fungal biomass, algal biomass, isotherms, kinetics.

1. INTRODUCTION

The toxic effects of heavy metals such as mercury, cadmium or lead require the treatment of industrial wastewater prior their discharge to the environment. Though precipitation processes are efficient at removing metal ions from solutions, these techniques are sometimes inappropriate for the treatment of dilute solutions for technical or economical reasons. Moreover, the production of toxic sludge as a by-product limits the interest of these processes: the precipitation results in a single pollution transfer. For these reasons, economical and efficient processes are still necessary to develop. Biosorption processes have been recognized as promising techniques, owing to the low cost and the great diversity of these materials. Since the early 80's many studies have focused on the use of materials of biological origin for the recovery of metal ions [1]. Living as well as non-living microorganisms have been used for metal recovery: algae [2-5], bacteria [6-7], fungi [8-12], and yeasts [13]. The identification of sorption sites on the cell walls of the microorganisms

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has been the motive for the increasing interest for metal uptake properties of the biopolymers entering in the composition of these cell walls: alginate [14], chitin and chitosan [15-16], or exopolysaccharides excreted by these microorganisms [17].

The present study focuses on a preliminary investigation of lead sorption using 5 fungi (*Aspergillus niger*, *Mucor miehei*, *Penicillium chrysogenum*, *Rhizopus arrhizus* and *Rhizopus conhii*), 2 algae (*Ascophyllum nodosum* and *Lessonia trabeculata*), 1 yeast (*Saccharomyces cerevisiae*) and 2 biopolymers (alginate and chitosan). The cell wall of selected fungi is characterized by the presence of chitin and/or chitosan material associated with proteins and other glucans. On the other hand, algal biomass may contain alginate (*L. trabeculata*) or fucoidan polymers (sulfate fucans, *A. nodosum*) [18-20]. Preliminary experiments focus on the study of the influence of the pH on 10 selected sorbents. Sorption isotherms and uptake kinetics are determined at pH 4 using alginate, *A. niger* and *A. nodosum*.

2. MATERIAL AND METHODS

2.1. Materials

The samples of *Aspergillus niger*, *Penicillium chrysogenum*, *Rhizopus arrhizus*, *Rhizopus conhii* and *Mucor miehei* were kindly donated by Gist Brocades (The Netherlands). They were supplied after being inactivated and dried. The particles were sieved and the fraction 125-250 μm was used for preliminary experiments. The brown alga *Ascophyllum nodosum* was collected on the Brittany coast while *Lessonia trabeculata* was collected on the Peru coast. The samples were dried and ground, the fraction 125-250 μm was used for experiments. The yeast (*Saccharomyces cerevisiae*) was obtained from local bakeries, as a commercial sample. Alginate was purchased from Janssen. Chitosan was supplied by ABER-Technologies (Brest-France) (Lot N°A17G28). Its characteristics were $\text{pK}_a = 6.2$, number average molecular mass, $\text{MW}_n = 125,000 \text{ g mol}^{-1}$, weight average molecular mass, $\text{MW}_w = 191,000 \text{ g mol}^{-1}$, and deacetylation percentage = 87%. Lead solutions were prepared by dilution of an atomic absorption standard solution (1 g Pb L^{-1}) supplied by Fluka (Germany). The metal was under the form of a nitrate-salt. The pH of the solutions was controlled with molar solutions of either sulfuric acid or sodium hydroxide. The ionic strength of the solution was adjusted by adding sodium nitrate at the final concentration 0.05 M.

2.2. Sorption procedure

For the study of the influence of the pH, 200 mL of solution containing 50 mg Pb L^{-1} was mixed with 40 mg of sorbent for 72 hours. This contact time was considered sufficient for reaching equilibrium. The pH was not controlled during sorption but its final value was measured. Samples were filtered on a filter membrane (pore size: 1.2 μm). The residual lead concentration in the filtrate was analyzed using an ICP-AES equipment (Jobin Yvon 2000, Jobin-Yvon, France). Sorption isotherms were carried out on alginate, *A. niger* and *A. nodosum*. A fixed volume of solution ($V: 200 \text{ mL}$), which pH was controlled with H_2SO_4 and NaOH solutions at different initial concentrations ($C_o, \text{ mg Pb L}^{-1}$: 9, 22 and 46) was mixed for 72 hours with increasing sorbent masses m (10-40 mg). After filtration, the samples were analyzed using ICP-AES equipment for the determination of the residual metal concentration, C_{eq} (mg Pb L^{-1}) and the mass balance equation was used for the determination of lead concentration in the sorbent, $q, \text{ mg Pb g}^{-1}$, $q = V/m (C_o - C_{eq})$. Sorption kinetics was determined using 1 L of solution at the concentration 25 mg Pb L^{-1} and 200 mg of sorbent. Samples were regularly collected, filtered and analyzed for lead content by ICP-AES.

3. RESULTS AND DISCUSSION

3.1. Influence of pH on lead sorption and selection of sorbents

Experiments were carried out at pH 3, 4, 5 and 6 with low metal concentrations to avoid precipitation artifacts. This part of the study served to select the best sorbents among the ten sorbents that were tested. Table 1 shows the change in the pH of the solution, the sorption efficiency and the sorption capacity.

Table 1

Influence of pH on sorption efficiency (SE, %) and sorption capacity (SC, mg Pb g⁻¹) for selected sorbents – Final pH (C₀: 50 mg L⁻¹; Sorbent dosage: 200 mg L⁻¹, NaNO₃: 0.05 M)

Sorbent	pH 3			pH 4			pH 5			pH 6		
	pH _f	SE	SC	pH _f	SE	SC	pH _f	SE	SC	pH _f	SE	SC
<i>A. niger</i>	3.3	44.4	103	4.8	58.0	129	6.0	43.1	107	6.1	54.6	102
<i>M. miehei</i>	3.1	22.2	52	3.9	10.2	23	4.4	39.5	95	4.5	34.5	74
<i>P. chrysogenum</i>	3.1	4.3	10	3.7	3.2	7	4.2	6.2	15	5.0	11.1	21
<i>R. arrhizus</i>	4.5	18.8	44	4.8	16.0	36	5.1	19.4	48	5.4	31.4	59
<i>R. conhii</i>	3.2	3.7	9	4.6	34.0	76	4.8	45.9	113	5.0	44.3	83
<i>A. nodosum</i>	3.2	41.8	97	5.0	48.6	108	5.4	59.7	149	5.6	68.4	127
<i>L. trabeculata</i>	3.1	11.4	26	4.0	12.0	27	4.9	13.7	34	5.2	23.8	45
<i>S. cerevisiae</i>	3.3	6.5	15	4.8	13.6	30	5.1	18.2	45	5.2	27.5	52
Alginate	3.2	88.5	205	4.2	55.2	123	5.1	56.0	140	5.9	31.5	59
Chitosan	5.2	8.1	19	5.5	10.1	22	5.7	17.7	44	6.0	21.5	40

Table 1 shows pH variation for selected sorbents. The sorbents can be classified in 3 groups: (a) those that systematically decreased the pH of the solution (*P. chrysogenum*; *M. miehei*); (b) those that systematically increased the pH of the solution (chitosan, *A. niger*); and (c) those that increased the pH when the initial pH was below 5-5.5 and decreased the pH for pH above pH 6 (*R. arrhizus*, *R. conhii*, *A. nodosum*, *L. trabeculata*, *S. cerevisiae*, alginate). Even in the same kind of sorbent (fungal, algae) the pH variations were not homogeneous in value and in trend, despite similar structures and compositions. In the case of industrial fungal biomass it may be explained by the treatments used for the inactivation of the microorganisms (thermal treatment versus chemical treatment) or by the presence of impurities (residues of flocculating and filtrating material). The greatest pH variations were observed with chitosan, especially at low initial pH.

The pH significantly influenced the sorption efficiency. However, the trends and the extent of the variation depended on the sorbent. In most cases, increasing the pH increased the sorption efficiency. In the case of *A. niger* and *R. conhii*, the sorption efficiency was almost independent of the pH, while in the case of alginate, the sorption efficiency tended to decrease with decreasing the initial pH. The best sorbents were *A. niger*, *A. nodosum*, *R. conhii*, *M. miehei*, and alginate. The optimum equilibrium pH was in most cases greater than pH 5, except for alginate. Indeed, in the case of alginate the sorption was much more efficient at acidic pH. Increasing the pH resulted in a decrease of the competition of protons with lead for sorption on the sorbents, while a mild pH was much more favorable to the chelation of lead by the ligands present on the biomass, and on amine functions of chitosan. The greatest sorption capacities were obtained at around pH 5-5.5 for *A. niger*, *A. nodosum*, *R. conhii*, with sorption capacities as high as 100-150 mg Pb g⁻¹ (0.5-0.75 mmol Pb g⁻¹). In the case of

alginate the sorption exceeded 200 mg Pb g⁻¹ (1 mmol Pb g⁻¹) at pH 3-3.5, but decreased at increasing the equilibrium pH. *A. niger*, *A. nodosum* and alginate have been selected for more complete sorption studies.

3.2. Sorption isotherms

Sorption isotherms have been carried out at pH 4 as the initial pH. The pH was controlled during the sorption. Figure 1 show lead sorption isotherms using *A. niger* and *A. nodosum*. The curves were modeled using the Langmuir (solid lines) and the Freundlich (dashed lines) equations:

$$\text{Langmuir equation: } q = \frac{q_m b C_{eq}}{1 + b C_{eq}} \quad (1)$$

where q , q_m are the sorption capacity and the maximum sorption capacity at monolayer coverage, respectively (mg Pb g⁻¹), b (L mg⁻¹) is the sorption affinity (proportional to the initial slope of the sorption isotherm curve).

$$\text{Freundlich equation: } q = k_F C_{eq}^{1/n} \quad (2)$$

where k_F and n are the parameters of the Freundlich model.

For both *A. niger* and *A. nodosum*, the best fit of experimental data was obtained with the Langmuir equation (Figure 1, and Table 2). Though the maximum sorption capacity and the affinity coefficient varied reciprocally for *A. niger* and *A. nodosum*, and the term $q_m b$, (i.e. the initial slope of the sorption isotherm curve) was comparable for *A. niger* and *A. nodosum*, (i.e. 97.0 and 97.8 L g⁻¹, respectively). These sorbents showed comparable sorption efficacy on the basis of equilibrium performance.

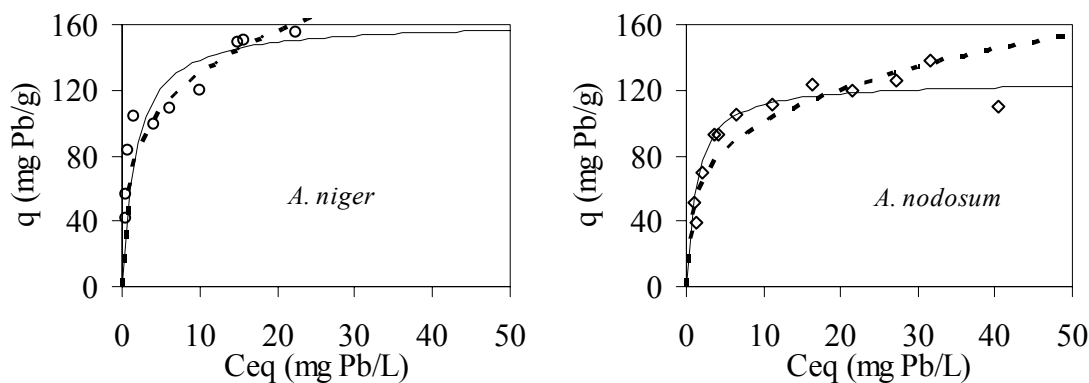


Fig. 1. Lead sorption isotherms on *A. niger* and *A. nodosum* at pH 4 (points: experimental data; dashed lines: modeling with the Freundlich equation; solid lines: modeling with the Langmuir equation).

In the case of alginate it was impossible to fit the experimental data with the models. Indeed, a great dispersion of sorption capacities was observed with changing the mass of the sorbent and the initial metal concentration (Figure 2). At using low initial metal concentration,

the sorption capacity was very low (below 25 mg Pb g⁻¹), while increasing the initial metal concentration, significantly increased the sorption capacity. However, for intermediary initial metal concentration (C₀: 22 mg Pb L⁻¹), unexpectedly, the sorption capacity decreased with increasing the residual concentration. At the highest initial metal concentration, again, the sorption capacity did not vary continuously with increasing the residual concentration.

Table 2

Lead sorption isotherms – Parameters of Langmuir and Freundlich models.

Sorbent	Langmuir Model			Freundlich Model		
	q _m	b	R ²	k	n	R ²
<i>A. nodosum</i>	125.4	0.78	0.979	53.85	3.73	0.788
<i>A. niger</i>	161.7	0.60	0.984	70.19	3.77	0.820

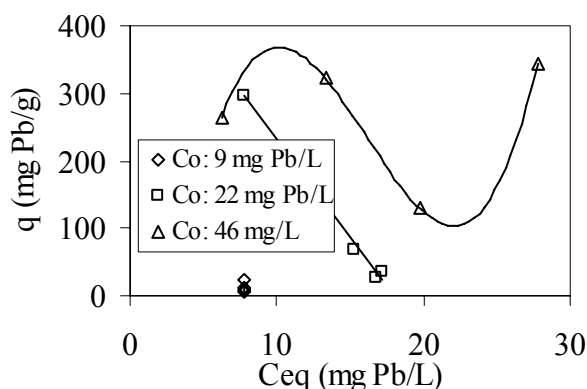


Fig. 2. Lead sorption isotherm on alginate at pH 4 (both initial concentration C₀ and sorbent dosage were varied to get the distribution of the metal between the two phases).

The experimental data were also worked on with plotting the sorption capacity and the sorption efficiency versus the sorbent dosage for each initial metal concentration (Figure 3, left and right panels, respectively). At low initial metal concentration, the sorption capacity and the sorption efficiency were not controlled by the sorbent dosage. At medium initial metal concentration, as expected increasing sorbent dosage resulted in a decrease in sorption capacity, however, increasing the mass of sorbent surprisingly decreased sorption efficiency. For the highest initial metal concentration, sorption capacity was almost constant at low sorbent dosage but seriously decreased at the highest sorbent dosage, while sorption efficiency reached a maximum when the sorbent dosage was 150 mg alginate L⁻¹. A first attempt has been made to explain this surprising behavior of alginate in relation with the dissolving of the biopolymer. The ability of alginate to sorb metal ions is well-documented but in most cases research has focused on the use of pre-formed alginate bead (gelled with calcium chloride, for example) [21], a few studies also dealt on the direct coagulation of alginate in metal ion solutions [22]. It is possible to suggest that lead sorption occurs by a dual mechanism involving the chelation of lead on functional groups of the biopolymer and by a gelation of the biopolymer, lead acting as a cross-linking agent. This ionic cross-linking / ionotropic gelation mechanism has been described by Dambies et al. in the case of chitosan gelation using molybdate as the cross-linking agent [23].

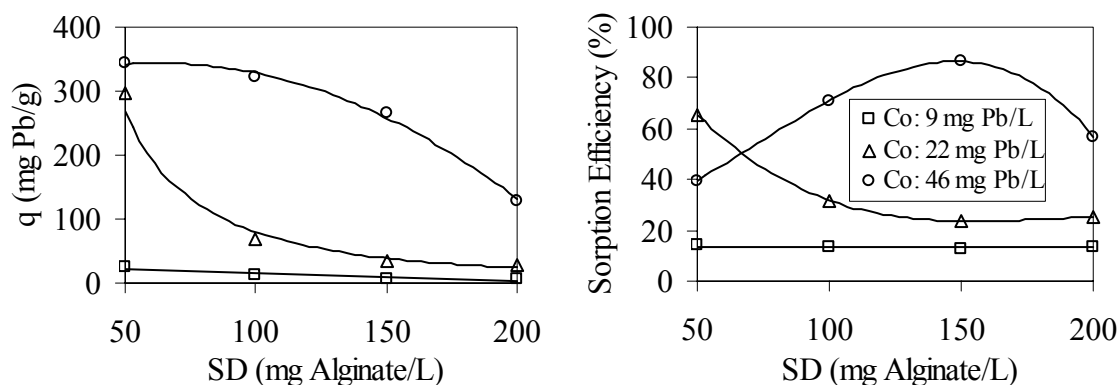


Fig. 3. Influence of sorbent dosage on uptake capacity and sorption efficiency at different initial metal concentrations (pH 4).

When there was an excess of polymer compared with lead, the amount of metal was not high enough to cross-link alginate chains. The biopolymer dissolved in acidic media and it was not able to form a stable network. Lead cations may be chelated to dissolved polymer chains and then they can not be removed at filtration and the sorption efficiency decreased. When the metal concentration increased, the cross-linking with lead ions was more efficient and the biopolymer gelled with a simultaneous immobilization of metal ions.

3.3. Sorption kinetics

Though the maximum sorption capacity and affinity are important parameters in the determination of the performance of a biosorption system, it is also necessary to take into account the uptake kinetics in the selection of the optimum sorbent. Figure 4 shows lead sorption kinetics for *A. niger* and *A. nodosum*, respectively. Equilibrium was reached after 4 hours of contact in the case of *A. nodosum*, while in the case of *A. niger*, more than 90 % of the total sorption was reached within the first 4 hours of contact, the sorbent continued to sorb small amounts of lead even after 24 hours of contact. It may be due to different sorption mechanisms, to diffusion limitations or to differences in the location of metal sorption. Tsezos and Volesky [24] showed in the case of uranium sorption on fungal biomass that the uptake involved different mechanisms including chelation, but also local precipitation of metal ions (in the membrane). The occurrence of successive different sorption steps could explain a longer time to be required for reaching the equilibrium. The sorption can be restricted to the external layer of the sorbent or can occur in the whole membrane: in this case the time required to penetrate, diffuse and be adsorbed can be significantly increased.

Uptake kinetics may be controlled by several mechanisms including the intrinsic sorption rate, but also resistance to diffusion. There are different steps in the mass transfer of the solute from the solution to the sorption sites: (a) bulk diffusion; (b) film mass transfer resistance; and (c) intraparticle mass transfer resistance. Providing a sufficient agitation (stirrer speed, reactor geometry) allows neglecting the bulk diffusion as the limiting step. Film diffusion and intraparticle diffusion are actually the main controlling steps. Though the separation of these two steps has no physical significance, it is possible to assume, as a simplification, that the preliminary stage (first minutes of contact) is controlled by film diffusion resistance while the later stage is mainly controlled by intraparticle diffusion resistance.

In a first approximation, the sorption kinetics (within the first minutes) may be modeled by a first-order kinetic equation [25]; and the kinetic parameter k_a (min^{-1}) can be obtained by:

$$\text{Ln} \left[\frac{C(t)}{C_o} \right] = k_a t \quad (3)$$

Puranik et al. [26-27] proposed a more sophisticated and appropriate model for the description of uptake kinetics under the following assumptions: (a) the particles are assumed to be spherical (uniformity in shape and size); (b) the bulk concentration of the solute is homogeneous in the reactor (correct mixing); (c) the intraparticle diffusion is negligible (sorption located at the surface of the sorbent); (d) instantaneous sorption at the surface of the particle (fast intrinsic sorption rate); (e) limited volume of solution; and (f) isothermal sorption mechanism described by either a Langmuir or a Freundlich equation. They used several equations, including the total mass balance equation:

$$W_s q(t) + C(t) = C_o \quad (4)$$

where W_s is the sorbent dosage (g L^{-1}), q is the sorption capacity (mg Pb g^{-1}), $C(t)$ is the bulk lead concentration (mg Pb L^{-1}), and C_o the initial metal concentration (mg Pb L^{-1}).

The change in the bulk concentration is proportional to the driving force for the sorption at the surface of the particle:

$$\frac{dC(t)}{dt} = -K_m a (C(t) - C_p(t)) \quad (5)$$

where K_m is the external film mass transfer coefficient (m min^{-1}), a is the specific surface area of the sorbent particles per unit volume of reactor ($\text{m}^2 \text{m}^{-3}$), and C_p is the concentration of the metal at the liquid/sorbent interface (mg Pb L^{-1}).

Combining the mass transfer resistance equation and the mass balance equation, they established the following equation:

$$W_s \left(\frac{dq(t)}{dt} \right) = K_m a (C(t) - C_p(t)) \quad (6)$$

The differentiation of the Langmuir equation applied for lead concentration at the interface (C_p) gave after simplification:

$$\frac{dq(t)}{dt} = \frac{dC_p(t)}{dt} \left[\frac{q_m b}{(1 + b C_p(t))^2} \right] \quad (7)$$

The combination of this equation with the preceding equation gave after simplification:

$$\frac{dC_p(t)}{dt} = \frac{K_m a}{W q_m b} \left[(C(t) - C_p(t))(1 + b C_p(t))^2 \right] \quad (8)$$

Using the dimensionless variables ($C^*(t) = C(t)/C_o$; and $C_p^*(t) = C_p(t)/C_o$), the change of metal concentration in the bulk solution with time might satisfy the system of first ordinary differential equations:

$$\frac{dC^*(t)}{dt} = -K_m a (C^*(t) - C_p^*(t)) \quad (9)$$

$$\frac{dC_p^*(t)}{dt} = \frac{K_m a}{W q_m b} [(C^*(t) - C_p^*(t))(1 + b C_p^*(t))^2] \quad (10)$$

$$\text{with the boundary conditions: } C^*(t=0) = 1 \quad \text{and} \quad C_p^*(t=0) = 0 \quad (11)$$

This system has been solved using Mathematica[®] package for the modeling of kinetics using the Langmuir coefficients from Table 2. The sum of the square of residuals has been minimized in order to get the optimum $K_m a$. Assuming that the sorbent particles were not porous, and that their (wet) density ρ (kg m^{-3}) was approximately 1050, the specific surface area of the sorbent particles per unit volume of reactor, a , can be calculated according to:

$$a = \frac{6SD}{d_p \rho} \approx 18 \text{ m}^{-1} \quad \text{where SD is the sorbent dosage (g L}^{-1}\text{)}. \quad (12)$$

Figure 4 (left panel) shows the modeling of experimental data for *A. nodosum* and *A. niger*, the kinetic parameters are given in Table 3. The sorption kinetics is quite well described by the modeling, especially in the first part of the curve. In the final stage, the residual concentration was slightly overestimated for *A. nodosum*. It may be due to an underestimation of the sorption capacity deduced from the Langmuir parameters. In the case of *A. niger* the modeling was not so good: the final concentration was dramatically underestimated and the initial part of the curve was not perfectly described as it was with *A. nodosum*. The worst fit of experimental data by this model may be explained by inaccurate modeling hypotheses, and especially an overestimation of the contribution of intraparticle diffusion.

Crank proposed a model whereby diffusion is controlled only by intraparticle mass transfer for well-stirred solutions of limited volume (V), assuming the solute concentration to be always uniform (initially C_o), the sorbent sphere to be free from solute, and the external diffusion to be negligible [28]. Under these conditions, the fractional approach to equilibrium (FATE) that is the total amount of solute M_t (mg g^{-1}) in a spherical particle after time t (min), expressed as a fraction of the corresponding quantity after infinite time (M_∞) is given by:

$$\text{FATE} = \frac{M(t)}{M(\infty)} = 1 - \sum_{i=1}^{\infty} \frac{6\alpha(\alpha+1)}{(9+9\alpha+q_n^2\alpha^2)} \text{Exp}\left[-\frac{Dq_n^2 t}{d_p^2}\right] \quad (14)$$

where D is the intraparticle diffusion coefficient ($\text{m}^2 \text{min}^{-1}$). The fractional approach to equilibrium, FATE, may be used to estimate the intraparticle diffusion coefficient D , when the external diffusion coefficient is neglected. α is the effective volume ratio, expressed as a

function of the equilibrium partition coefficient (solid/liquid concentration ratio) and is obtained by the ratio $C_{eq}/C_o - C_{eq}$. q_n represent the non-zero solutions of the equation:

$$\tan q_n = \frac{3 q_n}{3 + \alpha q_n^2} \quad (15)$$

The infinite terms are summed until the summation does not vary. This equation was used to determine the overall intraparticle diffusivity which best fit experimental data - minimizing the sum of the square of the differences between experimental results and calculated data. Tien pointed out that this equation is only justified when the sorption isotherm can be approximated by a linear equation [29]. However this simplified model will be sufficient to approach coefficient D. Figure 4 (right panel) shows that the equation fitted well experimental data, especially for *A. nodosum*. The simplified equation does not take into account the sorption capacity of the sorbent, the best fit of kinetic curves in the later stage of the sorption process was thus expectable. Intraparticle diffusion coefficients were of the same order of magnitude for *A. nodosum* and *A. niger*, close to $4 \cdot 10^{-12} \text{ m}^2 \text{ min}^{-1}$. The Biot number was very high (between 4500 and 15000), indicating that film resistance is negligible for these sorbents.

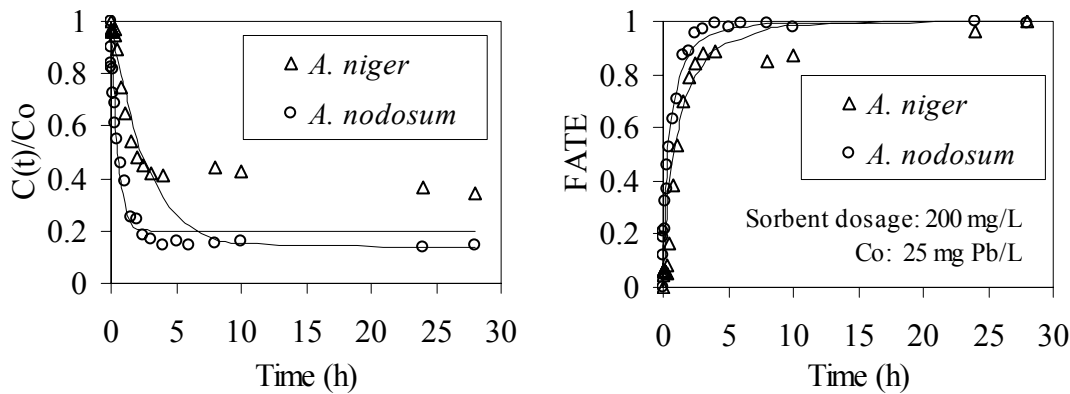


Fig. 4. Lead sorption kinetics on *A. niger* and *A. nodosum* at pH 4 (curves: modeling with external diffusion resistance model (left) and intraparticle diffusion resistance model (right)).

Table 3

Lead sorption kinetics – Parameters of the kinetic models (K_{ma} , min^{-1} ; K_m , m min^{-1} ; D , $\text{m}^2 \text{ min}^{-1}$) and Biot number (dimensionless).

Sorbent	First-order equation & Film Resistance			Crank equation (Intraparticle Diffusion)		Biot number
	$K_{ma} * 10^3$	$K_m * 10^3$	SSR	$D * 10^{12}$	SSR	$B_i = K_m d_p / D$
<i>A. nod.</i>	22.35	1.22	0.081	4.94	0.038	15400
<i>A. niger</i>	5.09	0.278	0.287	3.67	0.173	4700

SSR: Sum of Square Residuals : $\sum_{i=1, n} [(f(t_i)_{exp.} - f(t_i)_{calc.})^2]$, n is the number of experimental points, $f(t_i)_{exp.}$ and $f(t_i)_{calc.}$ are transforms of lead concentrations at time t_i on experimental data and modeled data, respectively.

4. CONCLUSIONS

A. niger and *A. nodosum* were selected for their high sorption for lead recovery from acidic solutions (around pH 4) with sorption capacities as high as 0.6-0.7 mmol Pb g⁻¹. Simple models were used for modeling sorption kinetics and evaluate the order of magnitude for mass transfer coefficients for external and intraparticle diffusion. The Biot numbers show that film diffusion can be considered as negligible. Alginate was also characterized by high sorption capacities (about 1.6-1.7 mmol Pb g⁻¹) when using high lead concentrations: it allows the gelification of the biopolymer. At low metal concentration, the amount of lead ions is not sufficient to maintain the stability of the polymer that dissolves in water and the sorption capacity strongly decreases.

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