



HAL
open science

Influence of the treatment of fungal biomass on sorption properties for lead and mercury uptake

Marketa Španělová, Lenka Svecova, Guibal Eric

► To cite this version:

Marketa Španělová, Lenka Svecova, Guibal Eric. Influence of the treatment of fungal biomass on sorption properties for lead and mercury uptake. 15th International Biohydrometallurgy Symposium (IBS 2003), Sep 2003, Athènes, Greece. hal-04755844

HAL Id: hal-04755844

<https://imt-mines-ales.hal.science/hal-04755844v1>

Submitted on 31 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Influence of the treatment of fungal biomass on sorption properties for lead and mercury uptake

M. Španělová^a, L. Švecová^{a*} and E. Guibal^{b*}

^a Institute of Chemical Technology, Department of Environmental Chemistry, Technická 5, 166 28 Prague 6, Czech Republic

^b Ecole des Mines d'Alès, Laboratoire Génie de l'Environnement Industriel, 6 avenue de Clavières, F-30319 Alès cedex, France

ABSTRACT

Aspergillus niger biomass, obtained as a by-product of fermentation processes, has been tested for lead and mercury sorption. Biomass was produced by two different ways of citric acid production: (a) surface growth, and (b) submerged growth. Their sorption properties have been compared to biomass subjected to an alkaline treatment. The influence of the pH has been studied to select the optimum pH for lead and mercury and pre-select the best sorbent samples. Optimum sorption performances for Pb were obtained with surface-grown biomass which was submitted to alkaline treatment, while with Hg biomass produced by submerged culture was preferred. For lead the experimental pH was set to pH 3, while for mercury the experimental pH was fixed to pH 6. Experiments were continued on selected sorbents by determination of sorption isotherms and uptake kinetics. The influence of experimental parameters (particle size, sorbent dosage, metal concentration) has been checked on sorption kinetics to evaluate the best operating conditions. In the case of lead sorption properties the excellent sorption properties characterized by fast sorption kinetics and high sorption capacities (close to 600 mg Pb g⁻¹) may be explained by the release of a cell component or a by-product of culture procedure (residue of growing media or sub-product of the fermentation process) that induces lead precipitation at long contact time.

Keywords: *Aspergillus niger*, waste biomass, sorption, lead, mercury.

1. INTRODUCTION

The reinforcement of the regulations concerning industrial wastewaters has been the motive to an increasing research for developing new sorption processes. Indeed, conventional techniques such as precipitation and ion-exchange are sometimes non-competitive or unable

* L. Švecová thanks the French Embassy in Prague for the financial support during her stay in France. E.Guibal thanks the European Community for financial support under Growth Program (3SPM project, Contract G1RD-CT2000-00300) for attending the IBS'03 conference.

to reach the regulation levels. There is still a need for alternative processes that should be cost-effective, and easy to manage. Biosorption that consists in using biological materials or microorganisms for the sorption of target molecules (metals, dyes, pesticides) has been widely studied since the early 80's. A great diversity of biomass material has been investigated for the sorption of metal ions from bacteria, fungi, algae [1], to agriculture waste by-products or bio-industry wastes [2]. Using dead biomass makes easier the control of the process and using waste materials reduces the cost of the material. For these reasons, fungal biomass has frequently been considered as a suitable biosorbent [3-7] since it is produced in huge amounts in the fermentation processes (citric acid production) and this biomass is poorly valorizable.

Fungal biomass may contain a wide range of functional groups including amine groups, carboxylic groups, and sulfur groups brought by cell constituents. For example fungal cell wall may be constituted by the assembling of chitin/chitosan layers (amine-rich), proteins (amino-acids), glucans [5]. Fungal biomass, especially from *Mucorales* group, has been considered as an alternative source for chitosan [8-10]: an aminopolysaccharide, which is commercially produced from crustacean shells, very efficient for metal recovery [11-14]. However, chitin and chitosan are strongly bound to other cell wall constituents such as glucans and proteins. While the association of chitin to proteins may be positive for sorption purpose since the amino-acids have potential sorption activity, the glucans have very weak potential for metal sorption. The immobilization of amine functions by linkage with glucans can significantly reduce the sorption activity of the material. Chemical treatments should be considered for "purifying" the biomass from this "inert" material [8-10,15-17]. The composition of the membrane is also tributary of the harvesting time and the growing conditions [18].

A preliminary study has been launched on the comparison of the sorbing potential of *Aspergillus niger* prepared under surface and submerged fermentation conditions used (a) as produced, and (b) after alkaline treatment. The sorption properties are investigated for lead and mercury removal from dilute solutions. First the influence of the pH is studied and these results serve to select the best sorbents for the recovery of these metals. Then the sorption properties of selected biomass are studied through sorption isotherms and uptake kinetics.

2. MATERIALS AND METHODS

2.1. Materials

Aspergillus niger biomass was supplied as an industrial waste from fermentation processes (citric acid production) by a local company (Czech Republic). Two different samples have been tested: one being obtained by a surface-growth procedure while the second sample was obtained by submerged culture. After being collected the samples were abundantly rinsed in order to remove residual compounds present in the culture media. The samples were then dried or submitted to an alkaline treatment to prepare 5 different materials. The treated samples were finally submitted to a water-rinsing step and dried. The experimental conditions for their preparation are listed in Table 1.

Table 1

Preparation characteristics of biosorbents

Sample	Culture conditions	Alkaline treatment (concentration)	Temperature	Time (h)
A	Surface	No	-	-
B	Surface	Yes (1 M)	Room	24
C	Submerged	No	-	-
D	Submerged	Yes (1 M)	Room	24
E	Submerged	Yes (10 M)	107 °C	6

Typically, the treatment was performed with 100 kg (wet weight, 20-25 % dry mass percentage) mixed with 500 L of sodium hydroxide solution at the appropriate concentration. After chemical treatment, the biomass was centrifuged, rinsed with water up to neutral pH and then dried in a fluidized bed dryer. The weight loss changed with the treatment. In the case of biomass B and D, which were selected for most of the experiments, the weight loss was 55 % and 80 %, respectively. The samples were ground and sieved before being used to prepare 4 different size fractions: $G1 < 125 \mu\text{m} < G2 < 250 \mu\text{m} < G3 < 355 \mu\text{m} < G4 < 510 \mu\text{m}$.

Lead chloride (Riedel-de-Haen, Germany) and mercury chloride (Fluka, Switzerland) have been used for the preparation of the solutions. Other reagents (hydrochloric acid, sodium hydroxide) were supplied by Carlo Erba (Italy).

2.2. Sorption procedures

The study of the influence of pH on sorption performance was carried out by mixing sorbent with metal ion solution at selected pH (controlled with HCl and NaOH) for 3 days. The final pH was measured and the residual concentration in the solution (after filtration on membrane; pore size: $1.2 \mu\text{m}$) was determined by ICP-AES (inductively coupled plasma atomic emission spectrometry). Sorbent dosage was fixed at 300 mg L^{-1} , while initial metal concentration was 50 mg Me L^{-1} . In the case of lead, the initial pH was not raised at pH 7 to avoid lead hydroxide precipitation.

For sorption isotherms, solutions were prepared at the appropriate pH (i.e. pH 3 for lead and pH 6 for mercury) controlled with HCl or NaOH, at different initial metal concentrations, C_o (mg Me L^{-1}), ranging between 10 and 200 mg Pb L^{-1} and between 10 and 100 mg Hg L^{-1} . The sorbent dosage was varied using a variable mass of sorbent m : 10 and/or 20 mg in a fixed volume of solution, V , 0.1 L). After 3 days of contact the solutions were filtered and the residual concentration (C_{eq} , mg Me L^{-1}) was determined by ICP-AES. The mass balance equation was used for calculating the sorption capacity, q (mg Me g^{-1}): $q = V/m (C_o - C_{eq})$.

For sorption kinetics, 1 L of solution (at given concentrations: 20, 50 or 100 mg Me L^{-1}) at selected pH was mixed with selected sorbent (at given sorbent dosage: 100, 200, 300 or 500 mg L^{-1}) for 3 to 4 days. Samples were regularly withdrawn and filtered on membranes and residual metal concentration was determined by ICP-AES.

3. RESULTS AND DISCUSSION

3.1. Influence of pH on sorption properties and biomass selection

A preliminary set of experiments was performed with standard conditions. This preliminary study was used to evaluate the efficiency of the different sorbents, to determine

the optimum pH and to check the influence of the biomass on the pH of the solution. Results are summarized on Figures 1 and 2 for lead and mercury sorption, respectively.

The contact of the biomass with metal ion solution significantly changed the pH of the solution, regardless of the type of metal. Significant differences were observed with the different biomass. With lead, biomass C is the only sorbent that decreases the pH of the solution at weakly acidic pH (i.e. pH 4-6). Biomass D hardly increased the pH (by less than 0.5 pH unit) over the whole pH range investigated. On the opposite hand, the other samples (biomass A, C, E) significantly increased the pH of the solution, especially at pH 4: in this case the pH can be increased up to 6.5-6.7 (biomass B). Above pH 5, pH variation was less significant: the biomass had a buffering effect around pH 6. Generally at acidic pH (below pH 4) the pH of the solution was not significantly changed (less than 0.3 pH unit): the alkaline charge of the sorbent and the influence of metal sorption (uptake of OH⁻ in relation with metal sorption, proton release) were not sufficient to change the pH.

For mercury sorption, the trends are generally similar, except for biomass C (for which the pH of the solutions was also decreased). The weak buffering effect of biomass was also observed at near-neutral pH. As expected the treatment of sodium hydroxide (regardless of NaOH concentration, temperature of the treatment and contact time) significantly impacted the pH of the solution. This may be explained by an insufficient washing/rinsing of the biomass after alkaline treatment or by the presence of citric acid released from the biomass (in the case of pH decrease). It is especially significant in the case of mercury sorption for which metal sorption was negligible, except in the case of biomass E (Figure 2 shows only sorption data for biomass E, for other biomass the sorption capacities were below 10 mg Me g⁻¹). So the pH variation was only attributable to acid-base properties of the biomass.

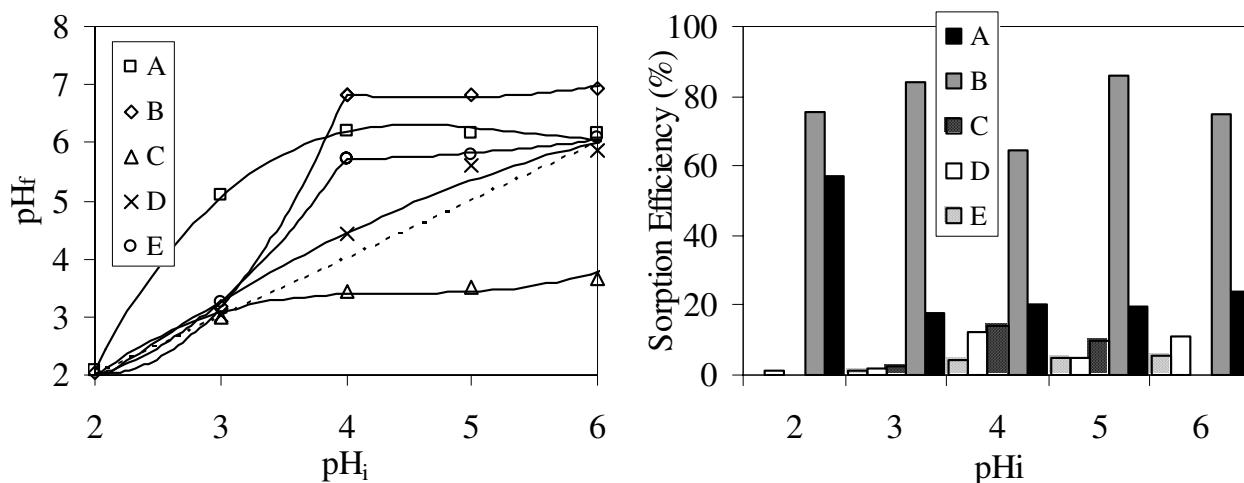


Fig. 1. pH variation during lead sorption (left panel) and sorption efficiency (right panel) in function of initial pH (Co: 50 mg Pb L⁻¹; Sorbent dosage: 300 mg L⁻¹).

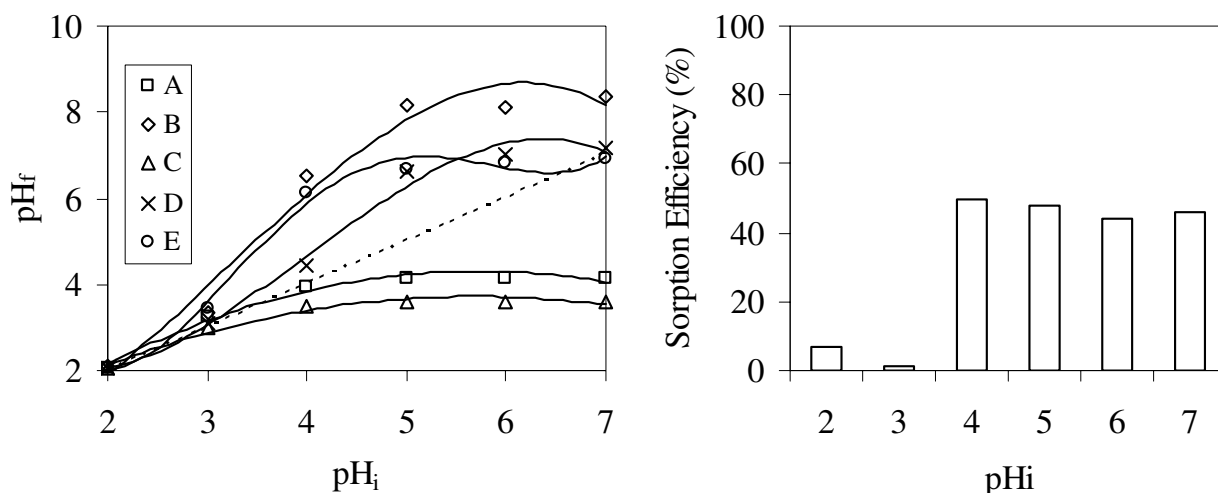


Fig. 2. pH variation during mercury sorption (left panel) and sorption efficiency in function of pH with biomass E (Co: 50 mg Hg L⁻¹; Sorbent dosage: 300 mg L⁻¹).

Lead sorption efficiency was only significant with biomass B, and to a lesser extent with biomass A (other biomass exhibited sorption efficiency below 20 % under selected experimental conditions). Since the biomass strongly increased the pH above pH_i = 4, and in order to avoid precipitation phenomena, the initial pH was selected at pH 3. The sorption efficiency was comparable at this pH to those observed at higher pH for biomass B. For these reasons biomass B was selected for further experiments using pH 3 as the optimum pH. It appears at this stage that biomass grown under surface fermentation conditions was more favorable to lead uptake, especially when submitted to alkaline treatment.

In the case of mercury uptake, sorption efficiency was negligible in most cases, except with biomass E (submerged fermentation procedure with strongly alkaline treatment). The strong alkaline treatment may drastically change the structure of the biomass. Such a strong treatment is used for the deacetylation of chitin to prepare chitosan, which is characterized by a higher affinity for metals than the raw material. We could expect this treatment being able to remove inert material from cell walls and to transform weakly active sorption sites to strongly reactive functional groups. Less drastic treatment conditions (lower concentration of NaOH, lower contact time, lower temperature) were not able to reach the same reactivity of the biomass for mercury. In this case mercury sorption was mainly efficient at pH equal or greater to pH 4: below pH 4, the sorption efficiency drastically dropped. It is important to observe that the sorption efficiency is significantly lower than the levels reached with lead. For further experiments on mercury sorption, biomass E was selected and experiments were performed at pH 6 (in order to minimize pH variation during metal sorption procedure).

3.2. Lead sorption isotherm

Figure 3 shows lead sorption isotherm at pH 3 using biomass B. The sorption isotherm is very favorable (almost rectangular). At very low concentration (below 3-4 mg Pb L⁻¹), sorption capacity was negligible. It may be explained by a possible complexation of lead ions by biological material released from the biomass; chelated lead is then less adsorbable on biosorbents. Above this limit concentration a sharp increase in the sorption capacity was observed up to a sorption capacity of about 550-600 mg Pb g⁻¹, followed by a plateau (when the residual concentration exceeded 10 mg Pb L⁻¹). Though under selected experimental

conditions (pH and metal concentration) there is no precipitation of lead under hydroxide forms, the shape of the curve (almost rectangular) may be indicative of a mixed adsorption/precipitation phenomenon. This may proceed by reaction of lead with some chelating/precipitating agents released from the biomass (phosphate used in the fermentation media; by-products from citric acid production such as oxalate ions).

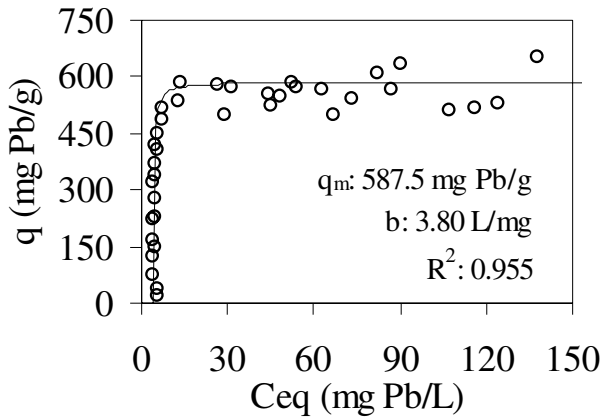


Fig. 3. Lead sorption isotherm at pH 3 using sorbent B (symbols: experimental points, lines: Langmuir modeling ($q = (q_m b C_{eq}) / (1 + b C_{eq})$) after correction of the residual concentration to take into account the non-null residual concentration due to a possible complexation of lead by dissolved compounds).

3.3. Influence of experimental parameters on lead sorption kinetics

Figure 4 shows the influence of lead concentration at two different sorbent dosages (pH 3) using biomass B. Sorption capacities have been plotted in function of the square root of time in order to compare sorption kinetic rates: this type of curve is frequently used to evaluate the contribution of intraparticle diffusion resistance [19]. In a first section of the curve corresponding to a latency of about 1-2 hours, the sorption remained negligible, after this period the sorption capacity linearly increased with the square root of time and the slope was of the same order of magnitude for initial concentrations of 50 and 100 mg Pb L⁻¹, significantly higher than those obtained at a metal concentration of 20 mg Pb L⁻¹. The latency decreased with increasing sorbent dosage.

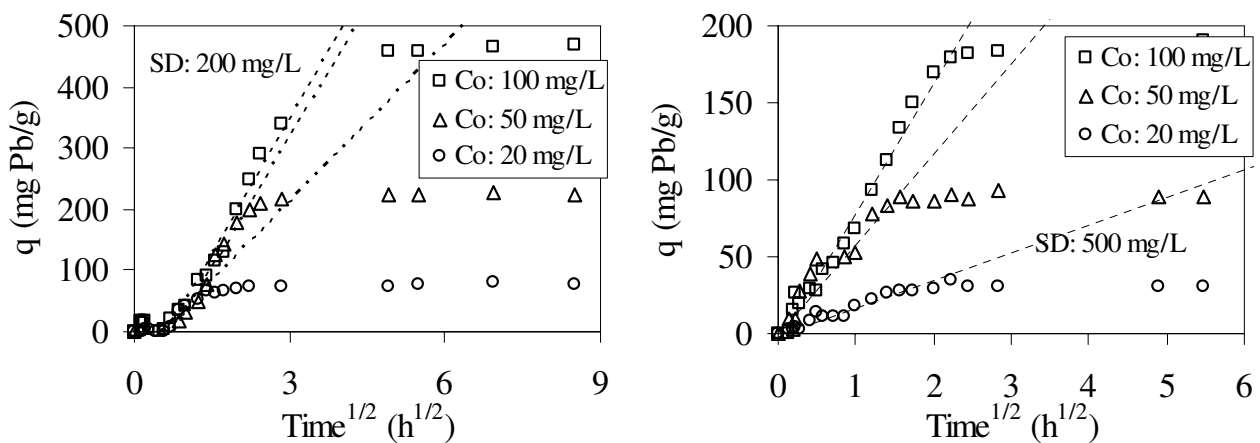


Fig. 4. Influence of lead concentration on sorption kinetics at pH 3 at 2 sorbent dosages (SD) (Sorbent B; G1 particle size).

Figure 5 (left) shows the influence of sorbent dosage on lead sorption kinetics (initial metal concentration: 100 mg Pb L^{-1}). The same trends were observed as in Figure 4. Increasing sorbent dosage slightly decreased the slope of the plot of sorption capacities in function of the square root of time: increasing the sorbent dosage increases the excess of sorption sites (compared to metal ions). As a consequence the residual concentration strongly decreased in the initial stage of the sorption process (after the latency period), then the concentration gradient decreased and the slope of the curve also diminished.

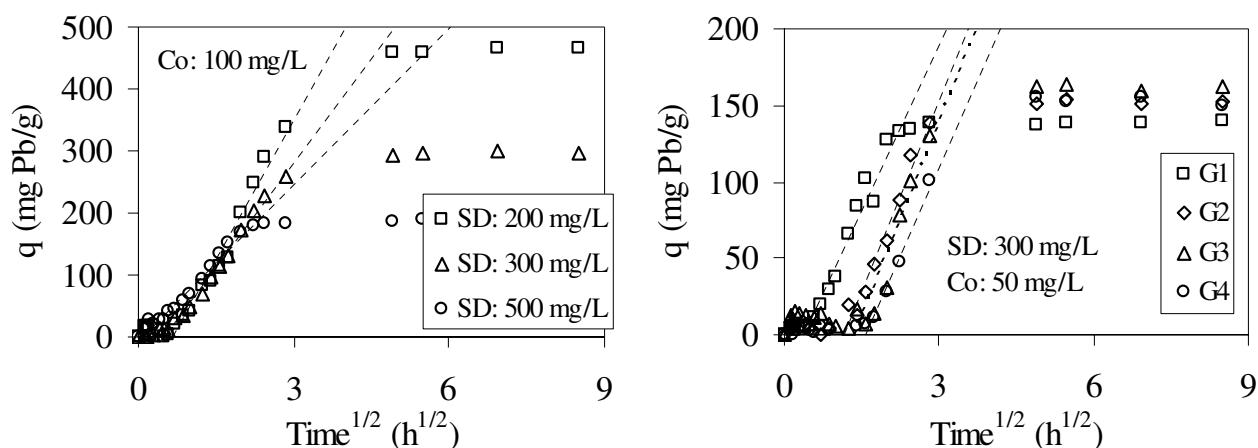


Fig. 5. Influence of sorbent dosage (left panel, G1 particle size) and sorbent particle size (right panel) on Pb sorption kinetics at pH 3 (Sorbent B; G1 particle size).

Figure 5 (right) shows the plot of sorption capacity as a function of square root of time for different particle sizes of biomass B at pH 3. The slopes of the curves were comparable (same order of magnitude) but the latency time increased with increasing the particle size of the sorbent. The shape of the kinetic curves is a bit unusual. It confirms that the mechanism involved in the removal of lead is not a simple sorption mechanism. Actually, at long contact time a trouble can be observed in the solution indicating the occurrence of precipitation phenomena (not due to hydroxide, but that could be explained by the presence of by-products as suggested above).

To verify this hypothesis the biomass was submitted to a new washing treatment with water and acidic water (pH 3). After 2 days of contact with the “washing” solution, the solution was filtered. The biomass was used for kinetic experiments under comparable experimental conditions to those selected above (pH, metal concentration, sorbent dosage; to be able to compare). A concentrated lead solution (1 g Pb L^{-1}) was added to the filtrate (to a final concentration of 50 mg Pb L^{-1}) and the solution was mixed for 3 days in order to verify the occurrence of precipitation phenomena. Actually, the precipitation was observed in the filtrate obtained from acidic solution treatment of biomass B (pH 3) after a few minutes of contact, when the biomass was treated with demineralized water, even after 2-3 days of contact the precipitation was very low (a few percent of initial metal concentration). Using the washed biomass resulted in slower sorption kinetics (Figure 6). At equilibrium the sorption efficiency was only 50 % (instead of 85 %), taking into account the fraction of metal precipitated in the experiments performed with the acidic filtrate (about 35-40 %, not shown): the mass balance is almost maintained.

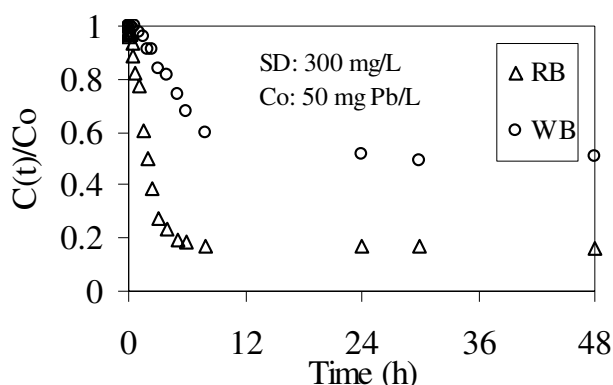


Fig. 6. Influence of acid-washing treatment on sorption kinetics (RB: raw biomass, WB: washed biomass).

3.4. Mercury sorption isotherm

Mercury sorption isotherms were performed at pH 6 using biomass E in presence of NaCl (0.1 M) and without salt addition (Figure 7). The addition of NaCl strongly reduced mercury sorption and changed the type of sorption model that fitted better experimental data.

Maximum sorption exceeded 250 mg Hg g^{-1} ; the Freundlich equation fitted better experimental data than the Langmuir equation: the curve can be characterized by an exponential trend and it was impossible to detect the plateau in the concentration range investigated in this study.

It is important to notice that similarly to experiments on lead, a sample of biomass was submitted to a complementary washing treatment with water at the pH of sorption experiments, the filtrate was collected and completed with concentrated mercury solution (to a final concentration consistent with those selected for sorption studies). In this case, no precipitation was observed.

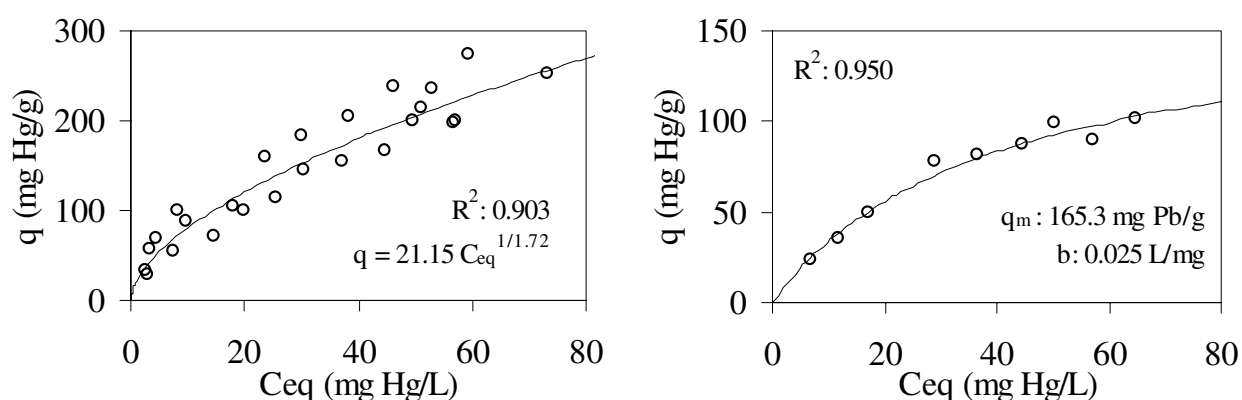


Fig. 7. Mercury sorption isotherm at pH 6 (left: without NaCl; right: with NaCl addition) using sorbent E (symbols: experimental points, lines: Langmuir or Freundlich modeling).

When NaCl was added to mercury solution, the sorption capacity was significantly decreased (about two times). In this case the Langmuir equation better fitted experimental data than the Freundlich model. The theoretical maximum sorption capacity was close to 165 mg Hg g^{-1} , higher than the maximum sorption capacity observed in the range of mercury concentration investigated in the present study (about 100 mg Hg g^{-1}). The addition of sodium

chloride influences the ionic strength of the solution. The influence of ionic strength is usually important in the case of ion-exchange mechanism. In the case of mercury sorption at pH close to neutrality metal is expected to be adsorbed by chelation on amine groups (less sensitive to ionic strength) or ion-exchange on carboxylic functions. The influence of sodium chloride may be interpreted by either the influence of ionic strength on the ion-exchange mechanism or by a change in the speciation of mercury (formation of chloro-complexes) that may affect its adsorbability.

3.5. Influence of experimental parameters on mercury sorption kinetics

The influence of experimental parameters (mercury concentration, sorbent dosage) on sorption kinetics has been investigated (Figure 8). Kinetic decay curves are plotted versus time together with the plots of sorption capacities versus the square root of time. As expected, at decreasing sorbent dosage, the sorption efficiency decreased but with low sorbent dosage (100 mg L^{-1} , not shown), at long contact time a partial release of mercury is observed, especially at high metal concentration and low sorbent dosage (SD: 300 mg L^{-1} ; but also at SD: 100 mg L^{-1} , not shown). This may explain some discrepancies between the results of sorption isotherms and equilibrium points of uptake kinetics. If the time of contact is not the same it can introduces some significant differences.

The initial section of the decay curves appeared to be independent of metal concentration. This first part corresponds to a step of the process that is controlled by external diffusion, while the second part of the curve is controlled by the resistance to intraparticle diffusion. Most significant differences were observed in the second stage of the process, indicating that sorbent dosage and metal concentration parameters mainly influenced mass transfer resistance to intraparticle diffusion. Even with a sorbent dosage as high as 500 mg L^{-1} , the sorption efficiency did not exceed 75-80 %.

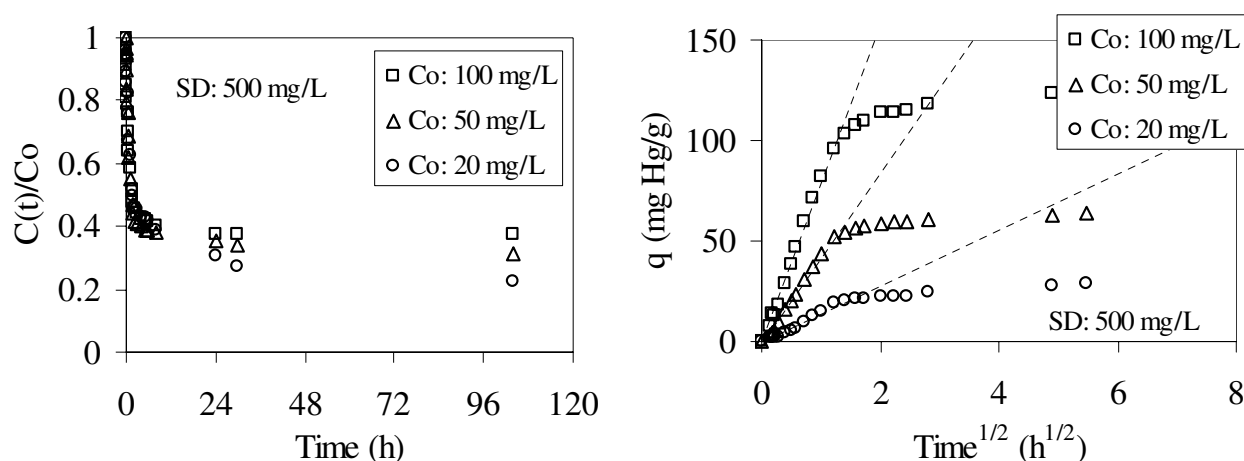


Fig. 8. Influence of mercury concentration on sorption kinetics at pH 6 at 2 sorbent dosages (SD) (Sorbent E; G1 particle size).

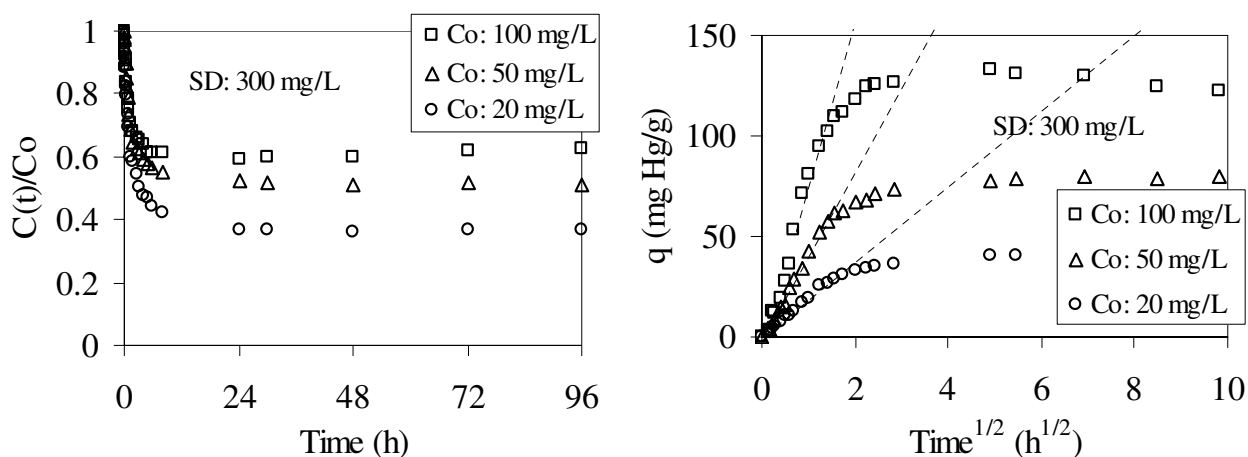


Fig. 8. Influence of mercury concentration on sorption kinetics at pH 6 at 2 sorbent dosages (SD) (Sorbent E; G1 particle size).

Particle size hardly influenced sorption kinetics (Figure 9). Regardless of the plot system ($C(t)/C_0$ versus time or q versus $t^{0.5}$), the curves were very close. Decreasing the size of sorbent particles allowed increasing the slope of the kinetic curves but the differences were not very marked.

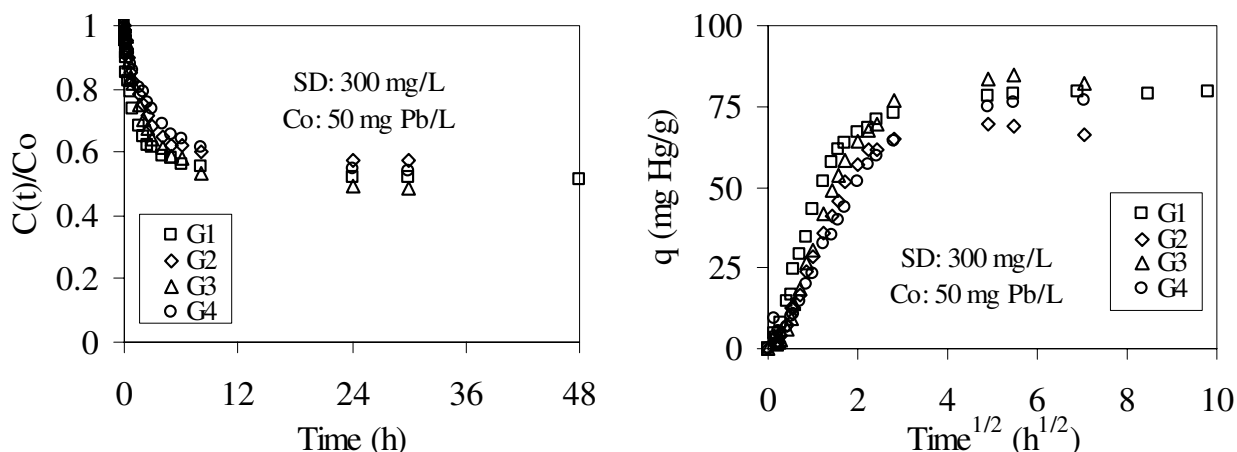


Fig. 9. Influence of particle size on mercury sorption kinetics at pH 6 (SD: 300 mg L^{-1} ; Co: 50 mg Pb L^{-1}).

At equilibrium the sorption capacities were very close: sorption did not occur only on the surface of sorbent particles (in this case the sorption capacity would be more sensitive to the external surface area of the sorbent) but also in the whole volume of the solution. But the sorption kinetics were not strictly controlled by the mass-transfer resistance for large particle.

4. CONCLUSIONS

Waste materials (fungal biomass) from industrial fermentation processes have been successfully used for the sorption of lead and mercury after being chemically treated (alkaline treatment). Best sorbents for mercury and lead sorption were obtained after being treated with NaOH solutions with different concentration, contact time and reaction temperature. While best results were obtained at pH 3 for lead, in the case of mercury sorption may be performed

at pH close to neutrality. High sorption capacities (between 1 and 2 mmol Me g⁻¹) were observed in the case of lead uptake but it appeared that a part of metal removal was due to a precipitation phenomenon probably due to a release of some sub-products or by-products of the fermentation process (phosphate, organic or inorganic; or oxalate). This illustrates the necessity to use a carefully washed material (especially industrial waste products) in order to avoid artifacts; and the care to take in the interpretation of experimental results. Sorption capacities in the case of mercury were lower, especially in the presence of NaCl that significantly reduced sorption capacities. Sorption kinetics were performed at different sorbent dosages: though the initial sorption is quite fast compared to other systems, 24 hours of contact were necessary to reach the equilibrium (due to low sorbent dosage, below 500 mg L⁻¹). Sorbent particle size has a negligible effect on equilibrium concentrations and kinetics.

REFERENCES

1. B. Volesky and Z. Holan, *Biotechnol. Prog.*, 11 (1995) 235.
2. S. Bosinco, J. Roussy, E. Guibal and P. Le Cloirec, *Environ. Technol.*, 17 (1996) 55.
3. M. Tsezos and B. Volesky, *Biotechnol. Bioeng.*, 24 (1982) 385.
4. E. Guibal, C. Roulph and P. Le Cloirec, *Wat. Res.*, 26 (1992) 1139.
5. A. Kapoor, and T. Viraraghavan, *Biores. Technol.*, 61 (1997) 221.
6. W. Lo, H. Chua, K.-H. Lam and S.-P. Bi, *Chemosphere*, 39 (1999) 2723.
7. W. Jianlong, Z. Xinmin, D. Decai and Z. Ding, *J. Biotechnol.*, 87 (2001) 273.
8. D.S. Wales and B.F. Sagard, *J. Chem. Tech. Biotechnol.*, 49 (1990) 345.
9. J. Synowiecki and N.A. Quawi Al-Khateeb, *Food Chem.*, 60 (1997) 605.
10. W.L. Teng, E. Khor, T.K. Tan, L.Y. Lim and S.C. Tan, *Carbohydr. Res.*, 332 (2001) 305.
11. E. Guibal, C. Milot and J. Roussy, *Sep. Sci. Technol.*, 35 (2000) 1021.
12. R. Bassi, S.O. Prasher and B.K. Simpson, *Sep. Sci. Technol.*, 35 (2000) 547.
13. J. Guzman, I. Saucedo, R. Navarro, J. Revilla and E. Guibal, *Langmuir*, 18 (2002) 1567.
14. M. Jaworska, K. Kula, P. Chassary and E. Guibal, *Polym. Int.*, in press (2003).
15. R.A.A. Muzzarelli, F. Tanfani and G. Scarpini, *Biotechnol. Bioeng.*, 22 (1980) 885.
16. A. Kapoor, and T. Viraraghavan, *Biores. Technol.*, 63 (1998) 109.
17. B.J. McAfee, W.D. Gould, J.C. Nadeau and A.C.A. da Costa, *Sep. Sci. Technol.*, 36 (2001) 3207.
18. S. Arcidiacono and D.L. Kaplan, *Biotechnol. Bioeng.*, 39 (1992) 281.
19. E. Guibal, I. Saucedo, J. Roussy, C. Roulph and P. Le Cloirec, *Water S.A.*, 19 (1993) 119.