Turk J Chem 26 (2002) , 441 – 452. © TÜBİTAK

Cadmium and Mercury Uptake by Immobilized *Pleurotus sapidus*

Yağmur YALÇINKAYA

Faculty of Science, Biology Department, Hacettepe University, 06532 Beytepe, Ankara-TURKEY M. Yakup ARICA

Faculty of Science, Biology Department, Kırıkkale University, 71450 Yahşihan, Kırıkkale-TURKEY

Levent SOYSAL, Adil DENİZLİ, Ömer GENÇ, Sema BEKTAŞ*

Faculty of Science, Chemistry Department, Hacettepe University, 06532 Beytepe, Ankara-TURKEY

Received 22.05.2001

Pleurotus sapidus basidiospores immobilized onto Ca-alginate beads were used for the removal of cadmium and mercury ions from aqueous solutions. The biosorption of Cd(II) and Hg(II) ions on the alginate beads and both immobilized live and heat inactivated fungal mycelia of Pleurotus sapidus was studied from aqueous solutions in the concentration range of $30-500 \text{ mg L}^{-1}$. The biosorption of Cd(II) and Hg(II) ions by the alginate and both live and heat inactivated immobilized preparations increased as the initial concentration of the ions increased in the medium. Maximum biosorption capacity for immobilized live and heat inactivated fungal mycelia of Pleurotus sapidus was found to be 96.57 mg g^{-1} (0.86 mmol g^{-1}) and 127.12 mg g^{-1} (1.13 mmol g^{-1}) for Cd(II) and 207.89 mg g^{-1} (1.04 mmol g^{-1}) and 287.43 mg g^{-1} (1.43 mmol g^{-1}) for Hg(II), respectively. The electronegativities and standard electrode potentials of the divalent ions of Group II elements show a definite trend with sorption capacity. Biosorption equilibria were established in about 1 h and were very well described by Langmuir isotherms. The temperature change between 15 and 45° C did not affect the biosorption capacity. The effect of pH was also investigated and the maximum uptake of metal ions on the alginate and both live and inactivated immobilized fungal mycelia were observed between pH 3.0 and 7.0. The alginate-fungus beads were regenerated using 10 mM HCl, with up to 97% recovery, the biosorbents were reused in three biosorption-desorption cycles without any considerable loss in the biosorption capacity.

Introduction

The metal-uptake ability of microorganisms has been known for a long time. It has been suggested that biomass could be used to decontaminate metal-bearing waste waters and to concentrate metals¹⁻³. Biological surfaces consist of different functional groups where coordination complexes with metal ions can be formed.

 $^{^{*}\}mathrm{To}$ whom all correspondence should be addressed.

Among these functional groups are carboxyl (-COOH), amide (-NH₂), thiol (-SH), phosphate (PO_4^{3-}) and hydroxide (-OH). When a metal ion in solution interacts with a solid surface it can be adsorbed by physical adsorption, associated with the weak forces of physical attraction such as van der Waals' forces or by chemical adsorption, associated with the exchange of electrons and the formation of a chemical bond between the adsorbent and the solid surface. The other possibility is the ion exchange which may take place between the incoming cation and hydrogen ions of functional groups at the surface. The ion-exchange mechanisms are expected to become less important as pH rises because most of the functional groups become dissociated if the pH is above a certain value. The inhibition of metal chelation with a decrease in pH was observed by several authors and in different biomasses. Thus it has been proposed that protons and metal ions can compete for the same sites⁴⁻⁶. It can be assumed that a metal ion binds to negatively charged groups or proton-occupied sites of the surface by a chemical, equilibrated and saturable mechanism. Therefore, proton-binding sites on fungal walls are available to metal ions as well.

Data selected from the referenced studies document that biomass from filamentous fungi such as *Aspergillus niger* and *Rhizopus oryzae*, yeasts such as *Saccharomyces cerevisiae*, algae such as *Chlorella regularis* and unicellular bacteria such as *Zoogloea ramigera* and *Pseudomonas aeruginosa* are capable of the uptake or binding of several metal ions. A metal loading capacity of greater than 15% of biomass (dry weight) has been defined as an economic threshold for practical applications of biosorption when compared with alternative methods such as traditional adsorption, ion exchange, chemical precipitation, solvent extraction, and reverse osmosis^{7,8}.

Researchers have previously described the immobilization of fungal spores in/on different matrices^{9,10}. Immobilization provides high cell concentration and the separation of treated water from biomass is easy. A good support material should be rigid and chemically inert, should bind cells firmly, and should have high loading capacity. Alginic acid is a heteropolysaccharide made of α -L-glucuramic acid and β -D-manuromic acids and is found in many algal species, especially ins brown algae. The overall composition and the sequence of monomers in the alginated polysaccharide vary extensively depending on the origin. This carboxylic polyelectrolyte is soluble from aqueous solutions and precipitates in the form of a coacervate in the presence of multivalent metal ions like Ca²⁺, Co²⁺, Fe²⁺, Fe³⁺, and Al^{3+ 11}. Alginate has been previously used as a support material for the immobilization of several enzymes and microbial cells¹².

Dead fungal cells can bind metals at levels greater than, equivalent to or less than live cells depending on the method used to kill the cells^{13,14}. However, it is well known that the use of heat inactivated biomass in industrial applications may offer some advantages over living cells, such as being less sensitive to heavy metal ion concentration and adverse operating conditions (i.e., pH and temperature).

In this work, the basidiospores of the fungus *Pleurotus sapidus* were entrapped using Na-alginate as the natural polymeric matrix. After vegetation of the entrapped basidiospores in the matrix, the immobilized live and heat inactivated fungal biomass was used for biosorption of cadmium and mercury ions from aqueous solutions in a batch system.

Materials and Methods

Microorganism and media

A white-rot basidiomycete strain, *Pleurotus sapidus*, was maintained by subculturing on malt dextrose agar slants. Spore suspensions for immobilization were freshly prepared from 7-day-old cultures, grown on malt dextrose agar slants at 30°C. The growth medium was prepared using deionized double-distilled water and was subsequently filter sterilized; the final pH at 25°C was adjusted to 4.5 (Table 1).

Constituents	Concentration (gL^{-1})
D-glucose	10.0
Yeast Extract	0.1
$\rm KH_2PO_4$	0.2
$MgSO_4.7H_2O$	0.5
$\rm NH_4H_2PO_4$	0.1
$CaCl_2.6H_2O$	0.1
NaCl	0.5
$MnSO_4.H_2O$	0.5
$FeSO_4.7H_2O$	0.1
$ZnSO_4$	0.1
$CaSO_4$	0.01

 Table 1. Composition of Growth Medium.

Immobilization of *Pleurotus sapidus* basidiospores

The immobilization of *Pleurotus sapidus* basidiospores via entrapment was carried out as follows: Na-alginate (2.0 g; from *Macrosytia pyrifera*, high viscosity, Sigma Chem. Co., USA) was dissolved in distilled water and then mixed with the fungal spore suspension (10 mL, about $1x10^9$ basidiospore mL⁻¹). The mixture was introduced into a solution containing 0.10 M CaCl₂ with a burette and the solution was stirred to prevent aggregation of the fungal spore entrapped Ca-alginate beads. The fungal spore entrapped beads (~ 4 mm) were cured in this solution for 1 h and then washed twice with 200 mL sterile distilled water. The beads with immobilized spores then transferred to the growth medium (100 mL) in a 250 mL flask and were incubated on an orbital shaker (150 rpm) at 30°C for 3 days. The mycelia growth in/on the beads was followed during the incubation period using a microscope. After a 3-day incubation period, the Ca-alginate beads with immobilized fungal mycelia were removed from the medium by filtration and washed twice with distilled water. It was then stored at 4°C until use in 5 mM CaCl₂ solution. Dry weights of the microbial growth in/on the immobilized preparations were determined by weighing (after drying in an oven at 50°C overnight) the alginate beads before and after cell growth.

Biosorption studies

The biosorption of Cd(II), and Hg(II) ions on the plain alginate beads and on the both immobilized live and heat inactivated *Pleurotus sapidus* (the heat inactivated preparation was obtained from immobilized live preparation after heat treatment at 90°C for 10 min) from water was investigated in batch biosorptionequilibrium experiments. The effects of the medium pH and the initial concentration of Cd(II) and Hg(II) ions on the biosorption rate and capacity were studied.

The effect of pH on the biosorption rate was investigated in the pH range of 3.0-7.0. The pH of the medium was adjusted with HCl or NaOH at the beginning of the experiment and not controlled afterwards. Metal ion solutions (200 mg L^{-1} for Cd(II) and 250 mg L^{-1} for Hg(II)) were prepared in 150 mM NaCl solution (25 mL) and alginate, and live or heat inactivated fungus entrapped in alginate beads was transferred into this medium and agitated magnetically at 400 rpm.

The effect of temperature on the biosorption capacity of the biosorbent was determined at pH 5.5 and the metal ion concentration was 200 mg L^{-1} for Cd(II) and 250 mg L^{-1} for Hg(II). The effect of the initial metal ion concentration on the biosorption was studied at pH 5.5 as described above.

Analytical procedure

The biosorption of Cd(II) and Hg(II) ions from aqueous solutions was studied in batch systems. Nitrates of the corresponding ions were used. After the desired incubation period (about 120 min), the aqueous phases were separated from the biosorbents and the concentration of Cd(II) and Hg(II) ions in these phases were measured. A Shimadzu AA-6800 Flame Atomic Absorption Spectrophotometer was used for the determination of cadmium. For mercury determination, The cold vapour technique was employed. Deuterium background correction was used and the spectral slit width was 0.5 nm. The working current/wavelength values for Cd and Hg were chosen as 8.0 mA/228.8 nm, and 6.0 mA/253.6 nm, respectively. The working conditions for mercury determination were as follows:

Concentration of $SnCl_2$:	1% (w/v)
Concentration of $KMnO_4$:	0.5% (w/v)
Concentration of H_2SO_4	:	5% (v/v)

The instrument response was periodically checked with metal ion standard solutions. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin of error.

The amount of metal ions adsorbed per unit mass of both empty and fungus immobilized alginate preparations (mg metal ions/g dry beads) was obtained using the following expression:

$$Q = \frac{(C_o - C)V}{M} \tag{1}$$

where Q is the amount of metal ions adsorbed onto the unit mass of the adsorbent (mg/g), C_o and C are the concentrations of the metal ions before and after biosorption (mg/L), V is the volume of the aqueous phase (L), and M is the amount of the adsorbent (g).

A known quantity of wet Ca-alginate or fungal immobilized preparations was used in the adsorption tests. After adsorption process, the adsorbents were dried in an oven at 50°C overnight and the dry weight of the preparations was used in the calculations.

Biosorption/Desorption

In order to determine the reusability of the alginate beads and immobilized fungal preparations, consecutive adsorption-desorption cycles were repeated three times by using the same biosorbent. Desorption of Cd(II) and Hg(II) ions was performed by 10 mM HCl solution. The alginate and immobilized fungal preparations loaded with metal ions were placed in the desorption medium and stirred at 400 rpm for 60 min at 25°C. The final Cd(II) and Hg(II) ion concentrations in the aqueous phase were determined by using an Atomic Absorption Spectrometer as described above. Desorption ratio was calculated from the amount of metal ions adsorbed on the immobilized preparations and the final metal ion concentration in the adsorption medium.

Desorption ratio was calculated from the following equation:

$$Desorption \ ratio = \frac{Amount \ of \ metal \ ions \ desorbed}{Amount \ of \ metal \ ions \ adsorbed}$$
(2)

Percent desorption values were obtained by multiplying the above ratio by 100.

SEM studies

Samples of Ca-alginate and *Pleurotus sapidus* immobilized beads were coated under vacuum with a thin layer of gold and examined by scanning electron microscopy (JEOL, Model JMS 5600).

Results and Discussion

Properties of the alginate based biosorbents

The Ca-alginate and *Pleurotus sapidus* immobilized Ca-alginate beads were prepared by the liquid curing method in the presence of Ca(II) ions and were used in the removal of metal ions from aqueous medium. The fungal biomass does not take up ions such Ca²⁺, Mg²⁺ and K^{+ 15}. Heavy metal removal by ion-exchange resins is sensitive to the presence of Ca²⁺, Mg²⁺ and K⁺ ions. Thus, the use of immobilized fungus in Ca-alginate beads may be advantageous over the ion-exchange resins when Ca²⁺, Mg²⁺ and K⁺ ions are present in take up medium or industrial waste water at high concentrations.

Alginate is a natural polymer that can easily be converted into hydrogels via crosslinking with divalent calcium ions. It was preferred over other materials because of its various advantages such as biodegradability, hydrophilicity, the presence of carboxylic groups, and natural origin. Additional advantages are its low density and mechanical stability, which make it highly suitable for many biotechnological applications. The alginate beads were very stable over the experimental pH range of 3.0-7.0. The operational stability of the support under specified experimental conditions is also a very important parameter in cells immobilization. One of the most important disadvantages of cell immobilization is the increase in the mass transfer resistance due to the polymeric matrix. Immobilized cell containing alginate do not have these disadvantages when compared with other support materials, such as polyvinyl alcohol and 2-hydroxyethylmethacrylate, because the presence of carboxylic groups in the alginate structure enhances the heavy metal ion adsorption capacity of the system with combinations of microbial cells.

The SEM micrographs of the plain Ca-alginate beads and *Pleurotus sapidus* immobilized beads are presented in Figures 1a and 1b. The alginate beads are spherical approximately 4 mm in diameter. The SEM micrograph of fungus immobilized alginate bead was completely different from the empty one and revealed a uniform fungal growth on the bead surface indicating that immobilization of basidiospore is not localized. This uniform distribution is an important criterion for the proper biosorption of heavy metal ions on the whole surface area of the fungus immobilized beads. Thus, immobilization of fungal cells in the alginate beads could also provide additional advantages over the freely suspended fungal cells, in batch culture fungal mycelia from individually distributed spherical clumps (\emptyset 2-4 mm). This tight packing of the fungal cells could also lead to diffusional restriction and less adsorptive sites for heavy metals than the alginate-fungal cells system.



Figure 1. SEM micrographs of (a) plain Ca-alginate beads and (b) Pleurotus sapidus immobilized beads.

The amount of entrapped fungus in the support was 0.107 g per gram beads. It was determined at the end of the five-day cultivation period, and no fungal biomass increase was detected after this period.

Biosorption of Cadmium and Mercury Ions

Adsorption Rate

Figure 2 shows the changes in the amount of Cd(II) and Hg(II) ions biosorbed with time, which were calculated by using Equation 1. The biosorption conditions are given in the figure legend. The initial slope of the curve reflects the biosorption rate. It should be noted that there was no precipitation in these groups of experiments. As seen here, high biosorption rates are observed at the beginning, and then plateau values (i.e., adsorption equilibrium) are gradually reached within 60 minutes.



Figure 2. Adsorption rates of (a) Cd(II) ions and (b) Hg(II) ions by plain Ca-alginate and *Pleurotus sapidus*. Adsorption conditions: amount of sorbent: 25 mg; volume of the biosorption medium: 25 mL; initial concentration of metal ions: 200 mg/L for Cd(II), 250 mg/L for Hg(II); pH: 5.5; temperature: 20°C.

Data on the adsorption kinetics of heavy metal ions by various sorbents have shown a wide range of adsorption rates. For example, Sobhan and Sternberg observed high degrees of cadmium biosorption during

the first 48 h by green microalgae¹⁶. The biosorption of cadmium onto pretreated biomass of marine alga Durvillaea potatorum has been studied and the biosorption process was very fast, with 90% uptake taking place within 30 min¹⁷. Shreedhara-Murthy and Ryan have investigated mercury, copper, cadmium, lead and uranium adsorption on cellulose-dithiocarbamate resins and reported that the adsorption rates were very slow¹⁸. Note that there are several parameters which affect the biosorption rate; such as the stirring rate of the aqueous phase, the structural properties of both the support and the biosorbent (e.g. protein and carbohydrate composition and surface charge density, topography and surface area), the amount of the sorbent, the properties of the ion under study (e.g. ionic radius), the initial concentration of ionic species and, of course, the existence of some other metal ions which may compete with the ionic species of interest for the active biosorption sites. Therefore, it is too difficult to compare the biosorption rates reported.

Effect of Initial Metal Ion Concentration

The metal ion biosorption capacities of the Ca-alginate and both immobilized live and inactivated fungus are presented as a function of the initial concentration of metal ions within the aqueous biosorption medium in Figure 3. This figure was prepared using the plateau values of the biosorption rate-curves (examples are given in Figure 2). The biosorption conditions are given in the figure legend.



Figure 3. Biosorption capacities of plain Ca-alginate and *Pleurotus sapidus* for (a) Cd(II) ions and (b) Hg(II) ions. Biosorption conditions: amount of sorbent: 25 mg; volume of the biosorption medium: 25 mL; pH: 5.5; temperature: 20°C; biosorption time: 60 minutes.

The amount of Cd(II) and Hg(II) ions adsorbed per unit mass of the biosorbent (i.e., biosorption capacity) increased with the initial concentration of metal ions, as expected. In order to reach the plateau values which represent saturation of the active sites (which are available for specific interaction with metal ions) on the biosorbent, in other terms to obtain the maximum biosorption capacity of the Ca-alginate and both immobilized live and inactivated fungus for Cd(II) and Hg(II) ions, the initial concentration of metal ions was increased up to 500 mg/L. As seen in Figure 3, the amount of Cd(II) and Hg(II) ions adsorbed on the plain alginate beads was 34.88 ± 1.03 mg/g and 31.46 ± 1.88 mg/g dry alginate beads respectively. The maximum biosorption capacity for immobilized live and heat inactivated fungal mycelia of *Pleurotus sapidus* was found to be 96.57 ± 2.44 mg/g (0.86 mmol g⁻¹) and 127.12 ± 3.64 mg/g (1.13 mmol g⁻¹) for Cd(II) and 207.89 ± 2.86 mg/g(1.04 mmol g⁻¹) and 287.43 ± 4.62 mg/g (1.43 mmol g⁻¹) for Hg(II), respectively.

The data in Table 2 indicate that the more electronegative metal ions will be more strongly attracted to the surface. Mercury has the highest adsorption capacity and the greatest electronegativity. In addition, the adsorption capacity of mercury is greater than that of cadmium and the same trend is shown by their respective reduction potentials. The two parameters, electronegativity and standard electrode potential, show a definite trend with adsorption capacity.

Ions	Coordination Number	Standard Reduction Potential vs NHE	Pauling Electronegativity
Cd^{2+}	6	- 0.403 V	1.69
Hg^{2+}	6	+ 0.854 V	2.00

Table 2. Selected Properties of the Studied Metal Ions

Different sorbents having a wide range of adsorption capacities for heavy metal ions have been reported. Shah and Devi used dithizone-anchored poly(vinyl pyridine) support and they reported a specific mercury adsorption capacity up to 0.72 mmol/g¹⁹. Liu et al. achieved 0.36 mmol Hg(II)/g adsorption capacity with N-hydroxymethyl thioamide resin²⁰. Cestari and Airoldi found 0.93 mmol Hg(II)/g with 3-trimethoxysilyl-1-propanethiol immobilized silica²¹. The maximum amount of adsorption capacity achieved was 0.25 mmol Hg(II)/g. Jyo et al. reported 0.20 mmol Hg(II)/g with phosphoric acid treated poly(glycidylmethacrylate-co-diviniylbenzene) beads²². Say et al. used dithiocarbamate-incorporated monosize polystyrene microspheres for adsorption of organomercury species, in which the maximum adsorption capacities were reported to be 0.61 mmol/g for CH₃HgCl, 0.57 mmol/g for C₂H₅HgCl and 0.10 mmol/g for C₆H₅HgCl²³. Özer et al. reported that the adsorption capacities of *Rhizopus arrhizus* and the living *E. Coli* strain were 71 mg Hg(II) g⁻¹ and 17.6 mg Hg(II) g⁻¹, respectively²⁴.

Equilibrium Studies

In order to optimize the design of a sorption system in order to remove metal ions it is important to establish the most appropriate correlations for the equilibrium curves. Two isotherm equations tested in the present study, namely Langmuir and Freundlich.

The most widely used isotherm equation for modelling equilibrium data is the Langmuir equation, which for dilute solutions may be represented as

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{3}$$

where q_e is the mass of solute adsorbed per mass of adsorbent used (mg adsorbed/mg adsorbent) and C_e is the equilibrium concentration of solute (mg/L or M). The constants K_L and a_L are the characteristics of the Langmuir equation and can be determined from a linearized form of the above equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{4}$$

Therefore, a plot of C_e/q_e versus C_e gives a straight line of slope a_L/K_L and intercept $1/K_L$. The constant K_L is the Langmuir equilibrium constant and the ratio a_L/K_L gives the theoretical monolayer

saturation capacity. The Langmuir equation is applicable to homogeneous sorption where each metal ionmicroorganism sorption process has equal sorption activation energy. The Langmuir equation obeys Henry's law at low concentrations.

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. The Freundlich equation is commonly presented as

$$q_e = aC_e^b \tag{5}$$

and the equation may be linearized by taking logarithms:

$$lnq_e = blnC_e + lna \tag{6}$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ enables the constant a and exponent b to be determined.

The Langmuir and Freundlich constants along with the correlation coefficients (R^2) were calculated from the corresponding plots for biosorption of Cd(II) and Hg(II) ions on the biosorbents and the results are presented in Table 3.

Table 3. Isotherm model constants and correlation coefficients for biosorption of Cd(II) and Hg(II) ions from aqueous solution.

Biosorbent	Langmuir			Freundlich		
	$a_L/K_L (mg/g)$	$K_L(x10^4) (mol/L)$	\mathbb{R}^2	a	b	\mathbf{R}^2
Active Pleurotus sapidus Hg(II)	208.3	2.51	0.9912	0.4	3.3	0.9518
Inactive Pleurotus sapidus Hg(II)	400	1.14	0.9948	12.79	1.83	0.9803
Active Pleurotus sapidus Cd(II)	100	6.61	0.9992	19.6	1.4	0.9408
Inactive Pleurotus sapidus Cd(II)	181.8	5.20	0.9918	18.6	1.1	0.9555

The correlation regression coefficients show that the adsorption process can be very well defined by the Langmuir equation.

Effect of pH and temperature on the biosorption capacity of the biosorbents

It is well known that metal ion adsorption on both non-specific and specific sorbents is pH dependent²⁵. The medium pH affects the solubility of metal ions and the ionization of the functional groups (i.e., carboxylate, phosphate, and amino groups) on the fungal cell wall. The carboxylate and phosphate groups carry negative charges that allow the microbial cells to be potent scavengers of metal ions ²⁶. In ous study, in order to establish the effect of pH on the biosorption of Cd(II) and Hg(II) ions onto the plain Ca-alginate beads and *Pleurotus sapidus* immobilized beads, the batch equilibrium studies were repeated at different pH values in the range of 3.0-7.0. Figure 4 shows the effect of pH on biosorption. The biosorption conditions are given in the figure legend. As seen here, biosorption of the Cd(II) and Hg(II) ions evaluated in this study

first increased with pH, and maximum biosorption occurred at about 6.0 and the interaction of the metal ions with the alginate and immobilized fungal cell wall component could be primarily with the carboxylate groups, both alginate and the cell wall component of the mycelia.



Figure 4. Effect of pH on the biosorption capacities of the Ca-alginate and *Pleurotus sapidus* fungus for (a) Cd(II) ions and (b) Hg(II) ions. Biosorption conditions: initial concentration of metal ions: 200 mg/L for Cd(II), 250 mg/L for Hg(II); amount of polymer: 25 mg; volume of biosorption medium: 25 mL; temperature: 20°C; biosorption time: 60 minutes.

The temperature of the adsorption medium could be important for energy-dependent mechanisms in metal biosorption by microorganisms. Energy-independent mechanisms are less likely to be affected by temperature since the process responsible for biosorption is largely physicochemical in nature. The biosorption of Cd(II) and Hg(II) by alginate and both immobilized live and inactivated fungus appears to be temperature independent over the temperature range tested (15-45°C). The similar to report by other researchers^{11,26}.

Desorption and Reuse

The desorption of the adsorbed Cd(II) and Hg(II) ions from the biosorbents was studied in a batch system. The metal ions taken onto biosorbents were eluted with 10 mM HCl. More than 97% of the adsorbed metal ions were desorbed from the biosorbents. In order to show the reusability of the biosorbents, an adsorptiondesorption cycle of metal ions was repeated three times using the same preparations. The adsorption capacities for all the biosorbents did not noticeably change (only a maximum 3% change was observed with the tested biosorbent) during the repeated adsorption-desorption operations. These results showed that alginate beads and both live and inactivated fungus entrapped biosorbents could be repeatedly used in heavy metal adsorption studies without detectable losses in their initial adsorption capacities.

Conclusion

In this study, cadmium and mercury uptake by immobilized *Pleurotus sapidus* was investigated. The performance of the biosorbent was examined as a function of the operating conditions, in particular equilibrium pH and initial metal ion concentration. The experimental evidence shows a strong effect of the experimental conditions. Maximum biosorption capacity values and biosorption/desorption experiments showed that the biosorbent used is very effective in recovery or removal of heavy metal ions from aquatic systems. When the ease of production and economical parameters are concerned, it was observed that immobilized *Pleurotus sapidus* is a very promising biomaterial the for removal or recovery of the metal ions studied.

References

- 1. G. M. Gadd and C. White, Trends Biotechnol. 11, 353-362 (1993).
- 2. E. Guibal, C. Roulph and C. Le Cloirec, Water Res. 8, 1139-1145 (1992).
- J. P. Huang, C. P. Huang and A. L. Morehart, Removal of Heavy Metals by Fungal (Aspergillus oryzae) Adsorption in: J.P. Vernet, ed. Trace Metals in the Environment I, 2nd Edition: Science Publishers. Amsterdam, Netherlands: Elsevier, 1994.
- 4. R. J. Doyle, T. H. Matthews and U. N. Streips, J. Bacteriol. 143, 471-482 (1980).
- 5. E. Fourest and J. C. Roux, Appl. Microbiol. Biotechnol. 37, 399-403 (1992).
- 6. C. Huang, C. P. Huang and A. L. Morehart, Water Res. 25, 1365-1371 (1991).
- J. A. Brierley, G. M. Goyak and C. L. Brierley, Considerations for Commercial Use of Natural Products for Metals Recovery, in: Eccles H and Hunt S, editors. Immobilization of Ions by Bio-sorption. Chichester, UK: Ellis Horwood, 105-117, 1986.
- 8. L. E. Macaskie, Crit. Rev. Biotechnol. 11, 41-112 (1991).
- R. H. Crist, J. R. Martin, D. Carr, J. R. Watson and H. J. Clarke, Environ. Sci. Technol. 28, 1859-1866 (1994).
- 10. Y. Sağ, M. Nourbakhsh and T. Kutsal, Process. Biochem. 30, 175-181 (1995).
- 11. N. Modifi, M. Aghai-Moghhadam and M. N. Sarbolouki, Process. Biochem. 35, 885-888 (2000).
- 12. E. Fourest and B. Volesky, Appl. Biochem. Biotechnol. 67, 215-226 (1997).
- J. L. Gardea-Torresdey, K. Tiemann, J. H. Gonzales, J. A. Henning and M. S. Towsend, J. of Hazardous Material 48, 181-190 (1996).
- 14. A. Kapoor, T. Viraraghavan and D. R. Cullimore, Biores. Technol. 70, 95-104 (1999).
- 15. J. M. Tobin, D. G. Cooper and R. Neufeld, J. Appl. Environ. Microbiol. 74, 821-824 (1984).
- 16. R. Sobhan and S. P. K. Sternberg, J. Environ. Sci. Health A34, 53-72 (1999).
- 17. J. T. Matheickal, Q. Yu and G. M. Woodburn, Water Res. 33, 335-342 (1999).
- 18. R. S. Shreedhara-Murthy and D. E. Ryan, Anal. Chim. Acta 140, 140:163 (1982).
- 19. R. Shah and S. Devi, React. Functl. Polym. 31, 1-10 (1996).
- 20. C. Y. Liu, H. T. Chang and C. C. Hu, Inorg. Chim. Acta 172, 151 (1990).
- 21. A. R. Cestari and C. Airoldi, J. Colloid. Interf. Sci. 195, 338 (1997).
- 22. A. Jyo, S. Matsufune, H. Ono and H. Egawa, J. Appl. Polym. Sci. 63, 1327 (1997).
- 23. R. Say, N. Şatıroğlu, E. Pişkin, S. Bektaş and Ö. Genç, Anal. Lett. 31, 511 (1998).

- 24. A. Özer, H. I. Ekiz, D. Özer, T. Kutsal and A. Çağlar, Process. Biochem. 32, 319-326 (1997).
- M. F. Benedetti, C. J. Milne, D. G. Kinninburg, W. H. Van Riemsddijk and L. K. Koopal, Environ. Sci. Technol. 29, 446-450 (1995).
- 26. E. Fourest and B. Volesky, Environ. Sci. Technol. 30, 277-302 (1996).