HEAVY METAL IONS REMOVAL BY BIOSORPTION-FLOTATION ON MYCELIAL WASTES

Ligia Stoica[1], G. Dima[1], O. Micu[1], D. Oancea[2], G. Oproiu[1]

[1] Department of Inorganic Chemistry, Polytechnic University of Bucharest
1 Polizu St.
sect. 1, Bucharest, Romania
e-mail: I.stoica@yankee.oxy.pub.ro

[2] Physical Chemistry Department
University of Bucharest, Romania

ABSTRACT

The aqueous systems arising from different industrial processes (i.e. mining industry, chemical and electrochemical industry, etc) have a complex composition, so they require the application of some efficient and economic purification methods. In the field of environmental pollution, some toxic metals (Cd, Pb) have received a great deal of attention.

The classical methods applied for removal of these heavy metal ions include precipitation as hydroxide or sulfide, followed by filtration, coprecipitation with $Fe(OH)_2$ reverse osmosis, ion exchange.

The paper presents a study regarding heavy metal ions removal by biosorption-flotation on mycelial wastes of Penicillium resulted in great quantities from pharmaceutical industry. Different preliminary treatments were applied to mycelial wastes in order to use them during biosorption-flotation experiments. Equilibrium sorption isotherms of Cd(II) and Pb(II) follow the typical Langmuir adsorption model.

The loaded inactive biomass was separated from the aqueous solutions by dissolved air flotation. The following parameters were studied for the biosorption-flotation process: pH, sorbent-metallic ion contact time and metallic ion concentration in order to obtain an effective separation of the loaded biomass separation to occur very well.

INTRODUCTION

Heavy metals can be removed from aqueous solutions by different physico-chemical processes according to the real pollution context. Some toxic metals (i.e. cadmium, lead) must be removed up to very low concentrations, less than 0.1 mg/l. These severe limits imposed for the effluents discharging require advanced purification processes for heavy metals removal.

The last ten years researches demonstrated that heavy metals removal from aqueous systems could be successfully accomplished by using active or inactive biomasses, the process being already known as "biosorption". Active and inactive biomasses have similar biosorption capacities (Brieley et al., 1989). Hence, the mycelial residues produced during many industrial fermentation processes like enzymes, flavours or antibiotics production, may be used as biosorbents at least for economically reasons.

Fungal mycelial residues were found to accumulate metals and radionuclids by physico-chemical and biological mechanisms including their binding by metabolites and biopolymers or specific polypeptides (Zoubilis and Matis, 1996). Biosorption on fungal cell walls was studied for many

metallic species (Gadd, 1988), the possibilities of subsequently metals desorption and biomasses reuse being also investigated.

If the biosorption process is operated in stirred tanks using a suspended biomass (Jackson et al. 1992), a subsequently solid/liquid separation stage is required. The specific characteristics of this kind of sorbat/sorbent system make difficult the separation by filtration (the process needs more time and may face filter blocking problems especially in the case of fine or ultrafine particles), centrifuging (apparent more expensive) or sedimentation (relatively slow process inadequate to biological materials which are usually of low density. Some flotation techniques were applied for microorganisms separation (Gadd and White, 1992) and the possibility of combining biosorption and flotation were also studied (Smith, 1989). Thus, flotation became of great interest among the bioseparation processes.

MATERIAL AND METHODS

Biomass and its preparation

A mycelial Penicillium residue, resulted from the fermentation process in pharmaceutical industry, was used as biosorbent. The biomass was previously treated by repeated washing and drying (in two different ways: simply drying or ketone drying); the size particles was less than 100μ.

The biosorption experiments were carried out in batch system. The samples of Cd(II) or Pb(II) solutions were shaken together with corresponding quantities of biomass in 50 ml flasks on a Braun shaker at a low constant rate (150 rpm)

Cadmium and lead solutions of different initial concentrations were prepared using p.a. reagents: $Cd(NO_3)_2.H_2O$; $Pb(NO_3)_2$; $CdCl_2.5/2H_2O$; $CdSO_4$.

Chemical analyses by AAS of the remaining solutions were used in order to assay the unremoved cadmium or lead. For pH regulation we used a Philips pH-meter and 0.1 M HCl or NaOH solutions.

Equilibrium biosorption evaluation and model

Biosorption metal uptake (q) is determined from the sorption system mass balance:

$$q = \frac{V(Ci - C_f)}{M} \qquad (1)$$

The Langmuir sorption model was applied to evaluate the isotherms, describing well the biosorption process. The equation can be written as:

$$q = \frac{bq_{max} C_f}{1 + bC_f} \qquad (2)$$

where C_f represents the final free metallic ions concentration, q_{max} is the maximum specific uptake and b is the Langmuir constant related to energy of adsorption.

Flotation process

The flotation process was carried out in a dissolved air flotation apparatus (Stoica, 1997).

Water saturated with air in the saturator and kept under pressure of 4.10^5 N/m^2 was introduced to the base of the cell. When releasing water to atmospheric pressure, fine air bubbles were generated, appropriated for solid/liquid separation.

IR analyses

To examine IR spectra of biomass before and after the biosorption-flotation process a IR-20 spectrophotometer was used. The high particulate samples were mixed with KBr and then pressed into a transparent disk. A pure KBr disk was used as a blank. Using this method, samples do not disperse radiation for 400-5000 cm^{-1} wave number range.

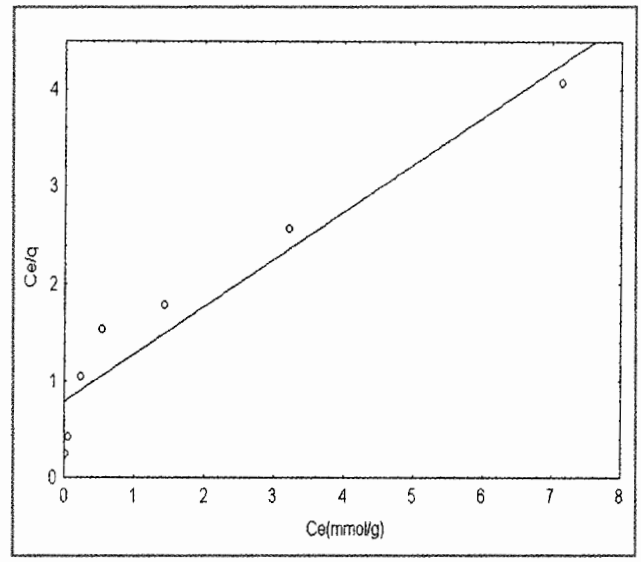

Figure 1a. Cd(II) sorption equilibrium isotherm.

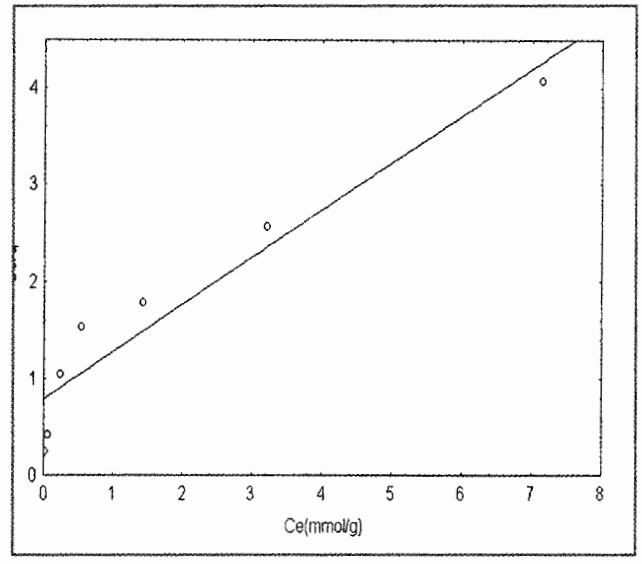

Figure 1b. Pb(II) sorption equilibrium isotherm.

RESULTS AND DISCUSSIONS

Cadmium and lead sorption isotherms

The sorption properties of mycelial Penicillium residues were evaluated from the experimentally obtained isotherms.

Sorption capacities obtained for the two metallic ions were expressed in terms of mmol M(II)/g biosorbent for a good comparison of the results. The respective values increase along with the increasing of the metallic ions initials concentrations.

In the range of low concentrations (under 100 mg/l), the biomass presents similar sorption capacities for the two metallic species (Figure 1) but in the range of high initials concentrations (over 500 mg/l) we observed a significant lowering of Pb(II) retention on the Penicillium biomass.

The equilibrium isotherm were drawn using the liniarised Langmuir equation.

Cadmium	q_{max}(mg/g)	b(L/mg)x10^3	q_{max}(mmol/g)	b(L/mmol)
Simply dried biomass	229.6	3.43	2.05	0.385
Ketone dried biomass	433.9	1.23	3.87	0.138
Lead				
Simply dried biomass	115.9	8.3	0.56	1.72
Ketone dried biomass	142.8	2.02	0.69	0.42

Table 1 Biosorption isotherm parameters.

The biosorption isotherms parameters were calculated from the liniarised Langmuir equation using the linear regression method for approximating the experimental data (with a regression coefficient $R \geq 0.95$). The calculated q_{max} values show the difference between the uptake capacity of different treated biomass for the two different metallic ions.

Biosorption-flotation parameters

As the organic sorbent is difficult to separate from the liquid phase particularly by filtration, the separation of loaded biomass by flotation was experimented, since the biosorbent presents a natural flotation tendency. After the biosorption stage the suspensions were transferred in a flotation cell and submitted to the DAF process.

The biosorption-flotation parameters are presented in comparison with the biosorption parameters.

Sorption			Sorption-flotation		
Sorption time(min)	C_f(mg/l)	R(%)	C_f(mg/l)	R(%)	Biomass R(%)
10	0.6	94	0.5	95	95
20	0.5	95	0.2	98	95
30	0.8	92	0.4	96	95

Table 3. %R= f(sorption time) dependence in Cd(II) recovery by sorption and biosorption-flotation processes ;C_i = 10 mg/l; pH = 7.

The dilution ratio (sample volume: water volume) was of 3:1. Cd(II) concentration and pH value were determined for the effluents. The biosorbent was the acetone dried Penicillium biomass.

Sorption			Sorption-flotation		
C_i(mg/l)	C_f(mg/l)	R(%)	C_f(mg/l)	R(%)	Biomass R(%)
100	17	83	16	84	95
50	5	90	4.5	91	95
10	0.5	95	0.2	98	95

Table 4. %R= f(CiCd(II)) dependence in Cd(II) recovery by sorption and biosorption-flotation processes; sorption time = 20 min.;pH = 7.

Sorption				Sorption-flotation				
C_i (mg/l)	Sorption time (min)	Sorption pH	C_f (mg/l)	Cd(II) R(%)	pH Sorpt-flot	C_f (mg/l)	Cd(II) R(%)	Biomass R(%)
10	10	6	2.8	72	6	1.9	81	95
10	10	7	0.6	94	7	0.5	95	95
10	10	8	0.85	91.5	8	0.65	93.5	95
10	10	9	0.9	91	9	0.8	92	95
10	20	6	0.9	91	6	0.85	91.5	95
10	20	7	0.5	95	7	0.4	96	95
10	20	8	0.8	92	8	0.6	94	95
10	20	9	1	90	9	0.8	92	95

Table 2. %R= f(pH) dependence in Cd(II) recovery by sorption and biosorption-flotation processes.

M(II)-biosorbent interactions

Biosorbent characteristics

Biosorption of cations is due to the net negative charge of the surface of the biomass. Indeed the cell wall of a biomass is constituted with carboxylic and hydroxylic groups which confer a global negative surface charge and an anionic ligands property.

Component	Component mg/100mg wall
Neutral zacharides	55.2
Glucose	36
Galactose	11
Manose	4
Aminohexose	20.1
Lipids	nd
Proteines	nd

Table 5. Chemical composition of cellular wall of P. chrysogenum.

The cellular wall have a high glucan content, most probably ß-1,3- glucan, with chitin as skeletal component (Demain et al. 1985).

IR spectra

The IR spectra of Penicillium biomass before and after biosorption and biosorption-flotation shows the characteristic absorption bands of glicosidic OH at 760-930 cm^{-1}, of OH from carbon hydrates at 1000-1200 cm^{-1}, of COO^- from peptides at 1400-1600 cm^{-1}, of C=O for amid bonds at 1650 cm^{-1}, of C=O from ammoniac's at 1720- 1750 cm^{-1} and of H_2O at 3000-3600 cm^{-1}.

After biosorption and biosorption-flotation a new band appeared at 710 cm^{-1} corresponding to the M-O bonds and others bands disappeared or are slightly shifted (1410 cm^{-1}), corresponding to the COO^- groups.

The adsorption intensities for each characteristic frequency are greater for the ketone dried biomass (named biosorbent 2) comparing to the simply dried biomass (named biosorbent 1), confirming the better experimental adsorption capacities (Stoica and Dima, 1999).

CONCLUSIONS

Biosorption –flotation may be applied for M(II) recovery from aqueous solutions, the efficiency being dependent on process optimal parameters. Even for more concentrated solution, the ketone pretreated biomass may ensure, in optimal work conditions, high values for M(II) recovery. The difficulties of separation the M(II) loaded sorbent from the liquid phase may be avoided if DAF technique is applied. This separation process offer the possibility of higher M(II) removals (comparing with the simple biosorption) and also high loaded biomass removals (over 95%, the remaining being mechanical losses) so the process permits the reuse of the biomass for a new cycle of biosorption-flotation. The flotation process does not require the presence of a collector.

The IR characteristic frequencies and their assignments confirm the existence of a M-O bond after biosorption and biosorption processes.

Sample	ν_s glic. α-1,4-OH	ν_{as} glic. α-1,4-OH	δ_{OH} (carbon hydrates)	ν_{COO^-} (peptide)	ν_{CO} (amide)	ν_{CO} (amino acids)	δ_{H2O}
Biosorb.1	758-793	917-930	1000-1200	1400-1608	1650	1724-1754	3100-3600
Biosorb.1+Cd ;pH:6.3	750	930	1030; 1050	1410	1640; 1660	1710;1730	3300-3500
Biosorb.1+Cd +flot;pH=6.3	750	930	1030; 1050	1390; 1410	1650; 1660	1740	3450-3550
Biosorb.1 +Pb	750	940	1040; 1160	1400; 1470	1650	1720-1740	3350-3450
Biosorb.2	758-793	917-930	1000-1200	1400-1608	1650	1724-1754	3100-3600
Biosorb.2+ Cd;pH:6.3	750	930-940	1000-1200	1380; 1410	1640; 1660	1720; 1740	3300-3400
Biosorb.2 +Cd+flot pH=6,3	750	930	1030; 1150	1390; 1410	1640; 1660	1710;1730	3250-3450
Biosorb2 +Pb	750	940	1040; 1160	1400; 1470	1650	1720;1740	3300-3400

Table 6 Characteristic infrared frequencies and assignments.

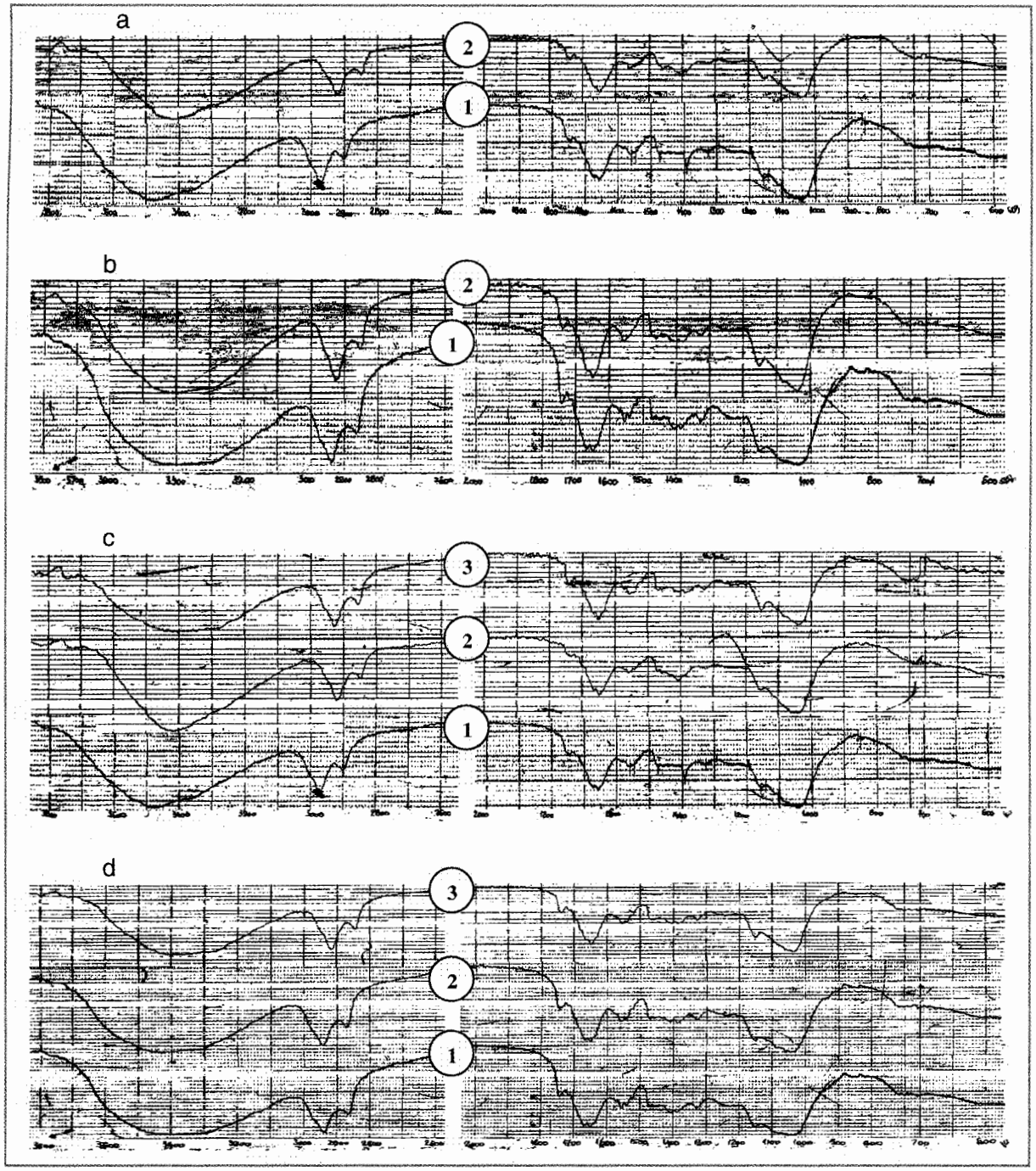

Figure 2. IR spectra for Penicillium biomass.
a: Biosorbent 1-Pb. 1) Biosorbent 1, 2) Biosorbent 1+Pb; b: Biosorbent 2-Pb. 1) Biosorbent 2, 2) Biosorbent 2+Pb
c: Biosorbent 1-Cd. 1) Biosorbent 1, 2) Biosorbent 1+Cd; ph = 6.3 3) Biosorbent 1+Cd+flot
c: Biosorbent 2-Cd. 1) Biosorbent 2, 2) Biosorbent 2+Cd; ph = 6.3 3) Biosorbent 2+Cd+flot

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