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Biosorption of Cr^{3+} from aqueous solution by a NaOH-treated bacterial dead *Streptomyces rimosus* biomass

A. Selatnia*, M.Z. Bakhti

Ecole Nationale Polytechnique d'Alger, Département de Génie Chimique, 10, avenue Pasteur, Belfort, B.P 182, EL-Harrach, Alger, Algeria

ABSTRACT

The chromium biosorption capacity of a *Streptomyces rimosus* biomass treated with NaOH (0.1M) was studied in the batch mode. After pre-treatment of biomass at the ambient temperature, optimum conditions of biosorption were found to be: a biomass particle size between 50 and 112μm, an average saturation contact time of 1h, a biomass concentration of 3g/L and a stirring speed of 250rpm .The equilibrium data could be fitted by Freundlich isotherm equation. Under these optimal conditions, 110mg Cr^{3+}/g biomass were fixed. © 2005 SDU. All rights reserved.

Keywords: Biosorption; Chromium; *Streptomyces rimosus*; Waste-water treatment

1. INTRODUCTION

Many industries such as coating, car, aeronautic and steel industries generate great quantities of waste water containing various concentrations of chromium. These concentrations are usually too low to be treated by standard methods. Chemical precipitation lead to the production of toxic sludge. Solvent extraction techniques are not profitable for a stream containing less than 1g/L of targeted heavy metals. On the other hand, ion exchange processes are too expensive due to the high cost of synthetic resins.

Antibiotic fermentation produces large amounts of semi-solid wastes which are normally disposed by incineration. Such semi-solid wastes, after granulation and a heat treatment, have been used to recover and remove heavy metals from waste water streams (Roux *et al.*,1990; Milande *et al.*,1993; Fourest *et al.*,1994; Fourest *et al.*,1996).These researchers tested several filamentous fungi (*Mucor miehei, Penicillium chrysogenum, Aspergillus niger* and *Rhizopus arrhizus*) to recover heavy metals from aqueous solutions.

In the literature, the capability of either living or non living organisms for fixing metal ions is widely described. Modak *et al.*(1996) showed that non living *Aspergillus niger* biomass attached to wheat bran was selective for the extraction of copper and zinc. Guibal *et al.* (1992) studied the biosorption of uranium by filamentous *fungus Mucor* and Gardea-Torresdey *et al.*(1996a) performed batch experiments with inactivated cells of *Mucor rouxii* for Cu+2 binding. Other studies were performed with different biomaterials as marine (Kuyucak and Volesky,1989 ; Hao *et al.*,1994 ; Leusch and Volesky,1995; Khoshmanesh *et al.*,1996; Chong and Volesky,1996), bacteria (Sautel *et al.*,1991 ; Urrutia and Beveridge,1993 ; Magao and Srivostava,1994 ; Butter *et al.*,1995; Engl *et al.*,1995 ; Sag and Kutsal,1995 ; Mishra *et al.*,1996 ; Singleton and Simmons,1996 ; Thomas and Macaskie,1996), chitosan (Jaanson-Cherrier *et al.*,1996) ; humic substances (Gardea-Torresdey *et al.*,1996b) and sewage sludge (Remacle *et al.*,1992 ; Solari *et al.*,1996). All these studies were done to remove and recover heavy metals from dilute aqueous streams by biosorption.

In the present work, dead *Streptomyces rimosus* biomass treated with NaOH(0.1M) was used in granulated form to remove Cr^{3+} from laboratory-made aqueous solutions. The effects of the physical and chemical parameters on the biosorption were studied and the chromium binding kinetics and mechanism were determined.

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* Corresponding author. E-mail: ammar_selatnia@yahoo.fr

2. DIFFUSION AND SORPTION MODELS

2.1. Sorption isotherms

The equilibrium of a solute between a liquid and a solid phase was described by various models of sorption isotherms such as the Langmuir and Freundlich models. These models suggest a monolayer sorption with lateral interactions between the sorbed molecules in the case of the Freundlich models: the energetic distribution of sites was heterogeneous, due to the diversity of sorption sites or the diverse nature of the metal ions sorbed, free or hydrolysed species. The Langmuir model supposes a monolayer sorption with an homogeneous distribution of sorption sites and sorption energies without interactions between the sorbed molecules.

The Langmuir model was described by the following equation:

$$q_e = q_m . \frac{b.C_e}{1 + b.C_e} \tag{1}$$

where

q_e is the adsorbed metal ion quantity per gram of biomass at equilibrium (mg/g).

q_m is the maximum amount of metal ion per unit weight of biomass to form a complete monolayer on the surface bound at high C_e (mg/g).

b is a constant related to the affinity of the binding sites (l/mg) .

The Freundlich model equation was of the form:

$$q_e = k.C_e^{1/n} \tag{2}$$

where k and n are the Freundlich's constants characteristic of the system.

2.2. Diffusion models

Sorption kinetics were mainly controlled by various steps including diffusion processes. 3 steps can be enumerated and applied to chromium removal (Fritz *et al.*, 1981; Hand *et al.,* 1983; Mc Kay, 1984).

Step 1 chromium transfer from the boundary film bordering to the surface of the particle;

Step 2 transfer of the chromium from the surface to the intraparticle actives sites;

Step 3 uptake of metal ion on the active sites, via complexation, sorption and intraparticle precipitation phenomena;

Step 1 describes film mass transfer resistance.

Step 2 is related to the intraparticle diffusion model.

Step 3 is a rapid, non limiting phase.

Various models of diffusion were studied, including single steps of external diffusion or intraparticle diffusion or combined phenomena (Van Vliet *et al.*,1980 ; Mattews and Weber, 1984 ; Mc Kay and Bino, 1988 ; Glover *et al.*, 1990; Mc Kay and Allen, 1990).

The aim of this study was to select the main limiting step in the overall sorption process.

2.2.1. External mass transfer diffusion model

This model, as an application of the Fickien's laws, expresses the evolution of the concentration of the solute in the solution C (mg/L), as a function of the difference in the concentrations of the metal ion in the solution C, and at the particle surface, C_S(mg/L), according to the equation 3 (Weber and Morris, 1962; Mc Kay and Poots, 1980; Mc Kay *et al.*, 1986).

$$\frac{dC}{dt} = -\beta . S. (C - C_S) \tag{3}$$

where

β is the mass transfer coefficient (m/s)

S the surface area of the biomass per unit solution volume (m^{-1})

The coefficients are determined after making some assumptions such as a surface concentration C_S negligible at t=0, a concentration in solution tending to the initial concentration C_0, and also negligible intraparticle diffusion. So the previous equation can be simplified to

$$S = \frac{6.m}{d_p . \rho_{app}} \tag{5}$$

where

m is the sorbent mass concentration in the solution (kg/m^3).

d_p particle size diameter (m).

ρ_{app} is the apparent density of the sorbent (kg/m^3).

2.2.2. Intraparticle mass transfer diffusion model

In this work, the models chosen refer to theories developed by Weber and Morris (1962), Mc Kay and Poots (1980) and Urano and Tachikawa (1991).

According to the intraparticle diffusion model proposed by Weber and Morris (1962), the initial rate of intraparticle diffusion was calculated by linearization of the curve $q=f(t^{0.5})$.

$$q=K_i.t^{0.5} \tag{6}$$

where

q is the amount of adsorbed metal ion on the biomass at time t (mg/g)

t time (s).

K_i is the diffusion coefficient in the solid (mg/g.s$^{1/2}$).

Another kind of intraparticle diffusion model was proposed by Urano and Tachikawa (1991). The sorption kinetics were modelled according to the following equation.

$$-\text{Log}_{10}\left[1-\left(\frac{q}{q_e}\right)^2\right]=\frac{4(\pi)^2.D_i.t}{2.3\ d_p^2} \tag{7}$$

where D_i is the diffusion coefficient in the solid (m^2/s).

2.3. Kinetic modelling

The first-order rate expression of Lagergreen(1898); Ho and Mc Kay(1999); Aksu (2001), based on solid capacity was generally expressed as follows:

$$-\text{Log}_{10}\left[\frac{(q_e-q)}{q_e}\right]=\frac{k_1}{2,3}.t \tag{8}$$

where k_1 is the rate constant of first-order biosorption (s^{-1}).

The first-order equation was generally applicable over the initial 20-30min of the sorption process.

The pseudo second-order equation is also based on the sorption capacity of the solid phase (Aksu, 2001; Ho and Mc Kay, 1983; Yakup *et al.*, 2001). The pseudo second-order kinetic rate was expressed as:

$$\left[\frac{1}{(q_e-q)}\right]=\left[\frac{1}{q_e}\right]+k_2.t \tag{9}$$

where k_2 is the rate constant of second -order biosorption (g/mg.s).

3. METHODS AND MATERIALS

S. rimosus biomass produced during oxytetracyclin antibiotic production was collected after fermentation. This biomass was washed with distilled water and dried at 50°C during 24 hours. It was then crushed and sieved in order to select a fraction with particle diameters between 50 and 112μm.This biomass was then treated with NaOH (0.1N) during 30 min and once again dried and sieved to obtain the particle size fraction between 50 and 112μm. The physical and chemical properties of this biosorbent are shown in Table1.

The biosorption tests were carried out in closed system. A known amount of Cr^{3+} prepared with $CrCl_3$ salt was added to the suspended biomass in solution until adsorption equilibrium was reached. Equilibrium and kinetic curves were plotted by monitoring the Cr^{3+} residual concentration as a function of time. A magnetic stirrer was used to homogenize the mixture. For all the experiments, initial Cr^{3+} and biomass concentrations were fixed at 100mg/L and 3g/L respectively.

Cr^{3+} residual concentrations in solution were determined using a Unicam 939 Atomic Absorption Spectrophotometer with a wavelength at 357.9nm.

All the experiments were carried out at unadjusted pH. Infrared Spectra were obtained with the help of a Perkin-Elmer FTIR1650.

Table 1
The Physical and chemical characteristics of the biomass

	Untreated biomass	NaOH-treated biomass
Particle size(μm)	50-112	50-112
Humidity (%)	3.2	4.4
Density	0.43	0.41
Surface area per unit solution volume (m^{-1})	516	542
Zeta potential (Volt)	-0.062	-0.082

4. RESULTS AND DISCUSSION

4.1. IR spectral analysis

In order to find out which functions were responsible for the chromium adsorption, IR analysis of the biomass was carried out. Figure 1 and 2 show the IR spectra and the various functional groups corresponding to the absorption bands. The frequencies of vibrations and their corresponding groups are presented in Table 2.

Table 2
IR absorption bands and corresponding possible groups

Frequency(cm^{-1})	Functional group
3431.58	-OH , -NH
2919.49	-CH
2852.92	-CH
1623.90	-COO$^-$, -C=O
1398.58	-COO$^-$
1111.81	-C-O , -C-N
666.29	-CH
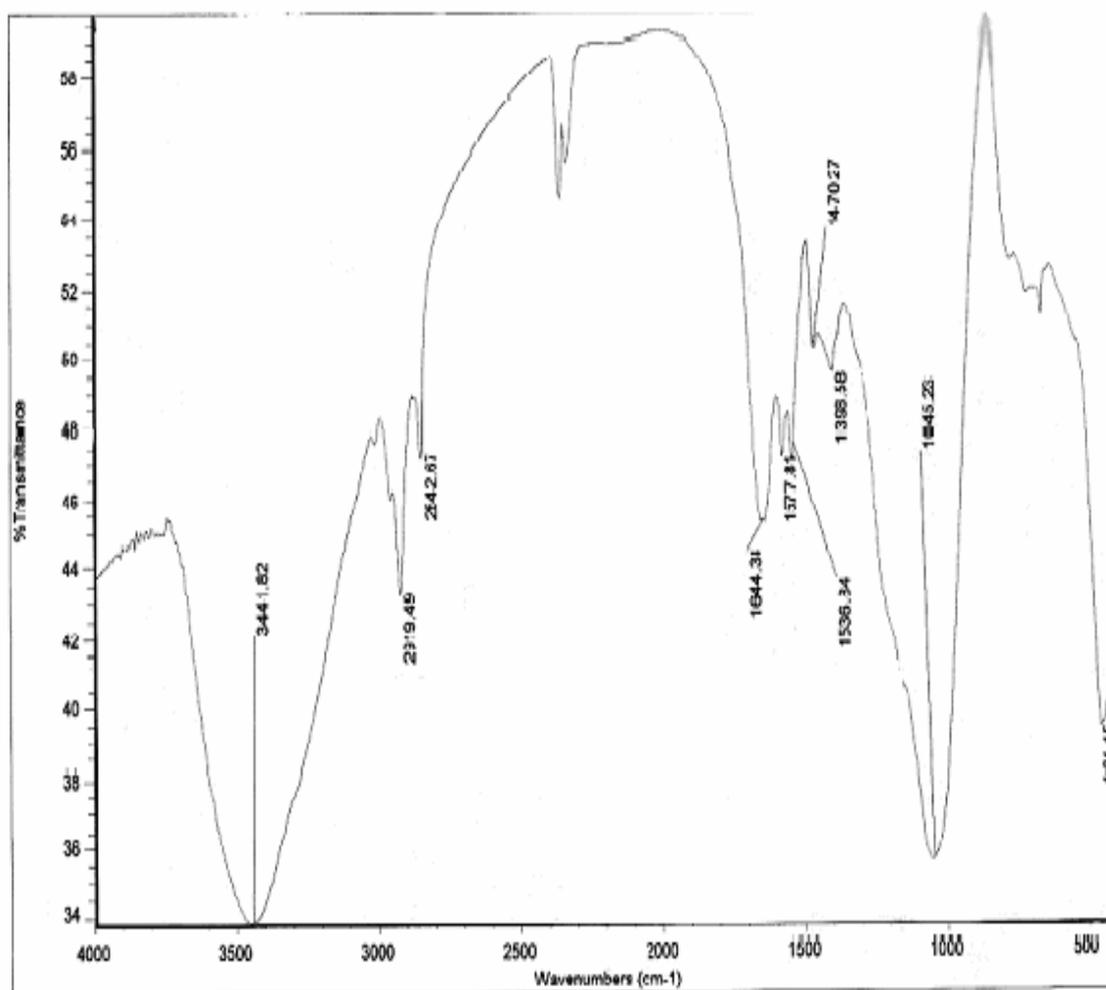
Figure 1. Spectrum 1: Infrared spectrum of the NaOH-treated biomass
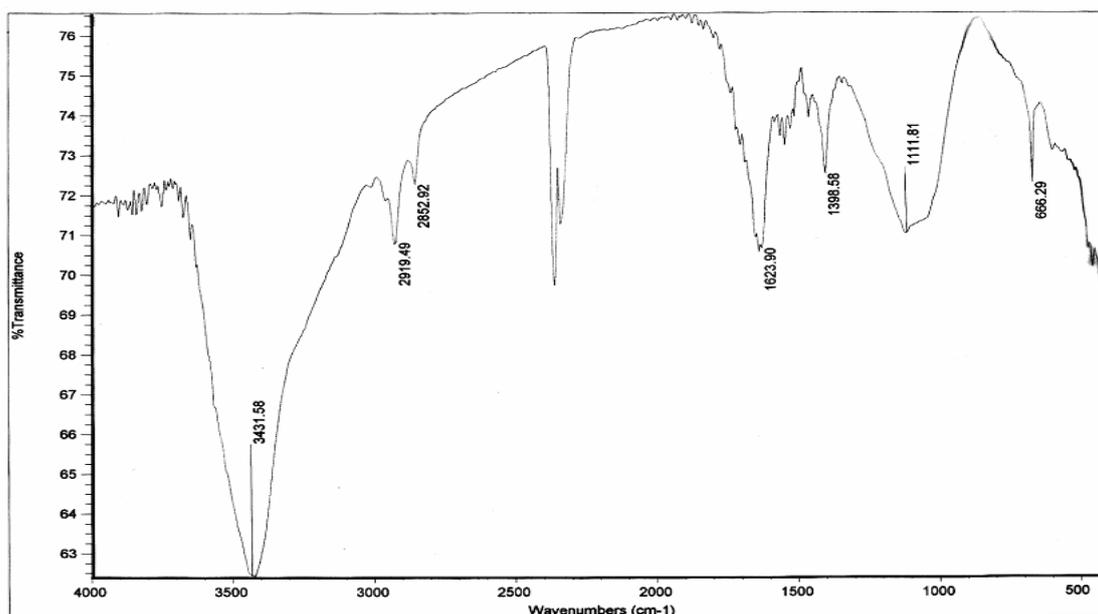
Figure 2. Spectrum 2: Infrared spectrum of untreated biomass

4.2. Chromium biosorption kinetics

As can be seen from Figure 3, chromium biosorption kinetics was very fast suggesting very active surface phenomena of the biomass. In fact, this biomass cell walls were made of great molecules (peptidoglycane) linked with techoïd acid and polysaccharides. These molecules possess functional groups which can adsorb heavy metals. These groups are of the type(-NH), carboxylate anions (-COO⁻), hydroxy (-OH) and others (-C-N), (-C-O), (-C-H),(-C=O) which present different affinities towards metallic ions. Figure3, shows adsorption kinetics of the biomass.
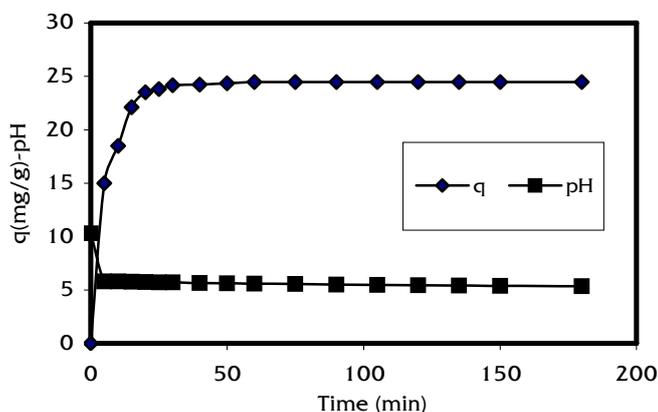
Figure 3.Time evolution of the biosorption capacity and pH during the experiments (ω=250rpm, $C_o(Cr^{3+})$=100mg/L, $C_{biomass}$=3g/L, PS : 50-112µm)

The metal biosorption depends strongly on the protonation or unprotonation of the functional groups on the cell wall i.e., carboxylic, hydroxyl and amino groups (Guibal *et al.*,1992; Sautel *et al.*,1991; Fourest and Volesky, 1997; Fourest and Roux, 1992). The ionic forms of the metal in solution and the electrical charge of the biomass depend of the solution pH.

The chemical treatment of the biomass with NaOH (0.1N) shows that in the sodium form, the ion exchange sites were more easily able to exchange this cation (Na+) with ions Cr^{3+} than when the ion exchange sites were protonated.

pH variations during the experiment are shown in Figure 3. The following deductions can be made:

➢ The adsorbed quantity tends to a value 24.47mg Cr^{3+}/g biomass, corresponding to pH of 5.4. At the very beginning of the experiment, the pH falls from 10.32 to a value of 5.4. This can be explained by H+ liberation of some compounds of the biomass in solution suggesting that the biosorption mechanism was a ion exchange type between H+ ions and Cr^{3+} ions.

➢ After a short time, solution pH stabilizes at the value of 5.4 and other biosorption mechanisms can occur. Among those, we can mention complexation , electrostatic attraction and ion exchange between Na+ ions and Cr^{3+} ions.

In our study, the biosorption mechanisms like ion exchange and complexation as well as electrostatic attractions seem to be the most occurring phenomena. Among the chemical groups possibly involved in such phenomena's were the (-COO⁻), (-OH), (-NH), (C-O-),(-C=O) groups, which were active sites for the Cr^{3+} sorption.

4.3. Biosorption rate constant

The adsorption kinetics over 30 min of the sorption process was found to be of the first order. The corresponding rate constant was found to be $k_1 = 2.5.10^{-3}$ s^{-1}.
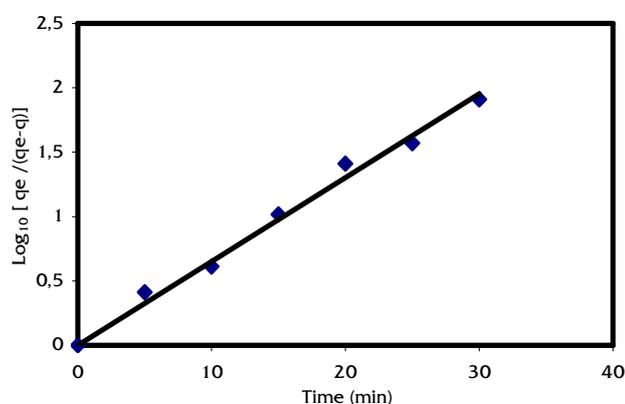

Figure 4. Log_{10}[qe/(qe-q)] versus time (t) for the NaOH-treated biomass.

4.4. External mass transfer coefficient

By plotting the slope values at C=0 of the plot (C/Co) =f(t) , we can deduce the values of the external mass transfer coefficients β. The corresponding value of the external mass transfer was β = $2.76.10^{-6}$ m/s. The low values of the external mass transfer coefficient means that the resistance to the external mass transfer was quite important.
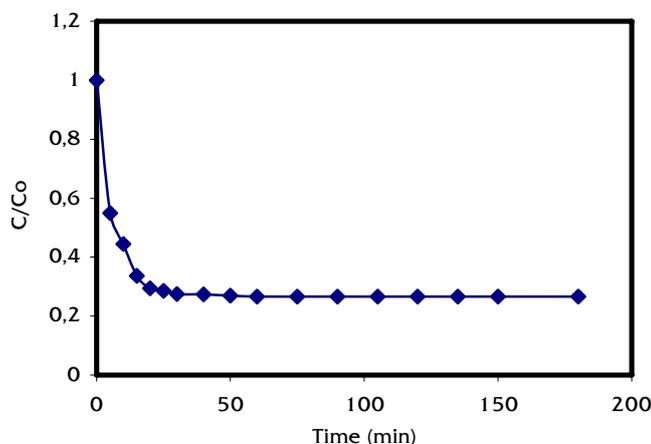

Figure 5. (C/C$_o$) versus time (t) according to the external mass transfer resistance model.

4.5. Intraparticle diffusion coefficient

When considering only the initial period according to Weber and Morris(1962) model, the rate constant of intraparticle diffusion K_i has been determined by a plot $q=f(t^{0.5})$.

The intraparticle diffusion coefficient D_i was computed by plotting $\text{Log}_{10}[1-(q/qe)^2]$ as a function of the time according to Urano and Tachikawa(1991) model.

Values of K_i and D_i are given in Table 3.

Table 3
Values of K_i and D_i for the NaOH-treated biomass.

	K_i (mg /g.s$^{1/2}$)	D_i (m^2/s)
NaOH-treated biomass	0.76	$2.85 . 10^{-13}$

The low values of K_i et D_i coefficients suggest that the intraparticle diffusion was negligible in comparison with the external mass transfer phenomena .
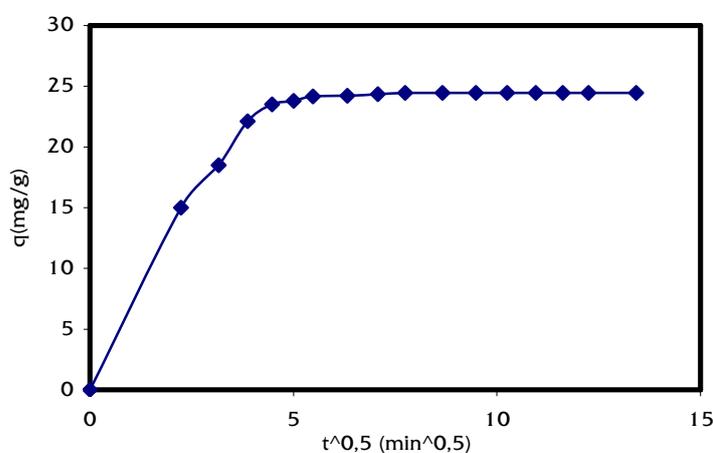

Figure 6. q versus t $^{0.5}$ according to the Weber and Morris model
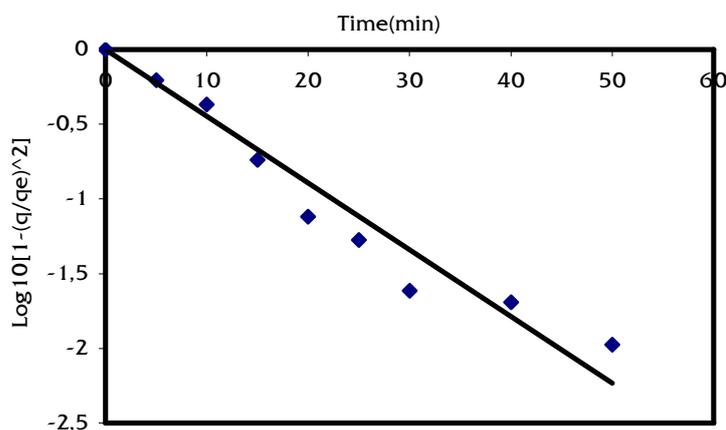

Figure 7. $\text{Log}_{10}[1-(q/qe)^2]$ versus time (t) according to the Urano and Tachikawa model

4.6. Effect of initial pH on Cr^{3+} biosorption

Figure8, below shows that the Cr^{3+} adsorbed quantity increases with increasing initial solution pH. This can be explained by the strong relation between the biosorption and the number of negative charges at the biomass surface which is itself related with the functional groups.

The maximum of the Cr^{3+} adsorbed quantity at the surface of the biomass was 25.2mg Cr^{3+}/g biomass. This maximum occurs at pH=11. There is a sharp increase of the adsorbed quantity from pH=4, which correspond to the dissociation of functional group or their deprotonation .

For low pH values, one may consider an adsorption competition between H+ protons and metallic ions on the active sites on the cell wall of the biomass, as it has been suggested by many others authors (Guibal *et al.,*1992; Sautel *et al.,*1991 ; Fourest and Volesky,1997 ; Fourest and Roux,1992 ; Benedetti *et al.,*1995,; Fourest and Volesky, 1996; Huang *et al.,*1988).
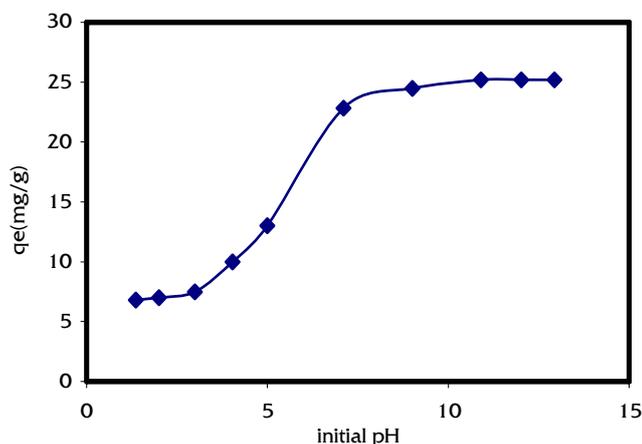

Figure 8. Effect of initial pH on the Cr^{3+} adsorption capacity by the NaOH-treated biomass (ω=250rpm, $C_o(Cr^{3+})$=100mg/L, C $_{biomass}$=3g/L, PS: 50-112µm)

4.7. Effect of stirring speed on Cr^{3+} biosorption

The effect of stirring speed on biomass adsorption capacity was studied. Optimal value of adsorption capacity was obtained for a stirring speed of 250rpm (Figure9). This stirring speed was used in all our experiments. A moderate speed gives the best homogeneity for the mixture suspension. At high stirring speed, vortex phenomena occurs and the suspension was no longer homogenous which makes the adsorption of Cr^{3+} difficult.
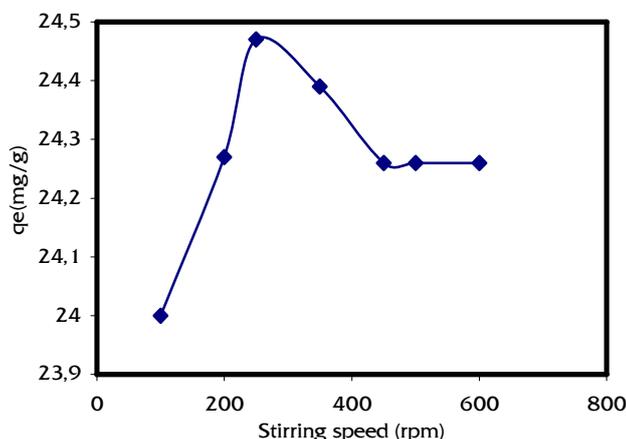

Figure 9. Effect of stirring speed on the biosorption capacity of the NaOH-treated biomass ($C_o(Cr^{3+})$=100mg/L, C $_{biomass}$=3 g/L, PS: 50-112µm)

4.8. Influence of biomass concentration

Figure10, shows the metallic ions elimination in weight per cent as a function of biomass concentration. This graph shows the increase of the metal ions removal with the concentration of the biomass. A plateau appears starting at a concentration of biomass equal to 3g/L. This can be explained by considering a partial aggregation which takes place at high biomass concentration causing a decrease of the actives sites.
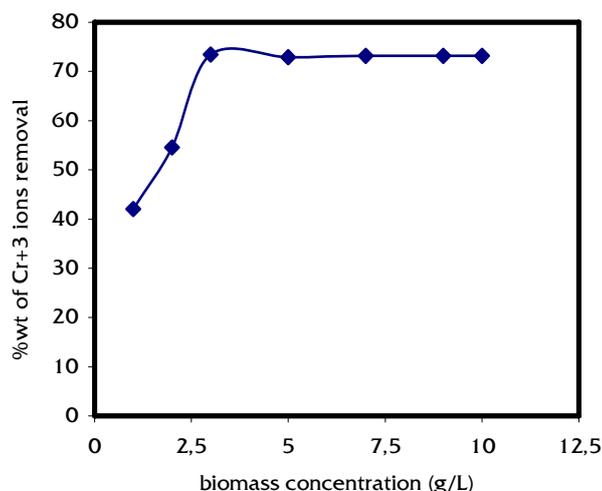
Figure 10. Effect of the biomass concentration on the biosorption capacity of the NaOH-treated biomass (ω=250rpm, $C_o(Cr^{3+})$=100mg/L, PS: 50-112μm)

4.9. Influence of the initial Cr^{3+} concentration

Many studies have shown that for low Cr^{3+} concentrations, the quantity of adsorbed Cr^{3+} par unit mass of biosorbent was directly proportional to the ionic concentration in solution.
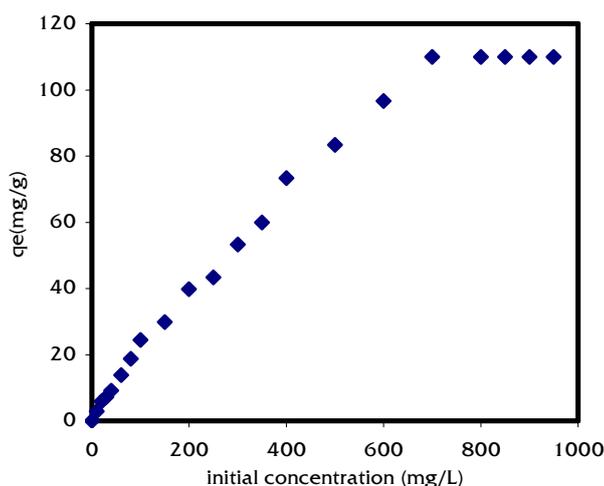

Figure 11. Influence of initial concentration of Cr^{3+} on the biosorption capacity of the NaOH-treated biomass (ω=250rpm, $C_{biomass}$=3g/L, PS: 50-112μm)

Figure 11 shows that the quantity of adsorbed Cr^{3+} per unit mass of biosorbent increases when the initial Cr^{3+} ions concentration increases.

This study shows that it possible the saturation of the active sites of the biomass and to obtain the maximum of Cr^{3+} ions adsorption capacity of the biomass. In our study, initial Cr^{3+} concentration varies from 20 to 800mg/L. As can be seen from Figure 11, the maximum quantity of adsorbed Cr^{3+} on biomass was around 110mg Cr^{3+}/g biomass.

4.10. Adsorption isotherm analysis

In order to optimize the biosorption process parameters, we have modelised the equilibrium curve (Figure 12). Two equations of isotherms of Langmuir and Freundlich were tested.
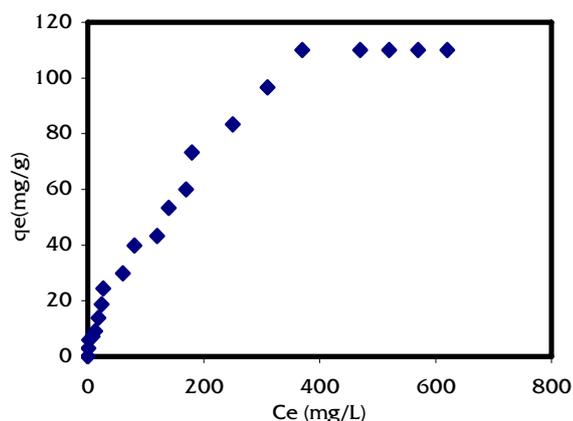
Figure 12. Adsorption data of Cr^{3+} onto the NaOH-treated biomass (ω=250rpm, C $_{biomass}$=3g/L, PS: 50-112μm)

The isotherm curve shows a limiting biosorption capacity attained at Cr^{3+} equilibrium concentration of about 370mg/L. Figure 13 and 14 are the transformed forms of these models which permit to calculate Langmuir's constants(q_m et b) and Freundlich constants(k et n) .
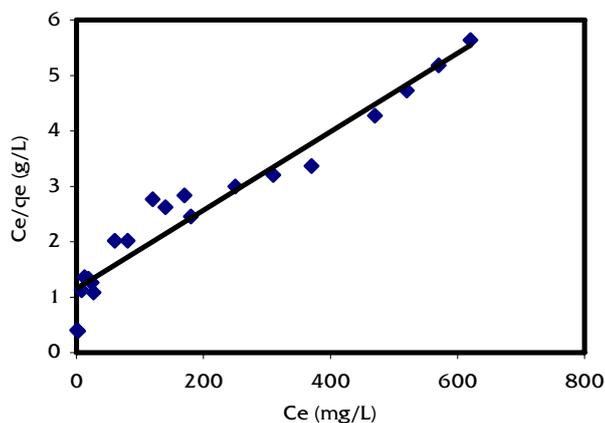

Figure 13. Application of the Langmuir equation to the adsorption data of Cr^{3+} onto the NaOH-treated biomass
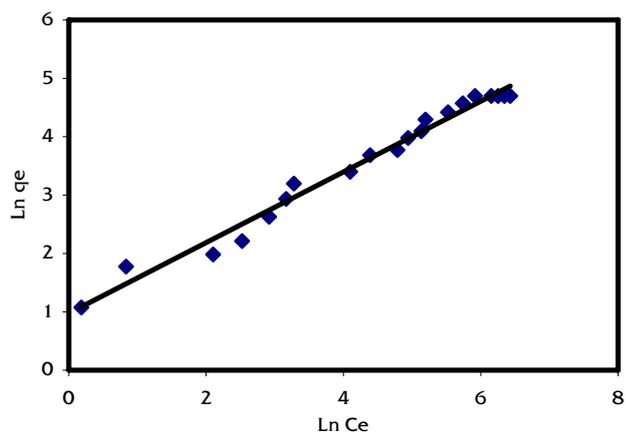

Figure 14. Application of the Freundlich equation to the adsorption data of Cr^{3+} onto the NaOH-treated biomass

Table 4 shows the values of the computed constants.

Table 4
Sorption isotherm coefficients of Langmuir and Freundlich models

Langmuir			Freundlich		
q_m (mg.g^{-1})	b(l.mg^{-1})	R^2	k(l.g^{-1})	1/n	R^2
140.85	6.2.10^{-3}	0.93	2.66	0.60	0.98

Values of coefficients of correlation R^2 shows that the Freundlich's models, fits best our experimental data.

5. CONCLUSIONS

S. rimosus dead biomass treated with NaOH (0.1M) was an efficient adsorbent of Cr^{3+} in dilute solutions. Up to 110mg of chromium can be fixed by each gramme of NaOH-treated biomass. The cell walls of this biomass contains anionic groups such as (-COO$^-$, -C-O, -NH, -C=O,-OH) whose adsorbent ability towards Cr^{3+} ions was fairly high. Adsorption was moreover influenced by various parameters such as initial pH, initial Cr^{3+} concentration, biomass concentration and stirring speed. The results obtained during this study show that this method of eliminating Cr^{3+} ions is very promising and confirm the technical and economic interest compared to the conventional processes such as the ion exchange on resins.

REFERENCES

Aksu, Z., Equilibrium and kinetic modelling of cadmium(II) biosorption by *C.vulgaris* in batch system: effect of temperature. Separation and Purification Technology, 2001, 21, 285-294.

Benedetti, M.F., Milne, C.J., Kinninburg, D.G., Van Riemsddijik, W.H., Koopal, L.K., Metal binding to humic substances. Application of the non-ideal competitive adsorption model. Environmental Science and Technology,1995, 29, 446-450.

Butter, T.J., Evision, L.M., Hancock, TY.C., Holland, F.C., Removal and recovery of cadmium from dilute aqueous streams by biosorption , elution and electrolysis, Proceedings 9th Forum for Applied Biotechnology,1995, 2581-2583, Gent, Norway.

Chong, K.H., Volesky, B., Metal biosorption equilibria in ternary system. Biotechnology and Bioengineering, 1996, 49, 629-638.

Engl, A., Tholmas, C., Kune, B., Biosorption of heavy metals by *paracoccus denitrificans*. Proceedings 9th Forum for Applied.Biotechnology,1995, 2589-2592,Gent, Norway.

Fourest, E., Canal, C., Roux, J.C., Improvement of heavy metals biosorption by micelial dead biomasses *Rhizopus arrhizus, Mucor miehei , Penicillium chrysogenum* : pH control and cationic activation. F.E.M.S.Microbiology Review,1994,14(4), 325- 332.

Fourest, E., Serre, A., Roux, J.C., Contribution of carboxyl groups to heavy metal binding sites in fungal wall. Toxicology Environmental and Chemistry,1996, 54(1-4),1-10.

Fourest, E., Roux, J.C., Heavy metal biosorption by fungal mycelial by-products. Mechanisms and influence of pH. Applied Microbiology Biotechnology,1992, 37,399-403.

Fourest, E., Volesky, B., Contribution of sulphonate groups and alginate to heavy metal biosorption by dry biomass of *Sargassum fluitants*. Environmental Science and Technology,1996, 30, 277-302.

Fourest, E., Volesky, B., Alginate properties and heavy metal biosorption by marine algae. Biochemistry and Biotechnology,1997, 67, 215-226.

Fritz, W., Merk, W., Schlünder, E.U, Competitive adsorption of two dissolved organics onto activated carbon-II. Adsorption kinetics in batch reactors. Chemical Engineering Science,1981, 36, 731-741.

Gardea-Torresdey, J.L., Cano-Aguilera, I., Webb R., Tiemann, K., Gutierrez-Corona, F., Copper adsorption by inactivated cells of *Mucor rouxii* : effect of esterification of carboxyl groups. Journal of Hazardous Materials,1996a, 48 , 171-180.

Gardea-Torresdey, J.L., Tang, L., Salvador, J.M., Copper adsorption by esterified and unesterified fractions of sphagnum peat moss and its different humic acid. Journal of Hazardous Materials ,1996b, 48, 191-206.

Glover, M.R.L., Young, B.D., Bryson, A.W., Modelling the binary adsorption of gold and zinc cyanides onto a strong-base anion exchange resin. International Journal of Mineral Processing,1990, 30, 217-228.

Guibal, E., Roulph, C., Lecloirec, P., Uranium biosorption by filamentous fungus *Mucor miehei*, pH effect on mechanisms and performances of uptake, Water Research,1992, 26(8), 1139-1145.

Hao, Y., Zhao, Y., Ramelow, G.J., Uptake of metal ions by non living biomass derived from marine organisms: effect of pH and chemical treatments, Journal of Environmental Science and Health, 1994, 29, 2235-2254.

Hand, D.W., Crittenden, J.C., Thacker, W.E., User-Oriented batch reactor solutions to the homogenous surface diffusion model. Journal of Environmental Engineering Division,1983, 109, 82-101.

Ho, Y.S., Mac Kay, G., Pseudo-second order model for sorption process. Process Biochemistry, 1983, 34, 451.

Ho,Y.S., Mac Kay, G., Water Research,1999, 33, 578.

Huang, C.P., Westman, D., Huang, C., Morehart, A ., Water Science and Technology,1988, 20,369.

Jaanson-Cherrier, M., Guibal, E., Roussy, J., Belanghe, B., Lecloirec, P., Vanadium(IV) sorption by chitosan: kinetics and equilibrium. Water Research,1996, 30(3), 465-475.

Khoshmanesh, A., Lawson, F., Prince, I.G., Cadmium uptake by unicellular green Microalgae. Chemical Engineering Journal,1996, 62, 81-88.

Kuyucak, N., Volesky, B., Accumulation of cobalt by marine alga, Biotechnology and Bioengineering,1989, 33, 809-822.

Lagergreen, S., Handlingar, 1898, 24, 1.

Leusch, A., Volesky, B., Influence of film diffusion on cadmium biosorption by marine biomass. Journal of Biotechnology, 1995, 43, 1-10.

Mc Kay, G., The adsorption of basic dye onto silica from aqueous solution-solid diffusion model, Chemical Engineering Science,1984, 39, 129-138.

Mac Kay, G., Allen, S.J., Peat as a Raw Material (Edited by Fuchman C.H., 1991). Proceedings at Bord NaMona Peat Research Center, Newbridge, Co Kildare,1990, 124-146.

Mac Kay, G., Bino, M.J., Adsorption of polluants from wastewater onto activated carbon based on external mass transfer and pore diffusion. Water Research,1988, 22, 279-286.

Mc Kay, G., Blair, H.S., Findon, A., Sorption of metal ions by chitosan. In Immobilisation of ions by Bio-sorption (Eds. Eccles H. and Hunt S.), Chichester, Ellis Horwood, U.K., 1986, 59-69.

Mac Kay, G., Poots, V.J.P., Kinetics and diffusion processes in colour removal from effluent using wood as an adsorbent. Journal of Chemical Technology and Biotechnology,1980, 30, 279-292.

Magao, R., Srivostava, S., Uptake by zinc in *Pseudomonas sp.* Strain UD626. Applied Environmental and Microbiology, 1994, 60, 2367-2370.

Mattews, A.P., Weber Jr ,W.J., Modelling and parameter evaluation for adsorption in slurry reactors. Chemical Engineering Communication,1984, 25, 157-171.

Milande, N., Roux, J.C., Fourest, E., Improvement of heavy metal from industrial wastes by filamentous fungi. Récents Progrès en Génie des Procédés,1993, 25, 19-24.

Mishra, S., Chaudhury, P., Roy G., Kinetics of Zn^{+2} adsorption by *Pénicillium sp.* Hydrometallurgy, 1996, 40, 11-23.

Modak, J.M., Natarajan, K.A., Saha, B., Biosorption of copper and zinc using waste *Aspergillus niger* biomass. Mineral and Metallurgy Process,1996,13, 52-57.

Remacle, J., Muguruza, I., Fransolet, M., Cadmium removal by strain of denitrificans isolated from metal-polluted pond. Water Research,1992, 7, 923-929.

Roux, J.C., Lhomme, B., Nexton, J., Lenon, G., Robillon, C., Biosorption of heavy metal from polluted waters by micellial dead biomass of filamentous fungus *Rhizopus arrhizus*. Proceedings of European Congress of Biotechnology, 1990, 325-328, Copenhagen, Danemark.

Sag, Y., Kutsal, T., Biosorption of heavy metals by *Zoogloea ramigera*: use of adsorption isotherms and a comparison of biosorption characteristics, Chemical Engineering Journal, Biochemical Engineering Journal,1995, 60, 181-188.

Sautel,G., Roulph, C., Leclerc, P., Cadmium biofixation by *Pseudomonas putida* Bacteria. Récents Progrès en Génie des Procédés,1991, 5, 203-208.

Singleton, I., Simmons, P., Factors affecting silver biosorption by an industrial strain of *Saccharomyces cerevisiae*. Journal of Chemical Technology and Biotechnology, 1996, 65, 21-28.

Solari, P., Zouboulis, A.I., Matis, K.A., Stalidis, G.A., Removal of toxic metals by biosorption onto nonliving sewage sludge. Separation Science and Technology, 1996, 31, 1075-1092.

Thomas, R., Macaskie, L.E., Biodegradation of tributyl phosphate by naturally occurring microbial isolates and coupling to removal of uranium from aqueous solution, Environmental Science and Technology,1996, 30, 2371-2375.

Urano, K., Tachikawa, H., Process development for removal and recovery of phosphorus from wastewater by new adsorbent-2 Adsorption rates and breathrough curves. Industrial Engineering and Chemical Research,1991, 30, 1897-1899.

Urrutia, M., Beveridge, T.J.,Remobilization of heavy metals retained as oxyhydroxides or silicates by *Bacillus subtilis* cells, Applied Environmental Microbiology,1993, 59 (12), 4323- 4329.

Van Vliet, B.M., Weber Jr, W.J., Hozumi, H., Modelling and prediction of specific compounds adsorption by activated carbon and synthetic adsorbents, Water Research,1980, 14, 1719-1728.

Weber, W.J. , Morris, J.C., Advances in water pollution research: Removal of biologically-resistant polluants from waste waters by adsorption. In Proceedings of International Conference on Water Pollution Symposium, Pergamon Press, Oxford, 1962, Vol.2, 231-266.

Yakup Arica, M., Kaçar, Y., Genç, Ö., Entrapment of white-rot fungus *Trametes versicolor* in Ca-alginate beads: preparation and biosorption kinetic analysis for cadmium removal from an aqueous solution. Bioresource Technology, 2001, 80, 121-129.