

Removal of Bi(III) and Zn (II) by nonliving *Streptomyces rimosus* biomass from nitric solutions

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ABSTRACT

The study reports the Bi³⁺ and Zn²⁺ species sorption onto various adsorbents from nitric synthetic solutions, a typical representative of waste effluents derived from non valid drugs lixiviate. Solid-liquid batch experiments carried out at 25°C to assess the adsorptive capacity of the sorbents indicate that nonliving *Streptomyces rimosus* biomass uptakes the metal species from solutions containing up to 100mg/l, at pH 1.9, at relatively fast kinetics. The biosorbent was loaded with about 7mg/g of Bi³⁺ and 15mg/g of Zn²⁺ after 2 hours contact time. Similar results were obtained with the mineral active carbon and the C25 strong cation exchanger. It was also found that prior treatment of the biosorbent with dilute solution of NaOH improved the sorption capacity of Bi³⁺ to up to 10mg/g. F.T.I.R spectra of the biomaterial gave bands which were assigned to potential binding groups of the amide I and amide II types, primary alcohol at C-6 and secondary alcohol at C-3. Characteristic related peaks were respectively observed at 3272-2950-2923, 1621-1536, 1010 and at 1409cm⁻¹. When adsorbed, both metal ions were quantitatively eluted and the biosorbent material regenerated by aqueous solutions of NaCl, 10g/l. Elution of Bi³⁺ ion was also obtained with nitric solution of Zn²⁺, 1g/l. © 2003 SDU. All rights reserved.

Keywords: Biosorption; *Streptomyces rimosus*; Bi³⁺; Zn²⁺; Environmental

1. INTRODUCTION

Heavy-metal containing effluents are very toxic on the aquatic media and their domestic use must be prohibited due to serious after-effects which are engendered after drinking (Seiler *et al.*, 1994). The poisonous effect of such solutes leads also to the total destruction or the inhibition of the microorganisms activity and hence reduces the efficiency of the self-purification or the bio-treatment operations of water (Arundel, 1995; Norbergs and Molin, 1983). With this regard, such aqueous effluents need specific treatments to remove all the metal species, even when their concentrations are low. These treatments are not only required for the potential hazard effect of the metal species on the environment but also because their economic value, i.e., most metallic baths present very important investment as raw material and demand recycling treatment for their reuse.

Mining and metal-processing waste waters which contain a substantial amount of metal ions such as Cu²⁺, Zn²⁺, Cr³⁺ or Ni²⁺, are considered to be the major sources of heavy metal contamination and the need for economic and effective methods for the removal of metals has resulted in the development of new separation technologies (Schneider and Rubio, 1995). However, it may be necessary to consider metallic pollution that comes from secondary sources like pharmaceutical industry where special emphasis involves no longer valid metallic or organo-metallic compounds containing drugs which may be judiciously valorized after incineration and leaching treatments. The bismuth derivatives are of a concern in this work. Such medicines like Anusol[®] (Parke-Davis) contain typically bismuth oxide, bismuth sub-gallate,

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zinc oxide, and some inorganic or organic excipients as kaolin, titan dioxide, magnesium stearate or castor oil.

The removal of the metallic species may be performed with various physicochemical operations such as precipitation, electrolysis, ion exchange or membrane techniques. However, the efficiency of some conventional separation methods is normally reduced due to complex composition of baths which prevent quantitative removal of the metal ions (Weiner, 1975) or because severe technical or economic constraints exist. Ion exchange and adsorption processes are the major methods used to remove these ions from diluted wastewater and are designed for reliable and versatile continuous or discontinuous processing. They have received widespread application in chemical and environmental engineering and are now recognized as a significant operation in the physicochemical treatment of water and wastewater.

The search for new technologies involving the removal of toxic metals from residual effluents has directed attention to biosorption which is now one of the applicable and most attractive treatment concepts for removal and separation of metal ions solutes, according to the metal binding capacities of various biological material such as bacteria, fungi, yeasts and algae (Volesky, 1986; Vegliò and Beolchini, 1997; Modak and Natarajan, 1995). Such materials like *Streptomyces rimosus*, *Saccharomyces cerevisiae* and *Ascophyllum nodosum* have been proved to be very effective for zinc, copper and nickel removal (Bakkaloglu *et al.*, 1998). The biosorption technique which has the capabilities of adsorption and ion exchange may be an alternative to these conventional processes and seems to be very attractive for heavy metals pollution monitoring (Sekhar *et al.*, 1998).

The study aims, first, to investigate the adsorption efficiency of *Streptomyces rimosus* biomass materials towards Bi^{3+} and Zn^{2+} species and reports on the appropriate conditions to meet the separation requirements when using this biomaterial. Furthermore, the obtained results are compared with sorption capabilities of conventional sorbents like the synthetic ion exchangers C25 (Duolite[®]) and Amberlite[®] IRC 50 (Rohm & Haas, U.S.A.) and the animal activated carbon of Merck[®] trade.

2. MATERIAL AND METHODS

As biosorbent, the nonliving *Streptomyces rimosus* biomass used for the oxytetracycline production was purchased from SAIDAL Antibiotical (Medea, Algeria) and used in dry form as washed raw biomaterial or after treatment by NaOH, 1% by weight. Commercially available synthetic cation exchanger resins, the strong C25 (Duolite) and the weak Amberlite[®] IRC 50 (Rohm & Haas) and mineral active carbon of Merck trade (18008 reference) were used as supplied. Otherwise, reagents of analytical grade were used herein in most experiments.

Adsorption experiments with Bi^{3+} and Zn^{2+} solutions of known concentration were conducted in glassware using GFL model 1083 mechanical shaker with thermostat bath. After the adsorption period, the supernatant was clarified by centrifugation and filtration and analyzed by atomic absorption spectroscopy with Pye Unicam, SP90 A instrument, and Shimadzu UV spectrophotometer, mini 1240, to determine the amount of zinc (λ : 213.9nm, AA) and bismuth (λ : 460nm, UV, according to the iodide complex (Charlot, 1974) and λ : 223.1nm, AA). The FTIR spectra of the biosorbent were recorded on Brüker, IFS 66/S, instrument fitted to Golden Gate measuring device according to the Attenuated Total Reflexion (ATR) spectroscopy. In this technique, a small amount of the sample, used without any particular preparation, is contacted ($\sim 1\text{mm}^2$) with an optically denser crystal (prism) made of ZnSe. The attenuated total reflexion of the propagating beam is analyzed.

In the kinetic study of the adsorption, samples were taken out of the shaker at regular intervals and after brief settling periods, the supernatant was analyzed. Next, in the determination of adsorption equilibrium curves of Bi^{3+} and Zn^{2+} onto the biomaterial, variable masses were contacted during 2 hours, at 25°C, with constant volume containing 100mg/l of metal-ion. After settling and filtration procedures, the supernatant was analyzed by the AA or the UV instruments.

3. RESULTS AND DISCUSSION

3.1. Kinetic studies

Preliminary kinetic test experiments were conducted for the adsorption of Bi^{3+} and Zn^{2+} onto the various adsorbents (C25 and IRC 50 cationic exchangers, mineral activated carbon and the *Streptomyces rimosus* biomass) from nitric solutions of pH 1.9, containing up to 100mg/l of metal ion. Extensive hydrolysis of Bi^{3+} is prevented in such conditions since precipitation of Bi^{3+} compounds occurs at weak acidic solutions of $\text{pH} > 4$. Figure 1 represents the distribution percentages of Zn^{2+} and Bi^{3+} metal species as a function of pH according to speciation based on the following reactions (1 to 6) and clearly indicates that Zn^{2+} , Bi^{3+} and BiOH^{2+} may be of concern to the sorption process from solutions at the above-mentioned pH.

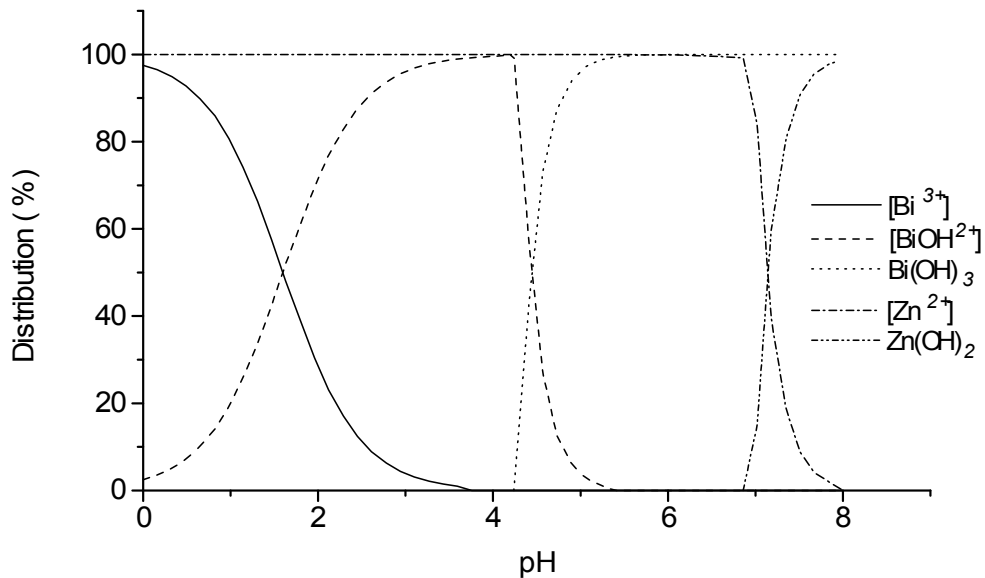
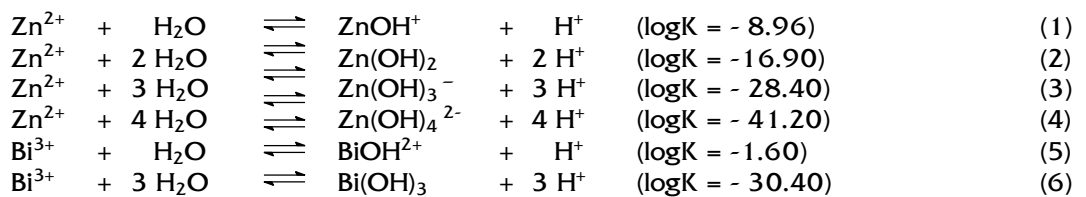


Figure 1. pH-distribution species diagram of Zn^{2+} , 0.0015M and Bi^{3+} , 0.0005M



The results obtained in the adsorption rate experiments show that in most cases the equilibrium was reached within few minutes (10-15min). With the regard to Bi^{3+} sorption from the acidic solutions, the mineral active carbon which was already proved to be useful in the metal species removal from aqueous media (Bal and Bal, 1997) and the *Streptomyces rimosus* biomass present high sorption capacity : over 7mg/g of the metal-ion were recovered on the biomass at 25°C, after 2 hours contact time. Sorption onto C25 of about 3mg/g resulted in very slow kinetics due to the highly porous structure of this resin. The IRC 50 resin was found to be less efficient in the test experiments from the nitric media of pH 1.9. The adsorption yields less than 0.5mg/g from solution containing 100mg/g of Bi^{3+} . Due to its weak cation exchanger characteristics, pH-limited efficiency is to be obtained at value lower than 4, so, inappropriate use of the resin is indicated in more acidic media.

When operated in batch system, the adsorption kinetics would be affected depending on many factors, such as porosity and particle size of the adsorbent, nature of solute, shaking speed, temperature, etc. (Mansour *et al.*, 1985). Species diffusion in the solid and the complex

formation rate in chelation and/or ion exchange processes are usually controlling steps. The adsorption load determination was, however, of a major concern herein.

3.2. Equilibrium studies

To produce the adsorption isotherms, which express the amount of Bi^{3+} and Zn^{2+} species adsorbed per unit weight of adsorbent as function of the equilibrium concentration in solution (C_e), the experimental results obtained at 25°C are plotted in Figures 2 and 3. From these figures, a first comparison indicates clearly that Zn^{2+} sorption onto the biomass is higher than that of Bi^{3+} . From single ion containing solution, the *Streptomyces rimosus* biomass was capable of accumulating up to about 15mg/g of zinc species and, as such, the biomass found to be more effective for removal of this metal ion becomes more suitable compared to conventional sludges, capable of biosorbing up to 5mg/g of Zn^{2+} from more appropriate pH solutions (Bux *et al.*, 1999). In other respects, prior treatment of the biomass with dilute solution of NaOH improved significantly the adsorption capacity of the biomaterial as it can be noted with Bi^{3+} sorption. Such treatment aims normally to the deproteinization of the biomass and, hence, producing crude polyglucosamines complexes which constitutes usually the cell wall of nonliving microorganisms (Majeti and Ravi Kumar, 2000).

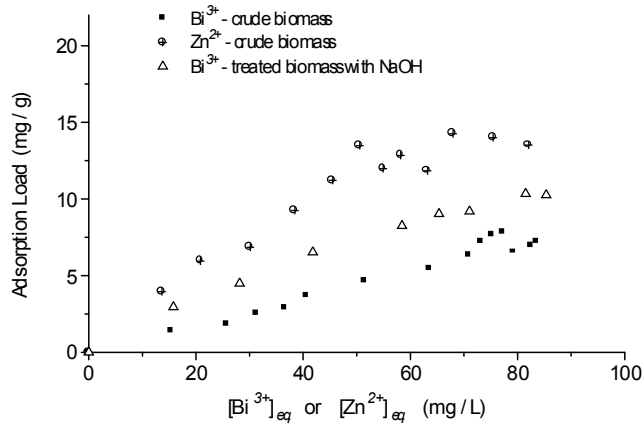


Figure 2. Adsorption equilibria of Bi^{3+} and Zn^{2+} by *Streptomyces rimosus* biomass ($\phi < 500\mu\text{m}$) from nitric solution, $[\text{Bi}^{3+}]_0 = 100\text{mg/l}$; $[\text{Zn}^{2+}]_0 = 100\text{mg/l}$; $\text{pH} = 1.9$; $T = 25^\circ\text{C}$; $t_{\text{ag}} = 2\text{h}$

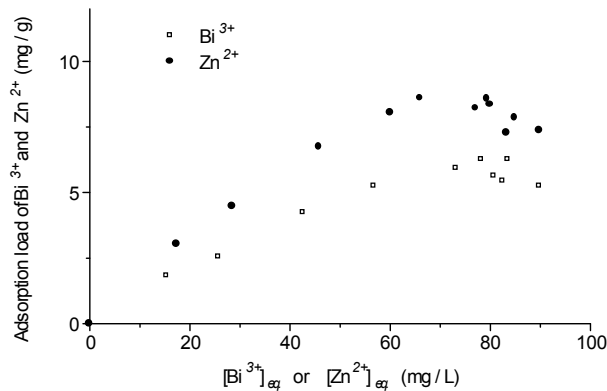


Figure 3. Adsorption equilibria of Bi^{3+} and Zn^{2+} mixture by *Streptomyces rimosus* biomass ($\phi < 500\mu\text{m}$) from nitric solution, $[\text{Bi}^{3+}]_0 = 100\text{mg/l}$; $[\text{Zn}^{2+}]_0 = 100\text{mg/l}$; $\text{pH} = 1.9$; $T = 25^\circ\text{C}$; $t_{\text{ag}} = 2\text{h}$

The sorption capacity of the used biomass toward Bi^{3+} and Zn^{2+} species from mixtures is in general preserved and slightly noticeable decreases are observed for the two metal ions. In this

context, biosorption extent of such species, which is in some cases selective (Sakaguchi and Nakajima, 1991; Tsezos and Volesky, 1982), seems to be here almost unaffected. Accordingly, Bi^{3+} as well as Zn^{2+} species are removed appreciably from binary acidic solutions. However, differences in sorption capacities are expected in streams because it is well-known that in general the presence of co-ions in multi-components combinations decreased the metal uptake.

F.T.I.R characterization of the biomaterial in his primary form (a) and treated with dilute NaOH solution (b) reveals the presence of effective chemical binding groups. Accordingly, Bi^{3+} and Zn^{2+} uptake kinetics, found to be relatively fast, indicate to chemical process which involves ion exchange and/or chelating phenomena, both are major biosorption mechanisms with precipitation and physical adsorption (Vegliò and Beolchini, 1997).

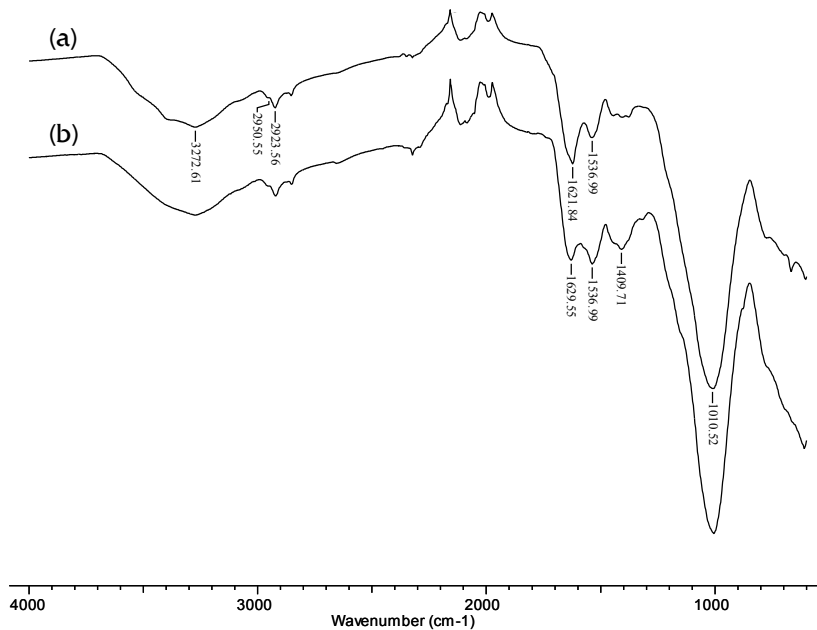


Figure 4. Recorded FTIR spectra of the *Streptomyces rimosus* biomass : (a), primary material and (b), treated material with NaOH, 1%

The spectra exhibit major peaks at 3272 , 2950 and 2923cm^{-1} which can be attributed to amide I, at 1621 and 1536cm^{-1} attributed to amide II, and very strong band at 1010cm^{-1} assigned to primary alcohol at C-6. Increased intensity of the peak at 1409cm^{-1} (spectrum b) attributed to secondary alcohol vibrations at C-3, may be a result of the NaOH treatment on the biomaterial. Correlating the F.T.I.R characteristics of the biomass and previous findings related to chitin derivatives (Gow, 1987), structural similarities provide evidence, in that, the used biosorbent is polysaccharide-based material with acetylated amino group ($-\text{NHCOCH}_3$); that is most indicative characteristics of chitin. These amino and carboxyl highly active with the hydroxyl content of biomaterial are likely to ensure potential interaction and offer particularly abundant metal-binding capacity.

3.3. Elution of adsorbed species

The possibility of using the biosorbent material in subsequent absorption-desorption cycles would be an attractive feature for practical applications of the biomass. Stripping of the adsorbed metal could be achieved by using an appropriate eluant and further yielding a concentrated solution of the metal of interest. The physicochemical phenomenon of metal biosorption, which was found here to be relatively rapid may be also reversible. Fortunately such behavior is the most common and the biomass has, thus, all that advantageous chemical characteristics of an ion exchange resin and activated carbon.

To study the regeneration of the sorbents, elution of adsorbed Zn^{2+} and Bi^{3+} species using aqueous solutions of sodium chloride (NaCl) and zinc sulfate ($ZnSO_4$) was examined. Aqueous NaCl solutions have proved in this work to be potential eluents for the adsorbed metal species. At the studied experimental conditions, significant elution yield was achieved with a solution of 10g/l of the compound. Elution yields of 88-94% were obtained from Zn^{2+} loaded biomass after 2 hours contact time. Adsorbed Bi^{3+} species onto C25 and IRC 50 cation exchangers were also brought back to solution quantitatively with the eluant.

Further investigations show that increasing concentration of Zn^{2+} in nitric media gives rise to favorable elution of the Bi^{3+} from the biosorbent. From this view point subsequent precipitation of low solubility Bi^{3+} compounds is prevented which may be of interest when treating the Bi^{3+} - Zn^{2+} mixtures. Figure 5 shows that complete elution of Bi^{3+} from 3.8mg/g loaded *Streptomyces rimosus* biomass is obtained when the Zn^{2+} concentration in the stripping solution is above 15mmol/l, i.e, corresponding to 1g/l.

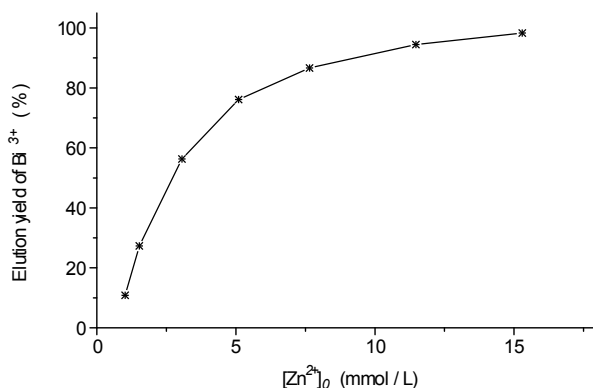


Figure 5. Elution yields of Bi^{3+} from *Streptomyces rimosus* biomass ($\phi < 500\mu m$) by aqueous solutions of Zn^{2+} of increasing concentration, $[Bi^{3+}]_0 = 3.8$ mg/g; $T = 25^\circ C$; $t_{ag.} = 2$ h

It is desirable that the elution is performed according to concentration change of one of the concerned solutes, as to allow suitable recycling of clean effluents. In the Bi^{3+} - Zn^{2+} systems, further separation of Bi^{3+} species from concentrated solutions may be achieved, for example, by precipitation.

4. CONCLUSIONS

The removal of Zn^{2+} and Bi^{3+} metal ions from aqueous acidic effluents by biosorption onto *Streptomyces rimosus* biomass is demonstrated here to be an useful alternative to conventional systems. The operation should be advantageous in the recovery of valuable metal solutes from non conventional metal-containing wastes such as needless or time-limited drugs, topic of this work. Significant loads which may be compared to those measured in mineral active carbons or strong cation exchangers systems are obtained quickly. In fact, the biomaterial contains many functional groups with O and N donor atoms, related to multi binding properties towards metal species.

The elution of Zn^{2+} and Bi^{3+} and the resulting regeneration of the biosorbent material are efficiently achieved with aqueous solution of NaCl. Nitric solution of Zn^{2+} was found to be of interest in the stripping of sorbed Bi^{3+} onto the biomass, leading to potential purification and separation purposes. Moreover, depending on the pH of Zn^{2+} and Bi^{3+} containing solutions, selective biosorption and feasible separation of Zn^{2+} species may be obtained at slightly acidic media at which Bi^{3+} species are completely precipitated.

REFERENCES

- Arundel, J., Sewage and industrial effluent treatment. Blackwell Science, Oxford (G.B.), 1995.
- Bakkaloglu, I., Butter, T.J., Evison, L.M., Holland, F.S., Hancock, I.C., Screening of various types biomass for removal and recovery of heavy metals (Zn, Cu, Ni) by biosorption, sedimentation and desorption. *Water Science and Technology*, 1998, **38** (6), 269-277.
- Bal, Y., Bal, K.E., Extraction and separation of Ni(II), Cu(II) and Zn(II) on activated carbon: Application to wastewater treatment. International conference on water problems in the mediterranean countries, 17-21 November, 1997, Nicosia, North Cyprus.
- Bux, F., Atkinson, B., Kasan, H.C., Zinc biosorption by waste activated and digested sludges. *Water Science and Technology*, 1999, **39** (10-11), 127-130.
- Charlot, G., Chimie analytique quantitative. 6th Edn, Masson, 1974, Paris.
- Gow, N.A.R., Gooday, G.W., Russel, J.D., Wilson, M.J.J., Infrared and X-ray diffraction data on chitins of variable structure. *Carbohydr. Res.*, 1987, **165** (1), 105-110.
- Majeti, L., Ravi Kumar, N.V., A Review of chitin and chitosan applications. *J. of Reactive and Functional Polymers*, 2000, **46**, 1-27.
- Mansour, A.R., Shahalam, A.B., Sotari, M.A., Parametric sensitivity study of multicomponent adsorption in agitated tanks. *Separation Science and Technology*, 1985, **20** (1), 1-20.
- Modak, J.M., Natarajan, K.A., Biosorption of metals using nonliving biomass - A review. *Minerals and Metallurgical Processing*, 1995, **12**, 189-195.
- Norbergs, A.B., Molin, N., Toxicity of cadmium, cobalt, uranium and zinc to *Zoogloea ramigera*. *Water Research*, 1983, **17** (10), 1333-1336.
- Sakaguchi, T., Nakajima, A., Accumulation of heavy metals such as uranium and thorium by microorganisms. In: Smith, R.W., Misra, M. (Eds.), *Mineral Bioprocessing*. The Minerals, Metals and Materials Society, 1991.
- Schneider, I.A.H., Rubio, J., New trends in biosorption of heavy metals by freshwater macrophytes. In: Jerez, C.A., Vargas, T., Toledo, H., Wiertz, J.V. (Eds.), *Biohydrometallurgical Processing*. 1995, University of Chile, Chile.
- Seiler, H.G., Sigel, A., Sigel, H., Handbook on metals in clinical and analytical chemistry. Marcel Dekker, Inc., 1994, New-York, USA.
- Sekhar, K.C., Subramaniam, S., Modak, J.M., Natarajan, K.A., Metal ions removal using a waste industrial biomass with reference to environmental control. *International Journal of Mineral Processing*, 1998, **53**, 107-120.
- Tsezos, M., Volesky, B., The mechanism of uranium biosorption by *Rhizopus arrhizus*. *Biotechnol. Bioeng.*, 1982, **24**, 385-401.
- Vegliò, F., Beolchini, F., Removal of metals by biosorption: a review. *Hydrometallurgy*, 1997, **44**, 301-316.
- Volesky, B., Biosorbent materials. *Biotechnol. Bioeng. Symp.*, 1986, **16**, 121-126.
- Weiner, R., *Epuration des eaux résiduaires dans la formation et la galvanisation des métaux*. Editions Eyrolles, 1975, Paris.