Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 146 (2007) 86–90
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Mathematical models applied to the Cr(III) and Cr(VI) breakthrough curves

Margarita Ramirez C. [a,*], Mônica Pereira da Silva [b], Selma G. Ferreira L. [b], Oscar Vasco E. [a]

[a] *Universidad Pontificia Bolivariana, Facultad de Ingeniería Química, CIBIOT, Circular 1ª, N° 70-01 Medellín, Colombia*
[b] *Escola de Química, Universidade Federal do Rio de Janeiro, Brazil*

Received 3 May 2006; received in revised form 28 November 2006; accepted 30 November 2006
Available online 5 December 2006

Abstract

Trivalent and hexavalent chromium continuous biosorption was studied using residual brewer *Saccharomyces cerevisiae* immobilized in volcanic rock. The columns used in the process had a diameter of 4.5 cm and a length of 140 cm, working at an inlet flow rate of 15 mL/min. Breakthrough curves were used to study the yeast biosorption behavior in the process. The saturation time (t_s) was 21 and 45 h for Cr(III) and Cr(VI), respectively, and a breakthrough time (t_b) of 4 h for Cr(III) and 5 h for Cr(VI). The uptake capacity of the biosorbent for Cr(III) and Cr(VI) were 48 and 60 mg/g, respectively. Two non-diffusional mathematical models with parameters t_0 and σ were used to adjust the experimental data obtained. Microsoft Excel tools were used for the mathematical solution of the two parameters used.

Keywords: Biosorption; Models; Breakthrough curves; Chromium; *Saccharomyces cerevisiae*

1. Introduction

Due to the development of industrial activities, there is an increase in the content of heavy metals inside the effluents heading towards rivers, generating 2.4 million tonnes of As, Cd, Cr, Cu, Hg, Ni, Pb, Sc, V and Zn [1], which affect the water quality. Chromium is a transition metal located in group VI-B of the periodic table. Although it is able to exist in several oxidation states, the most stable and common forms are the trivalent Cr(III) and the hexavalent Cr(VI) species, which display quite different chemical properties [1]. Biosorption technology comes as an answer to the reduction of water toxicity [2], its processes are based in the ability of a microorganism to adsorb a metal in solution by several physical-chemical processes through the cell's wall; this process does not always involve biomass metabolism, and that is why it does not matter if the microorganisms are dead or alive for the development of such processes [3–5]. The physical–chemical processes involved in biosorption are usually identified as ion exchange, complexation, coordination, chelation, micro-precipitation or adsorption, due to the removal of the metal from the solution [6].

Continuous packed bed column systems are the most suitable and economic ways to remove heavy metals, offering an alternative treatment for the removal and recovery of heavy metals in aqueous systems [2,4].

Breakthrough curves are necessary for the adsorption column design, due to the information about the dynamic behavior of the metal concentration of the effluent in time [4,5]. Another important factor for the column design is the maximum capability of adsorption of the metallic ion with a specific amount of biomass, this process is studied with the help of sorption isotherms [3,5].

Mathematical models were created for the adjustment of experimental breakthrough curves, and the dynamic behavior prediction of the column in biosorption processes.

These models are useful for the sizing and optimization of the industrial scale process using laboratory data; mathematical models also enable the response and mechanisms prediction of the system [7].

The aim of the present survey is to study the chromium biosorption process using *Saccharomyces cerevisiae* as the biosorbent in a support of volcanic rock, by analyzing the behavior of the experimental breakthrough curves for each one of the stable oxidation states of chromium using the two

* Corresponding author. Tel.: +57 4 415 90 20; fax: +57 4 411 87 79.
E-mail addresses: mramirez@upb.edu.co, margarita.ramirez@upb.edu.co (M. Ramirez C.).

0304-3894/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2006.11.056

parameters (dose–response) mathematical model proposed by Belter in Brady et al. [8] and modified by Chu [9].

2. Materials and methods

2.1. Biosorbent

The biosorbent used for the chromium removal was the residual yeast *S. cerevisiae* originated in the brewery industry Cervecería Unión S.A./Colombia

2.2. Metal solution preparation

The Cr(III) solutions were prepared using $KCr(SO_4)_2{\cdot}12H_2O$ (MERCK), and Cr(VI) solutions were prepared using $K_2Cr_2O_7$ (JT BAKER) with concentrations of 300 mg/L and 200 mg/L, respectively, the solutions concentrations were measured using atomic absorption spectroscopy in a Perkin Elmer 3100 spectrophotometer.

The initial values of the trivalent and hexavalente concentrations of chromium solutions were obtained from the real solutions of the leather industry of Antioquia (Colombia) and the values of pH were adopted of the experimental results in batch after making a response surface designs that optimizes the value of the parameters in the biosorption process, the results were analyzed by means analysis of the variance and *t*-test of student as it is to Carmona et al. [10].

2.3. Breakthrough curve

A PVC pipe of 4.3 cm of diameter was the building material of the column with volcanic rock, porous structure, originated in the jean washing industries as the packing material with a length of 140 cm. The column was filled with volcanic rock up to a height of 120 cm, approximately 85% of the total volume of the column, and the void fraction within the column was 0.67, i.e., total porosity, calculated like water volume added divided volume of the bed.

The immobilized microorganisms were pumped and recycled into the column as a suspension with a biomass concentration of 155 g/L for a period of 8 days, period in which the yeast is adhered strongly on the interstices of volcanic rock. The amount of immobilized biomass was determined by quantifying the biomass concentration each day taking a known volume and bringing it to a dry weight, from here find the concentration that has the solution and less the initial concentration, during the 8-day of immobilization process until the amount of biomass in the samples were maintained constant.

The initial volumetric flow used in this paper was calculated from Eq. (1), with base in the results in batch. When we use a volumetric flow under observe preferential channels and died zones, which cause difficulties in the repetition data. Consequently other values of volumetric flows were used.

$$Q = \frac{Mq}{Ct_{eq}} \tag{1}$$

where Q is volumetric flow (mL/min), M the biosorbent mass (g), q the metal uptake capacity (mg metal/g biosorbent), C the inlet metal concentration (mg/L) and t_{eq} is the time to reach the equilibrium (min).

Subsequently, the uptake capacity was determined as shown in Eq. (2).

$$q_{eq} = \frac{q_{tot}}{X} \tag{2}$$

where q_{eq} is biosorbent uptake capacity for metal ion, q_{tot} the total quantity of adsorbed metal ion (mg) and X is the biosorbent mass (g).

Values for total quantity of adsorbed metal ion after final time were 2956 and 3691 mg for Cr(III) and (VI), respectively, the biosorbent mass and immobilized volcanic rock mass in the column were both 61.4 g. The values for the uptake capacity were 48 mg/g for Cr(III) and 60 mg/g for Cr(VI).

Initially, the value of the flow of 6 mL/min, then was increased to 15 mL/min. The results using flow of 6 mL/min are in Fig. 1.

In order to apply the model it is necessary that the rupture curve present rupture time and saturation time. The rupture curves vary according to the flow, one of those variations is the form and the inclination that the curve displays from each one of these points, therefore, when varying the flow, vary the parameters of the model to gamma.

The inlet volumetric flow was of 15 mL/min and it was supplied at the upper section of the column with a peristaltic pump (Cole Palmer, model 77201-60), using a latex pipe L/S 13 with an inner diameter of 0.8 mm. The Effluent samples where collected at the bottom of the column using a sample collector programmed for the duration of the assays, all the samples where submitted to analysis to determine the final metallic ion concentration (C_F).

The initial inlet conditions for the metallic solution were 300 mg/L and 200 mg/L of Cr(III) and Cr(VI), respectively, with a pH value of 4.34 for Cr(III) and 1.66 for Cr(VI) [10].

2.4. Mathematical modeling of breakthrough curves

The biosorption experimental data adjustment for continuous systems used in this process is the one suggested by Thomas in Volesky [11,12], thermodynamically obtained models [2], mass transfer and diffusional models [2,3,12–18], BDST (bed depth

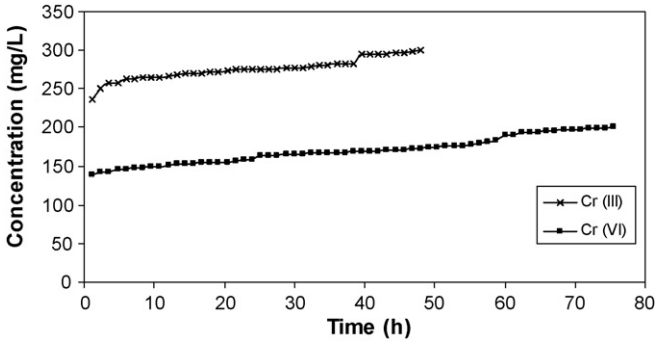

Fig. 1. Breakthrough curves for Cr(III) and Cr(VI) using 6 mL/min inlet volumetric flow.

service time) [6,19–21] and scientific models [4] among others, are very complex in their mathematical solution due to the determination of some diffusional parameters in the equations involved in the description of the biosorption process [1,2].

The models used in this survey were the ones developed by Belter and Cussler and modified by Chu [9], as it is shown in Eqs. (2)–(4).

$$\frac{C_e}{C_i} = \frac{1}{2}\left(1 + \text{erf}\left[\frac{t - t_0}{\sqrt{2}\sigma t_0}\right]\right) \quad (2)$$

$$\frac{C_e}{C_i} = \frac{1}{2}\left(1 + \text{erf}\left[\frac{(t - t_0)\exp(\sigma(t/t_0))}{\sqrt{2}\sigma t_0}\right]\right) \quad (3)$$

$$\frac{C_e}{C_i} = \frac{1}{2}\left(1 + \text{erf}\left[\frac{(t - t_0)\exp(-\sigma(t/t_0))}{\sqrt{2}\sigma t_0}\right]\right) \quad (4)$$

where erf(x) is the error function of x, t the residence time inside the column, t_0 the temporal parameter which indicate time needed for the outlet metal concentration to be the half of the one inlet metal concentration and σ is the standard deviation of the linear part of the breakthrough curve.

The model parameters t_0 and σ can be estimated by fitting Eqs. (2)–(4) to experimental breakthrough data.

Microsoft Excel® tool was used for the mathematical solution of the above equations. t_0 and σ were estimated by replacing in Eqs. (2)–(4) data from the experimental breakthrough curves. Before using the data of the breakthrough curve obtained experimentally, all the data in the curve should be normalized, this means that, the breakthrough curve must be presented in terms of the dependence in time of the relation between the final and initial chromium concentrations (C_f/C_0).

3. Results and discussion

The breakthrough curves, normalized concentration defined as the measured concentration divided by the inlet concentration is plotted against time in Fig. 2, and shows the amount of chromium present in the solution (both oxidation states) was removed with *S. cerevisiae* (as the biosorbent) inside a continuous packed bed column system. The S shape and the appearance of the breakthrough point describe a typical behavior of biosorption inside fixed bed column systems. The sorption process for Cr(III) and Cr(VI) did not happen very fast; this can be concluded from the behavior of the curve that didn't show a linear vertical behavior between the breakthrough point and the saturation point. The breakthrough point for each one of the ions of chromium is identified well in Fig. 2. According to Treybal [21], the time to reach breakthrough point decreases due to several factors; as the fixed bed length decreases, the normal size of the biosorbent increases, the volumetric flow increases through the column or having no solute concentration at the inlet stream.

The Cr(VI) concentrations in the effluent, were higher than zero, this could be attributed to the initial flow rate conditions that could have been too high. According to Treybal [21] and Aksu et al. [22] the flow rate is an important factor involved in the biosorption process.

Breakthrough point observed for Cr (III) ions was early than that for Cr(VI) ions, possibly the chemical properties of Cr(VI) and Cr(III) are different. Cr(VI), considered the most toxic form of Cr, is usually associated with oxygen as chromate (CrO_2^{-4}) or dichromate ($Cr_2O_2^{-7}$) ions. In contrast, Cr (III) in the form of oxides, hydroxides or sulfates, is much less mobile [23]. Most cells are impermeable to Cr (III) probably because it forms water insoluble compounds in non-acidic aqueous solutions [23], similar justification was exposed for Travis et al. [24].

The experimental data shown in Fig. 2 were adjusted to the mathematical models proposed by Chu [9] in Eqs. (2)–(4). According to Chu [9], variables such as the inlet flow rate, column length and average size of the sorbent were not used to develop Eq. (2), and it was also empirically correlated to simulate the dynamic response of the column at different experimental conditions.

The equations described previously were used to fit the experimental data obtained in the chromium—yeast system employed. These equations do not use diffusional coefficients; they only use the error function (erf) to describe the process as well as the standard deviation (σ) of lineal part. These equations are only appropriate in the cases that the system chromium—yeast are favorable (when the breakthrough curve evidences an S shape), and this is shown in discontinuous systems in the isotherm building process, in which there is a maximum chromium removal capacity by *S. cerevisiae* [25]. In the cases that the biosorption system is unfavorable it is necessary to use other mathematical models that include the diffusional coefficients such as Treybal describes them [21].

Eqs. (2)–(4) were applied to adjust the models to breakthrough curve obtained in the process of biosorption of Cr(III) and Cr(VI), by using *S. cerevisiae* due to the isotherms for the same process gave favorable curves, such as it shown by Carmona [10]. They were used to model the experimental breakthrough curves for Cr(III) and Cr(VI), and the results are shown in Fig. 2.

The model shown in Eq. (2) is capable to describe the symmetric breakthrough curve behavior. When symmetric or asymmetric curves are obtained Eqs. (3) and (4) are employed for the modeling of the process.

The curves of rupture for Cr(III) showed symmetric behavior to the difference of the curve for Cr(VI) that was asymmetric, possibly due to the Cr(VI) before to be totally attracted by the yeast, first is convert to Cr(III) [23].

For Cr(VI), the behavior of the breakthrough curve was asymmetric, showing a well adjustment to the models described by Eqs. (2) and (4), the best values of standard deviation, however, this last one describes the curve starting at time (t) equal to zero, allowing a simulation or prediction more adjustable to the model expressed by Eq. (2). As it was mentioned previously Eqs. (3) and (4) were modified by Chu [9] so that the experimental data would fit better, no matter if the curve is symmetrical or asymmetrical.

There are several papers in literature [2,4,11–14] that use mathematical models to fit experimental data obtained in con-

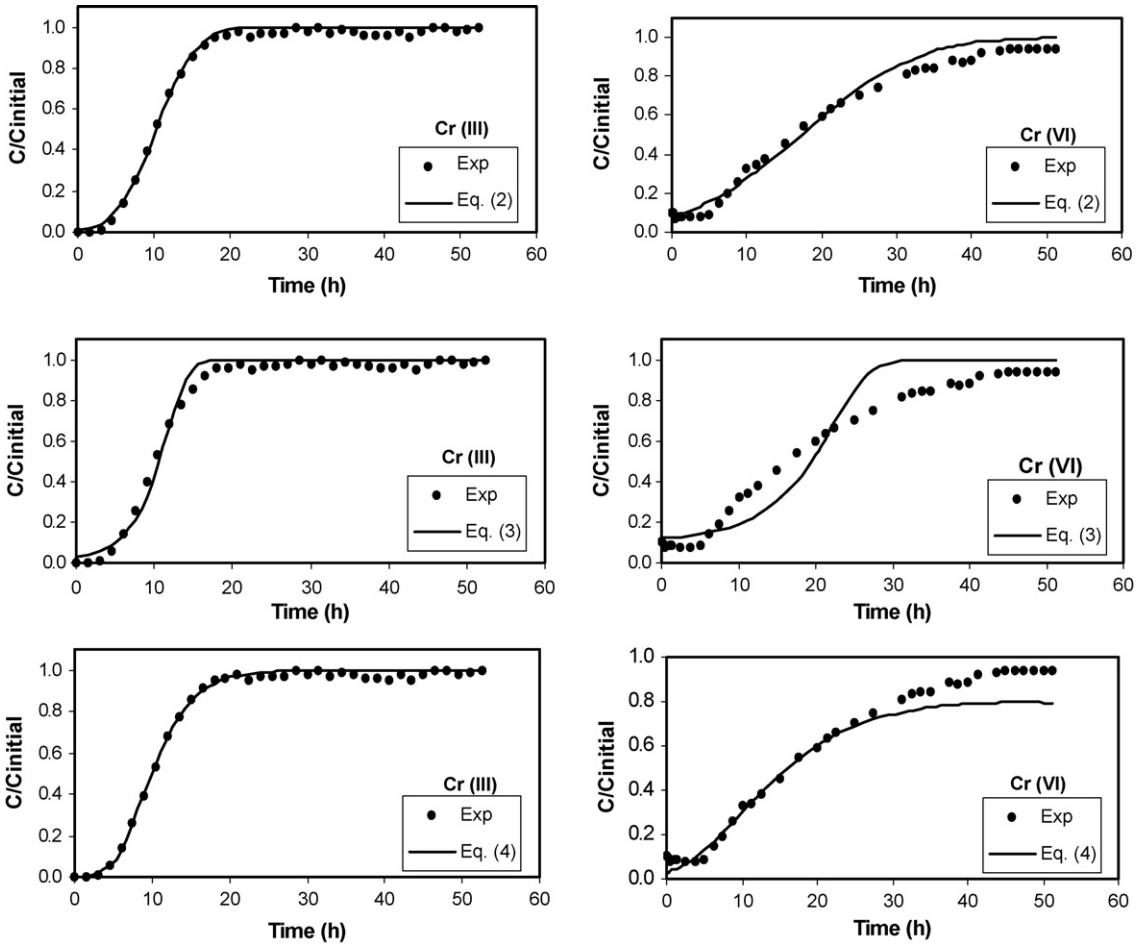

Fig. 2. Models obtained for the breakthrough curves for Cr(III) and Cr(VI) using Eqs. (2)–(4).

tinuous biosorption systems. Da Silva et al. [26] made Cu(II) biosorption assays using *Sargassum sp.* in batch and continuous systems, demonstrating the suitability of the system by the building of sorption isotherms. Researchers have made several assays in packed bed columns to demonstrate the symmetry of the breakthrough curves, furthermore, they use mass transfer mathematical models to adjust experimental data. The results obtained showed the sensibility to breakthrough curve adjustment. The mathematical models employed for such predictions were complex and depended on assumptions like; the radial dispersion was negligible, and in addition the finite volume technique and Dassal code were used for the mathematical solution of the differential equations present in the model.

Although, the mathematical models involving diffusional coefficients to adjust the experimental data are sensible and well fit, they are complex in their mathematical development, whereas, the models described in Eqs. (2)–(4) are more suitable for calculations and experimental data fitting.

Sigma, t_0 and standard deviation of lineal part data for trivalent and hexavalent chromium, were obtained from Fig. 1, is shown in Table 1.

The use of the methodology proposed by Chu, facilitates the use of the error function (erf), which is inside Microsoft Excel package.

Table 1
Sigma (σ), t_0 and standard deviation

	Cr(III)			Cr(VI)		
	t_0	Sigma (σ)	R^2	t_0	Sigma (σ)	R^2
Eq. (1)	10.29	0.40	0.9968	17.25	0.70	0.9802
Eq. (2)	10.68	0.54	0.9863	19.43	0.85	0.8388
Eq. (3)	10.03	0.30	0.9988	15.93	0.52	0.9821

4. Conclusions

The use of immobilized *S. cerevisiae* in volcanic rock (high porosity) is suitable for the biosorption of each one of the oxidation states of chromium. The breakthrough curve for Cr(III) describes more symmetry, however, the Cr(VI) breakthrough curve shows a breakthrough point in a time of 40 h, higher than the one reported by the Cr(III) that was of 15 h.

The breakthrough curve for Cr(VI) describes an asymmetric behavior, and the model that gave the best fit was the one given by Eq. (4), allowing a much better simulation or prediction than the one given by Eq. (2).

The breakthrough curves for chromium biosorption with *S. cerevisiae* as the biosorbent, were described by Eqs. (3) and (4), showing a better adjustment to the experimental data than the

last one of the models used, because of the time zero correction given by the model.

The applicability of the mathematical models used does not require complex mathematical manipulations; this makes a great difference between the mass transfer balance models used to describe the biosorption processes.

Acknowledgements

Margarita Enid Ramírez Carmona expresses her acknowledgements to: COLCIENCIAS/Colombia, CIBIOT, Universidad Pontificia Bolivariana/Colombia and Escola de Química, UFRJ/Brasil.

References

[1] F.A. Veglió, A. Esposito, A.P. Reverberi, Standardisation of heavy metal biosorption tests: equilibrium and modelling study, Process Biochem. 38 (2003) 953–961.
[2] K.Y. Gin, Y.Z. Tang, M.A. Aziz, Derivation and application of a new model for heavy metal biosorption by algae, Water Res. 36 (2002) 1313–1323.
[3] B. Volesky, Biosorption of Heavy Metals, CRC Press, Florida, 1990.
[4] Y. Sag, A. Yalcuk, T. Kutsal, Use of a mathematical model for prediction of the performance of the simultaneous biosorption of Cr VI and Fe III on Rhizopus arrhizus in a semi-batch reactor, Hydrometallurgy 59 (2001) 77–87.
[5] Y. Guangyu, T. Viraraghavan, Heavy metal removal in a biosorption column by immobilized *M. rouxii* biomasa, Biores. Technol. 78 (2001) 243–249.
[6] K. Vijaya raghavana, J. Jegana, K. Palanivelub, M. Velan, Removal of nickel(II) ions from aqueous solution using crab shell particles in a packed bed up-flow column, J. Hazard. Mater. B113 (2004) 223–230.
[7] Z. Aksu, F. Gönen, Biosorption of phenol by immobilized activated sludge in a continuos packed bed: prediction of breakthrough curves, Process Biochem. 39 (2004) 599–613.
[8] J.M. Brady, J.M. Tobin, J.C. Roux, Continuous packed bed biosorption of Cu^{2+} ions: application of a simple two parameter mathematical model, J. Chem. Technol. Biotechnol 74 (1999) 71–77.
[9] K. Chu, Improved fixed bed models for metal biosorption, Chem. Eng. J. 97 (2004) 233–239.
[10] M. Carmona, M. Antunes, S. Gomes, Bioadsorción de Cr+3 y Cr+6 empleando levadura residual de la industria cervecera, Ingeniería Química (2003) 53–65.
[11] B. Volesky, I. Prasetyo, Cadmium removal in a biosorption column, Biotechnol. Bioeng. 43 (1994) 1010–1015.
[12] B. Volesky, Biosorption process simulation tools, Hydrometallurgy 71 (2003) 179–190.
[13] A. Pethkar, K. Paknikar, Recovery of gold from solutions using cladosporium cladosporioides biomass beds, J. Biotechnol. 63 (1998) 121–136.
[14] E. Trujillo, Transferencia de masa Fundamentos y aplicaciones, Environ. Sci. Technol. 25 (9) (1991) 1559–1594.
[15] Z. Aksu, Kutsal, Determination of kinetic parameters in the biosorption of copper(II) on *Cladophora* sp., in a packed bed column reactor, Process Biochem. 33 (1) (1998) 7–13.
[16] F. Beglio, F. Beolchini, L. Toro, Kinetic modeling of copper biosorption by immobilized biomass, Ind. Eng. Chem. Res. 37 (1998) 1107–1111.
[17] D. Kratochvil, B. Volesky, Multicomponent biosorption in fixed beds, Water Res. 34 (12) (2000) 3186–3196.
[18] D. Kratochvil, B. Volesky, G. Demopoulos, Optimizing Cu removal/recovery in a biossorption column, Water Res. 31 (9) (1997) 2327–2339.
[19] Z. Zulfadhly, M. Mashitad, S. Bhatia, Heavy metals removal in fixed-bed column by the macro fungus *Pycnopous sanguineus*, Environ. Pollut. 112 (2001) 463–470.
[20] T. Muraleedharan, et al., Application studies of Biosorption for monazite processing industry effluents, Biores. Technol. 49 (1994) 179–186.
[21] R. Treybal, Operaciones de transferencia de masa. Operaciones sólido fluido, McGraw-Hill, España, 1998.
[22] Z. Aksu, F. Gönen, Z. Demircan, Biosorption of chromium (VI) ions by Mowital®B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon, Process Biochem. 32 (2002) 175–186.
[23] C. Cervantes, et al., Interactions of chromium with microorganisms and plans, FEMS Microbiol. Rev. Chem. 25 (2001) 335–347.
[24] J. Travis, et al., Effects of hexavalent chromium on the survival and cell cycle distribution of DNA repair-deficient *S. cerevisiae*, DNA Repair 1 (2002) 617–627.
[25] B. Volesky, J. Webera, J.M. Parkb, Continuous-flow metal biosorption in a regenerable Sargassum column, Water Res. 37 (2003) 297–306.
[26] E. Da Silva, et al., Modeling of copper (II) biosorption by marine alga *Sargassum* sp. in fixid-bed column, Process Biochem. 38 (2002) 791–799.