THE PROCESS OF BIOSORPTION OF HEAVY METALS IN BIOREACTORS LOADED WITH SANITARY SEWAGE SLUDGE

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Abstract - This work on the process of biosorption of nickel and chromium in an ascendant continuous-flow, fixed packed-bed bioreactor of sanitary sewage sludge was conducted in a search for solutions to the environmental problem caused by heavy metals. Analysis of the results demonstrated that the absorbent had an extraordinary capacity for biosorption of the heavy metals studied at about 9.0 pH of the effluent, with a removal percentage of over 90.0% for the two metals. Chemometric study results demonstrated that 20 days of the experimental system function were sufficient for achieving the maximum efficiency of sorption of the heavy metals studied by the sanitary sewage sludge employed.
Keywords: Heavy metals; Biosorption; Sanitary sewage sludge; Bioreactors.

INTRODUCTION

The indiscriminate use of natural resources has caused serious problems of contamination of aquatic ecosystems, principally due to chemical pollution of organic and inorganic origins, especially by the organochlorinated compounds and heavy metals. The pollution of an aquatic environment can alter its physical, chemical and biological characteristics, jeopardizing the quality of water for human consumption (Marques et al., 1996). Of the variety of existing pollutants, heavy metals have received special attention, since some of them are extremely harmful to a large variety of organisms when they exceed the limit permitted by environmental legislation and/or the quantities assimilable by these organisms (Laws, 1993).

The conventional methods for treatment of effluents contaminated with heavy metals involve physicochemical processes such as flocculation, precipitation, electrolysis and crystallization. However, these processes are very expensive and generate new products, merely resulting in a transfer of the metal from one medium to another, but not providing a definitive solution (Volesky, 1990; Hughes, 1975; Kratochvil and Volesky, 1998). The search for cheaper and definitive solutions led to the development of new technologies based on the utilization of organic substrates for removal of heavy metals by the process of sorption (Gadd, 1992).

Sorption of the dissolved metals based on the chemical activity of microbial biomass or of dead vegetable residues, known as biosorption, furnishes the basis for a new technology for removal and recovery of these metals (Kratochvil and Volesky, 1998).

The term "biosorption" refers solely to technological application of natural systems that have existed for thousands of years. Due to the high polluting capacity of modern society in recent years these processes have been used to the benefit of mankind. "Biosorption" can be defined as the removal of metallic ions by means of passive adsorption or complexation by live biomass or organic waste (Eccles, 1995).

The inactive or dead microbial biomass can serve as a basis for the development of biosorbent materials capable of the concentration and recuperation of heavy metals. These new biosorbents can be regenerated and reutilized and are selective, efficient, cheap and competitive with artificial products. Therefore they have a potential application in operations of environmental control and recovery of the metal (Volesky, 1990). One of these biosorbents, sanitary sewage sludge obtained from the treatment of municipal sewage, which is composed of mineral salts and organic and inorganic compounds, has a strong attraction for metals due to the presence of humic acid in the organic matter (Arican et al., 2002). These substances are rich in negatively charged functional groups, such as carboxylic acids and phenolic and alcoholic hydroxides, which are the biosorption sites for metals in solution.

Sanitary sewage sludge is an organic solid waste produced by human activity, which after drying contains organic matter rich in oxygenated functional groups that capture heavy metals by the action of electrostatic forces and of chemical bonds. This favors its utilization as a strong biosorbent for metals in biosorption columns (Qiao and Ho, 1996; Valdman and Leite, 2000).

Biosorption experiments in bioreactors can very expensive due to the detention time and functioning of the system, principally by utilization of sophisticated techniques of analysis that increase the experimental cost. Therefore, during recent years the utilization of experimental planning for better reproducibility and accuracy of the data has stimulated the development of mathematical and statistical techniques and the computational software for data analysis and adjustment of scientific experimental results. One of these techniques is chemometrics, which can be defined as the application of mathematical and statistical methods in the planning or optimization of procedures and in

obtaining chemical information through analysis of relevant results (Vogel et al., 2000). This type of technique offers a powerful method that is essential for the study of an experimental system and its optimization. In biosorption studies chemometrics can be used in the prediction and the optimization of the performance of biosorbents in the sorption of metallic species (Brown et al., 1996; Barros Neto et al., 1995).

The objectives of this work were to study the process of biosorption of nickel and chromium in column bioreactors loaded with two types de absorbents (sewage sludge and sand) and to use chemometric techniques (fractional factorial planning and response surface) for optimization of this biosorption process.

MATERIALS AND METHODS

Materials

The sanitary sewage sludge (SS) was obtained from an UASB (upflow anaerobic sludge blanket) reactor and then packed in a rectangular fiberglass box for air drying. This sludge was turned over daily to facilitate drying, which occurred in a period of 14 days. The dry SS was triturated and sieved through a mesh ($\varnothing$ = 4 mm) and packed in plastic bags. The sand (RS) used for loading the reactor was collected from a river bed and passed through a sieve with a 4 mm mesh diameter.

Experimental System

The experimental system consisted of four ascendant, continuous-flow, fixed packed-bed bioreactors with a circular section constructed of PVC tubes with a 100 mm internal diameter and a height of 260 mm (Figure 1). The reactors were provided with plastic taps ($\varnothing$ = 12 mm) and polyethylene tubes ($\varnothing$ = 12 mm) for feeding the solution and for taking the liquid effluent samples. The effluent flow was controlled by a system adapted from one used in hospitals for intravenous application of physiological serum (serum equipage kit). Crushed stone (gravel) was used in the lower part of each reactor a as filter, thus preventing outflow of the biosorbent. Two of the four reactors were loaded with SS and the other two with RS, with 100.0g of the absorbent in each reactor. The four reactors were operated for 30 days at a daily flow rate of 100 mL day^{-1} of the metal solutions. All the experiments were conducted at room temperature ($\approx$ 25°C).
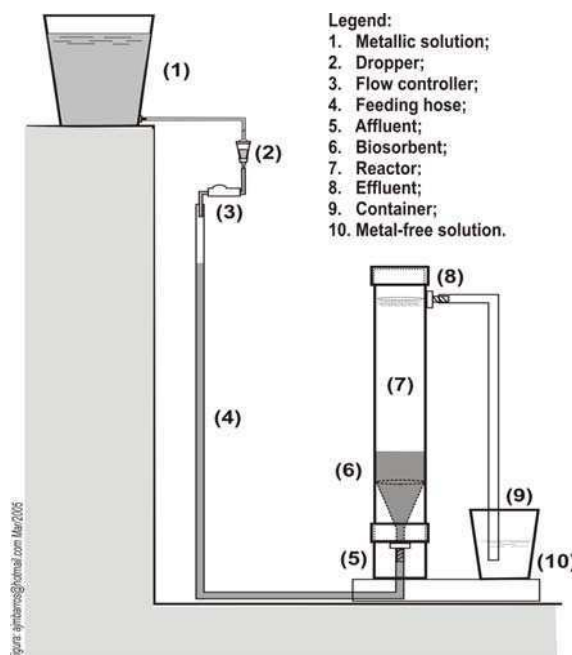
Figure 1: Schematic representation of one of the reactors used for biosorption.

Biosorption Process

Two reactors, one loaded with SS and the other with RS, were fed with a solution of 10.00 ± 0.15 mg Cr^{3+} L^{-1} of chromium(III) chloride, and the other two reactors with the same profiles were fed with a solution of 10.00 ± 0.15 mg Ni^{2+} L^{-1} of nickel(II) chloride.

During the 30-day period of operation the four reactors were monitored daily using the following parameters: metal ion concentration of the affluent and effluent solutions, pH of the effluent solutions, biosorption capacity (q) and removal efficiency (E) of the metal ions by the biosorbents.

The biosorption capacity (q mg/g) of metallic ion biosorbed in milligram per gram of dry mass of the biomass and the removal efficiency ($E \%$) of metallic ions were calculated with Eq. (1) and (2), respectively (Volesky, 1990).

$$q = \left(\frac{C_i - C_f}{m} \right) V \qquad (1)$$

$$E = \left(\frac{C_i - C_f}{C_i} \right) 100 \qquad (2)$$

where C_i is the initial concentration of the metallic ion in the affluent of the reactor (mg L^{-1}); C_f, the final concentration of the metallic ion in the effluent of the reactor (mg L^{-1}) collected every 24 h; m, the

mass of the biosorbent in the reaction mixture (g) and V, the volume of the reaction mixture (L).

Analytical Determinations

The pH of the effluent from the reactor was measured once daily during the period of operation of the experimental system by the potentiometric method in accordance with APHA et al. (1998) using a pH-meter Tecnal model TEC2. The electrical conductivity was determined once daily by the electrometric method in accordance with APHA et al. (1998) using a conductometer Analyser 600.

Concentrations of the heavy metals in the affluents and effluents were determined daily with a UV-Visible Coleman 395D spectrophotometer, using the dimethylglyoxime method for Ni(II) at 530nm (Padmavathy et al., 2003) and the potassium dichromate method for Cr(III) at 440nm adapted from Vogel et al. (2000). The concentrations were calculated from the calibration curves (from 0.0 to 0.5 mg Ni^{2+} L^{-1} for nickel and from 0.0 to 12.0 mg $Cr^{3+}.L^{-1}$ for chromium).

Chemometric Study of the Data

To study the effects of the five factors (variables) on the response variable of the biosorption system under study, the two levels 2^n factorial planning technique was used, observing the possible combinations of n factors in the experiment. Only

four factors were used for obtaining more accurate and precise results on the biosorption of the metals. The results of the experimental planning were analyzed using the mathematical tool MATLAB 6.5 for Windows to obtain the linear and quadratic models for the biosorption process. The models were optimized by the response surface technique with has the objective of finding the best conditions of the variables for the maximum response of sorption capacity (Box et al., 1978; Bruns and Faigle, 1985).

RESULTS AND DISCUSSION

Process of Biosorption

Figure 2 contains the results on biosorption capacity (q) and as effluent pH as a function of operation time of the reactor loaded with SS and fed with nickel(II) solution. It can be observed that the biosorption capacity, initially at around 7.6×10^{-3} mg g^{-1}, finally increased to 12.8×10^{-3} mg g^{-1}, whereas effluent pH increased from 5.1 to 9.0, correspondingly. The data demonstrate that the sorption capacity of the biosorbent for nickel was high when the pH of the effluent attained 9.0 after a 15-day period of operation.

Figure 3 shows the profile for biosorption and for effluent pH as a function of time for the reactor loaded with SS and fed with chromium(III) solution during the period of operation of the reactors. The behavior was similar to that of the reactor fed with nickel solution, showing that chromium had an initial biosorption of 12.0×10^{-3} mg g^{-1} and a final biosorption of 13.5×10^{-3} mg g^{-1}, corresponding to the initial and final effluent pH values of 5.5 and 8.9, respectively.

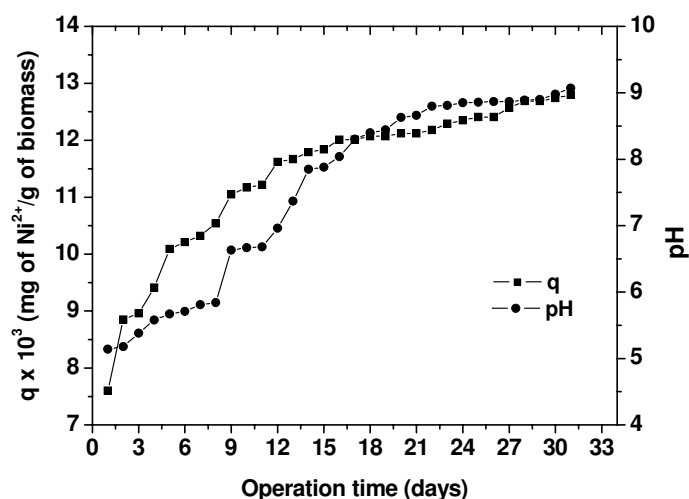**Figure 2:** Biosorption of nickel(II) ion in SS as a function of reactor operation time.
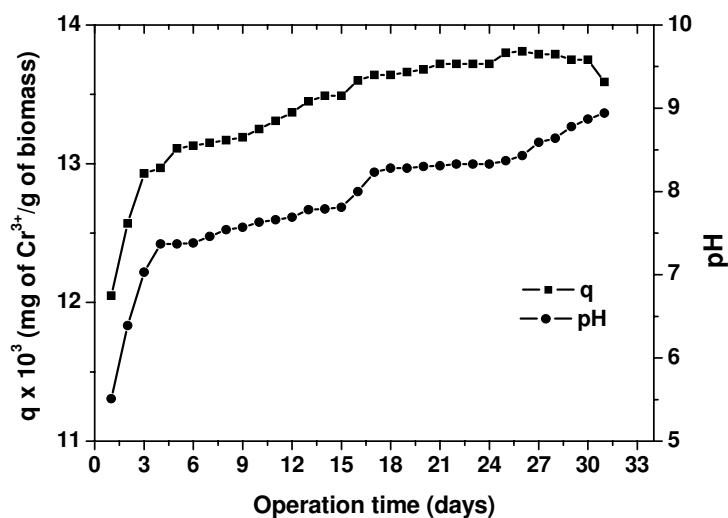

Figure 3: Biosorption of chromium(III) ion in SS as a function of reactor operation time.

The retention capacity of the cations in the vertical columns loaded with SS is directly related to the biosorption of metals by the absorbent by physisorption and chemisorption phenomena caused by liberation of vacant sites on the surface of the sanitary sewage sludge. The sorption of the metals by the biomass was lower in the first samples monitored and increased progressively with operation time. Similarly the variation in pH from acidic to basic, due to the freeing of cationic species from the absorbent surface by hydrolysis, resulted in retention of the heavy metals with the increase in negative charge on the absorbent surface.

Results obtained by Petroni et al. (2000), who studied the retention of zinc and cadmium in peat columns, showed similar pH changes. Vilar et al. (2005) studied biosorption of lead(II) by *Gelidium* alga and by agar extraction residue and obtained results similar to those in the present work. Lee and Yang (1997) reported similar results for removal of copper(II) utilizing apple waste. While investigating the mechanism of biosorption of nickel in activated sludge Arican et al. (2002) also obtained a variation in pH similar to that obtained in this work.

In Figures 4 and 5 the percentages of removal of the metals as a function of operation time of the reactors loaded with SS and RS and fed with solutions of nickel and chromium, respectively, are presented.

The data obtained during operation of the reactors loaded with SS varied from 54.6 to 92.5% with an average removal of 82.4% for the reactor fed with the nickel solution, whereas for the reactor that received an affluent flow of chromium ion, the average removal was 90.5% with a variation from 60.8 to 96.1%. For the reactors loaded with sand, the data varied from 40.4 to 68.4% for the reactor fed with the nickel ion solution and from 29.6 to 46.8% for the reactor with chromium ion, with average removals of 60.9% and 44.0%, respectively. The higher capacity for sorption of the cations by SS was related to its organo-mineral composition with a higher proportion of bonding sites for organic and inorganic systems. Such sites are absent in the inert material; therefore only a surface retention of the cations between the RS surface and the metallic ions by the physisorption process occurred.

The reactors loaded with sand removed less of the metals, which may be ascribed to the lack of organic material responsible for formation of complexation bonding with the metals. Therefore, in these reactors containing inert material the predominant process was adsorption due to the absence of bonding sites of biological origin.

Similar behavior was observed by Petroni et al. (2000) in their studies on removal of cadmium and zinc using turf as biosorbent. Barros Jr et al. (2002) verified that the biomass of a fungus attained 94% of its saturation capacity and about 84% of its biosorption capacity. Our results for biosorption of the metals by SS are similar to those obtained by these researchers.
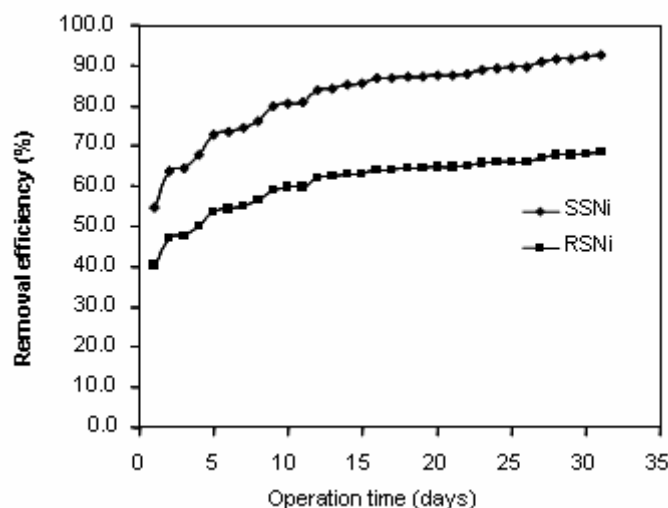

Figure 4: Removal efficiency and residual concentration of Ni(II) ion in the SS and RS as a function of operation time, where SSNi is the nickel sorbed by the sanitary sewage sludge and RSNi is the nickel sorbed by the sand.
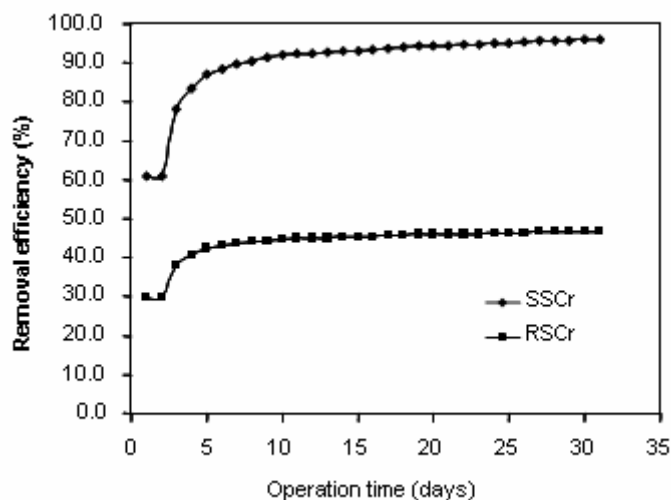
Figure 5: Removal efficiency and residual concentration of Cr(III) ion in the SS and RS as a function of operation time, where SSCr is the chromium sorbed by the sanitary sewage sludge and RSCr is the chromium sorbed by the sand.

Chemometric Evaluation

Sorption capacity, concentration of effluent metal, pH and electrical conductivity were used to study the efficiency of biosorption of nickel and chromium by the SS biomass, utilizing the fractional factorial planning technique. The high and low levels of the variables studied in the experimental design for biosorption of the metals by the substrate are presented in Table 1.

Applying the computational tools of the program MATLAB 6.5, it was possible to determine the linear model (equation 3) from the variables obtained by the data shown in Table 2. This model can be used to predict the interactions between the studied parameters discussed above for the response function Y (sorption capacity).

$$Y = 8.5767 - 0.1859pH - 0.4061EC + \\ +0.6284q + 0.6308M_{Effluent} \tag{3}$$

The linear model had a quadratic regression coefficient (R^2) of 0.7000 with a significance level of 95% of for the value of F calculated for the linear model, which was equal to 69.97. The calculated value of F is 30.2 times the tabulated value ($F_{(10/21)}$=2.31), thus permitting utilization of the response surface method (isoresponse curves), which according to Box et al. (1978) and Barros Neto et al. (1995) offers better reproducibility in obtaining the quadratic model. This statement was supported by the linear model diagram of the residuals (Figure 6), which showed the quadratic tendency of the deviations of the data for the response variable of the system under study. The quadratic model obtained from use of the response surface is given by Equation 4, which was calculated by a mathematical tool in MATLAB 6.5.

$$Y = 1.7750 + 0.2773OT + 1.1739pH - \\ -0.0048(OT)^2 + 0.0137OTpH - 0.0504(pH)^2 \tag{4}$$

The residuals of the experimental data are presented in Figure 6. The behavior shown in the figure demonstrates that the biosorption system has a quadratic tendency, since the residuals are distributed curvilinearly around the center (zero), justifying the use of the study of the quadratic model of the data.

Table 1: Levels of the factors applied to the experimental design.

Factors	High Level (+)	Low Level (-)
pH	8.90	4.11
EC (mS cm^{-1})	2.18	0.38
Q (mg g^{-1})	1.175	0.121
M$_{Effl}$ (mg L^{-1})	3.913	0.389

EC - electrical conductivity;
q - sanitary sewage sludge capacity of biosorption of the metallic ions;
M$_{Effl}$ - final concentration of the effluent metal from the reactor.

Table 2: Matrix of the experimental data.

| Experiments	OT (days)	pH	EC (mS cm^{-1})	M$_b$ (mg L^{-1})	M$_{Efl}$ (mg L^{-1})	q (mg g^{-1})
1	0	5.51	1.28	7.83	2.17	0.96
2	2	6.96	2.18	7.24	2.76	0.89
3	4	4.11	0.55	6.09	3.91	0.74
4	6	8.86	1.27	9.17	0.83	0.12
5	8	8.33	0.38	9.44	0.56	1.15
6	10	8.89	1.30	8.82	1.18	1.08
7	12	6.39	0.39	8.33	1.67	1.02
8	14	6.93	1.37	9.17	0.83	1.12
9	16	8.78	0.38	9.56	0.44	1.17
10	18	8.90	1.37	9.25	0.75	1.13
11	20	8.90	1.23	9.61	0.39	1.17
12	22	5.58	1.45	9.36	0.64	0.90
13	24	7.54	0.40	9.22	0.78	1.13
14	26	8.87	1.25	8.88	1.12	1.09
15	28	8.85	1.19	9.27	0.72	1.13
16	30	7.66	1.29	7.98	2.02	1.13

OT - operation time;
EC - electrical conductivity;
M$_b$ - biosorbed metal;
M$_{Efl}$ - final concentration of the effluent metal from the reactor;
q - biosorption capacity.
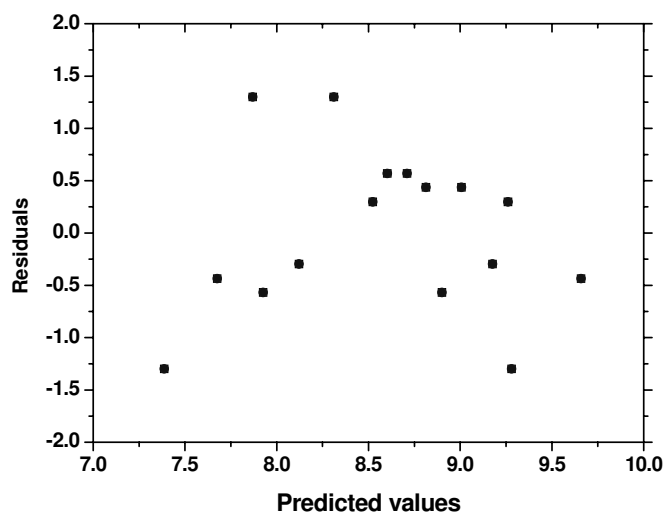
Figure 6: Residuals of the linear model.

In Figure 7 a normal distribution of the data around the center of the parabola followed by the residuals obtained in the quadratic model can be observed. Therefore, optimization of the biosorption of heavy metals becomes feasible for this study. This observation was strengthened by the F-test, as demonstrated above.

Residuals found in the statistical analysis of the response variable data were systematically distributed around zero (Figure 8), which demonstrates that the variables studied in this experiment interact. Therefore,

the residuals for the quadratic model do not appear to be inadequate, justifying use of the quadratic model in the experimental design.

These distributions of the residuals around zero, observed in Figures 6, 7 and 8, were also observed in studies carried out by Barros Jr. et al. (2002). Menezes et al. (2002) studied the process of biosorption of copper by baker's yeast using the experimental design and found behavior for the residuals produced in linear and quadratic fits similar to that found with the sanitary sewage sludge.
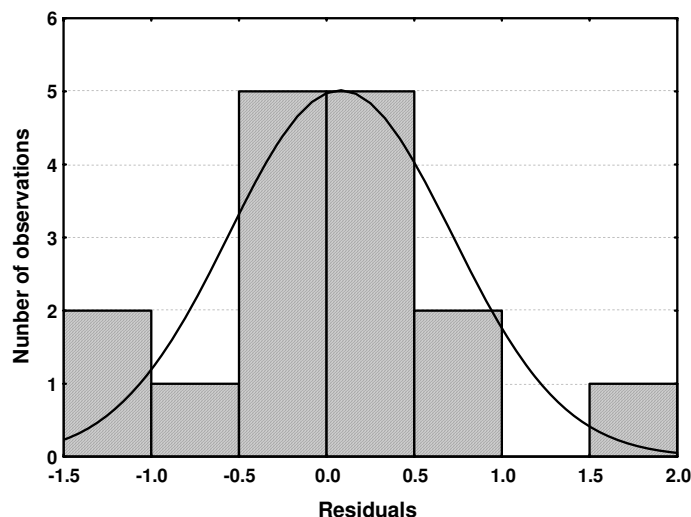
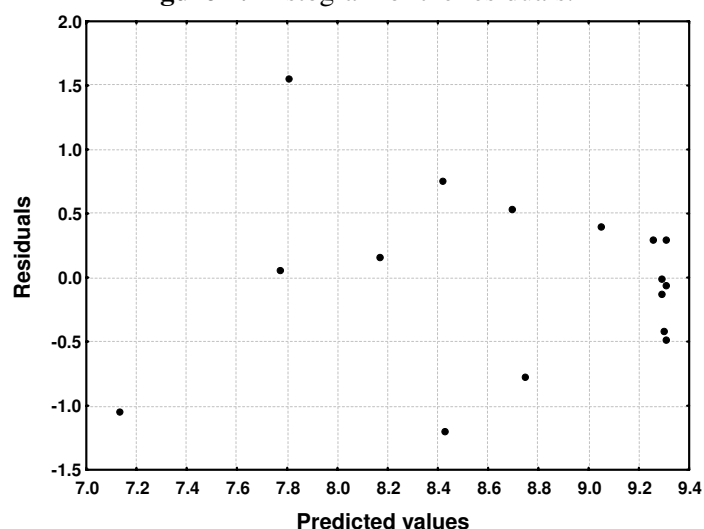**Figure 7:** Histogram of the residuals.

Figure 8: Residuals of the quadratic model for response variable Y.

The principal effects of biosorption of metal (Y) by the biomass and the interactions between them for the system under study can be studied by analysis of response surface (isoresponse) curves, as shown in Figures 9 and 10. This can verify the best operation time of the system for biosorption of nickel and chromium by observing the behavior in relation to the values obtained for pH, electrical conductivity and sorption capacity. Thus the response surface techniques can be used to obtain the point of maximum interaction between these variables, when there is a correlation between them (Barros Neto et al., 1995; Box et al., 1978).

Figure 9 shows the isoresponse curve of interaction between operation time, pH and the metal biosorbed by the sanitary sewage sludge. For biosorption of 10 mg.L^{-1} of nickel and chromium, the pH value was found to be around 9.0 with completion of the removal process in an operation

time of about 15 to 20 days. Therefore, by taking into consideration the results shown on the isoresponse surface, the experiment could be optimized in less time than the period for which the reactor system of was operated.

The study results on the isoresponse curve (Figure 10) show that for the interaction of operation time, electrical conductivity and amount of metal biosorbed, the maximum retention of the metal occurred for 20 days of operation. The results for operation time are similar to those suggested by Figure 9.

Barros Jr et al. (2002) studied the process of biosorption of cadmium by *Aspergillus niger* and showed that it could be obtained with the quadratic model and isoresponse curves similar to those in this work. In the other study, similar behavior was found by Menezes et al. (2002) with the same experimental planning for optimization of the process of copper biosorption by baker's yeast.
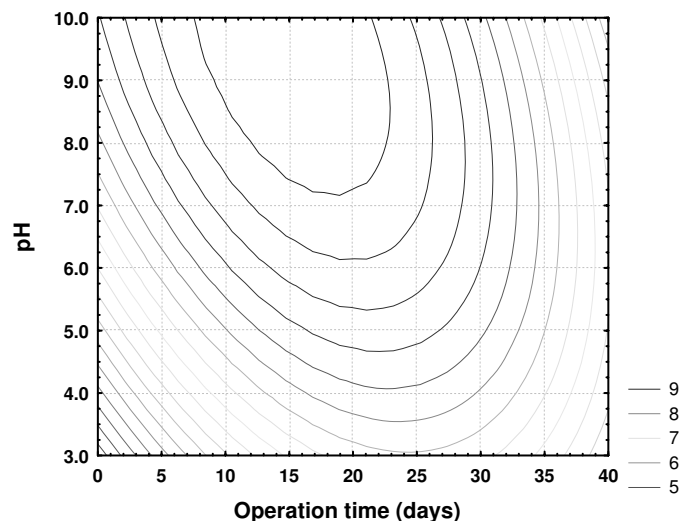
Figure 9: Isoresponse surface of the metal biosorbed by SS (mg.L^{-1}) as a function of operation time (days) and pH.
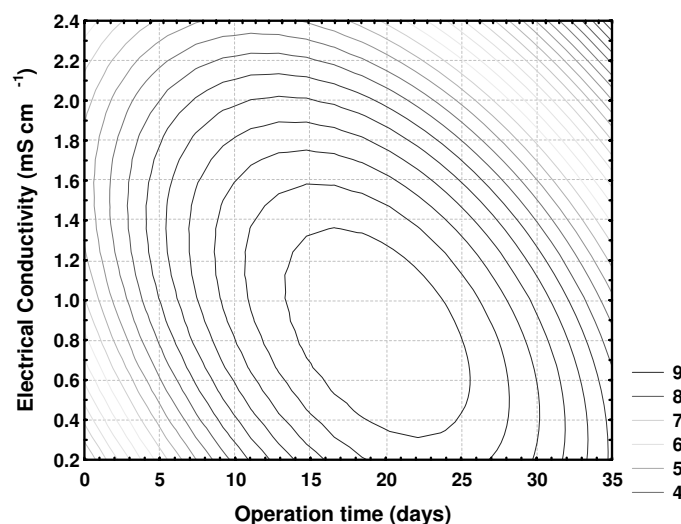

Figure 10: Isoresponse surface of the metal biosorbed by SS (mg.L^{-1}) as a function of operation time (days) and electrical conductivity (mS.cm^{-1}).

CONCLUSIONS

Analyzing the data from this work, the following conclusions can be drawn:

Biosorption of the metallic ions was more intense in the columns loaded with sanitary sewage sludge than in the columns with inert material, which may be ascribed to the more effective complexation due to chemisorption and physisorption phenomena produced by the organic and inorganic compounds in this type of biosolid;

Removal of the ions from the aqueous solution by the sanitary sewage sludge tended to achieve ion-exchange equilibrium between the absorbent surface and the metallic solution when the biosorption process stabilized in the reactors after about 20 days of operation, confirmed by the chemometric study conducted with the experimental results obtained in this research;

The highest efficiency of the biosorption system loaded with sanitary sewage sludge was at pH 9.0; this should have occurred by hydrolysis of the absorbent during the process of biosorption of the heavy metals;

The chemometric study of the results demonstrated that the system is better represented by the quadratic model than the linear one. The isoresponse curves demonstrated that the operation

time of the reactor could be optimized for a 20-day period.

ACKNOWLEDGEMENTS

NOMENCLATURE

SS   sanitary sewage sludge;
RS   river sand;
SSNi   nickel sorbed by the sanitary sewage sludge;
RSNi   nickel sorbed by the sand;
SSCr   chromium sorbed by the sanitary sewage sludge;
RSCr   chromium sorbed by the sand;
UASB   upflow anaerobic sludge blanket

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