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Biosorption of heavy metals in upflow sludge columns

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Abstract

The present study was carried out for evaluating the retention behavior of sanitary sewage and sand in relation to chromium and nickel ions in upflow reactors. It was found that the sludge presented a greater assimilation of the metals studied when compared to the inert material, probably due to the presence of anionic groups, which favors adsorption and complexation processes. Thermal analyses of the samples showed a shift in the decomposition peaks of the "in natura" sludge, when compared with those of the samples spiked with the metals, confirming the possibility of interactions between the heavy metals and the anionic groups present in the sludge.
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1. Introduction

At present, one of the most serious problems faced the nature is the chemical pollution of organic and inorganic origin catalyzed by the presence of heavy metals and organochloride products. The pollution of an aquatic medium can cause changes in physical (turbidity, color, temperature, viscosity, surface tension), chemical (chemical oxygen demand, pH, acidity, alkalinity, dissolved oxygen, toxicity level, nutrients) and biological characteristics, compromising the water quality for human consumption (Clarisse et al., 1999). Among the various contaminants, heavy metals have received special attention, since some of them are extremely toxic for a large variety of organisms, even at very low concentrations (in the order of mil-ligrams or micrograms per liter) (Laws, 1993; Sawyer et al., 1994).

The general technical procedure adopted consists of treating the effluents contaminated with heavy metals by physicochemical processes, such as flocculation and/or precipitation, electrolysis and crystallization. However, these processes are expensive and generate new products or simply transfer of the metal from one medium to another, not propitiating the definitive solution of the problem. The pursuit for economical and definitive solutions has led to the development of new technologies based on the utilization of organic substrates as absorbents of heavy metals in a process called sorption (Gadd, 1992; Muniz and Leite, 1999; Pinto et al., 2001).

Sorption processes are very important in bioreactors for promoting the accumulation of metallic species on an absorbent by means of adsorption and absorption phenomena. These processes can be used for capturing the chemical species and they act in two distinct manners. The first process, adsorption, consists in the attraction of molecules of a solute by vacant sites of substrate surface,

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fixing them in these sites owing to the action of physical processes (physisorption) and chemical bonds (chemisorption). Whereas, the absorption process involves separation of a contaminant from a gaseous, liquid and solid phase to another phase (Valdman and Leite, 2000; Brito et al., 2001).

The sorption of dissolved metals may also occur by the biochemical activity of microbial biomass or of dead vegetable residues, which is called as biosorption (Eccles, 1995). It is a promising route for the removal and recovery of metals (Muniz and Leite, 1999; Barros Jr. et al., 2002).

According to Eccles (1995), bioaccumulation includes all the processes responsible for the removal of metals by live cells (bacteria, fungi, algae and others), in which the processes of biosorption along with bioprecipitation and intracellular accumulation are included. There is a second concept that considers the bioaccumulation as a system, which exclusively involves the mechanisms that depend on the cellular metabolism (Gomes et al., 1998).

Organic solid wastes serve as a base for the development of adsorbent materials (biosorbents) with a high potential of concentration and recovery of heavy metals (Volesky, 1989; Kratochvil and Volesky, 1998). The development of these new biosorbents is interesting, as they can be regenerated, reutilized and they are selective, efficient, cheap and competitive with those of artificial products. Among these new biosorbents, the municipal wastewater sludge has gained more importance because it is a residual sediment formed from wastewater treatment, and for possessing organic (carboxylic acids, phenolic and hydrolytic compounds, and others) and inorganic (compounds of nitrogen, sulfur, phosphates, ferric and others) compounds, which favor the implementation of these processes. Besides this, the sludge does not present an additional cost on treatment of effluents, since it is a waste produced during the conventional treatment process of wastewater.

According to Arican et al. (2002), the strong attraction of the metals by the wastewater sludge occurs due to the formation of humic acids by hydrolysis of the organic material present in the sludge, as these substances present functional groups, such as carboxylic acids, hydroxyls, phenolic and alcoholic groups, which function as anionic legends responsible by the sorption sites that capture the metals in solution. However, the use of the sludge as a biosorbent of heavy metals presents some difficulties principally arising from the presence of eggs of parasites in the dry sludge, besides resistant organisms of pathogenic bacteria and protozoa, and also, seeds of harmful plants could be an obstacle for its use as a substrate. The significant elimination of these residues and microorganisms by thermal treatment gives more safety to the destruction to these remains and living beings sensible to heat (Branco, 1986), besides promoting favorable changes in the physical and chemical properties of the wastewater sludge.

The present study aims at evaluating the sorptive behavior of wastewater sludge (WS) and river sand (RS) in relation to the ions Ni(II) and Cr(III) in continuous upflow column reactors. Besides this, to evaluate the thermal stability of the compounds formed on wastewater sludge during the process of biosorption, two techniques of thermal analysis (thermogravimetry – TG and differential scanning calorimetry – DSC) were used.

2. Methods

2.1. Experimental system

The experimental system for this work was installed and operated in the Environmental Sanitation Laboratory, located at the Experimental Station for Biological Treatment of Sanitary Sewage (EXTRABES) of the Center for Sciences and Technology, Paraíba State University, in the City of Campina Grande, Paraíba, in Northeastern Brazil.

The wastewater sludge was collected from an UASB reactor, followed by packing in a rectangular fiberglass box for air drying. This sludge was turned around daily to facilitate the drying, which occurred during a period of 14 days. The dry WS was made to powder and sieved through an 18 mesh (US standard) and packed in plastic bags. The results of physico-chemical analyses, performed by the methods standardized by APHA (1995), are shown in Table 1. The RS used for loading the reactor was collected from a river bed, passed through an 18 mesh sieve and washed with deionized distilled water.

The experimental system consists of four cylindrical upflow reactors with 2.0 L of capacity each and having a useful volume of 1.0 L. The reactors were built from PVC tubes of 100 mm internal diameter. Out of the four reactors, two were loaded with sludge and the other two with RS, with 100 g of the absorbent in each reactor. The four reactors were operated for 30 days, with a flow of 100 mL day^{-1} of CrCl$_3$ solution for two reactors (one loaded with WS and the other with RS), and similarly the other two were fed with a solution of NiCl$_2$, both solutions had a concentration of 10.00 ± 0.15 mg L^{-1} of the metal. All the experiments were realized at room temperature (≈ 25 °C).

Table 1
Physico-chemical characterization of the wastewater sludge sample

Parameters	
Moisture (%)[a]	8.8
pH	6.6
Alkalinity (mg CaCO$_3$ L^{-1})	340.0
Total solids (%)	91.2
Fixed solids (%)	43.9
Volatile solids (%)	47.3
Total organic carbon (%)	26.3
Chemical oxygen demand (mg kg^{-1})	1133.0
N$_{total}$ (mg kg^{-1})	26.3
P$_{total}$ (mg kg^{-1})	18.1
S$_{total}$ (mg kg^{-1})	29.3
Fe (mg kg^{-1})	23.8

[a] The percentage is calculated on dry mass.

2.2. Kinetic evolution

The biosorption capacity of the sludge is expressed as milligrams of biosorbed ion per gram of dry mass of the biomass (q mg/g) and the removal efficiency of metallic ion ($E\%$) was calculated by Eqs. (1) and (2), respectively (Volesky, 1989).

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

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

where C_i, initial concentration of the metal ion in the influent of the reactor (mg L^{-1}); C_f, final concentration of the metallic ion in the effluent of the reactor (mg L^{-1}) collected every 24 h; m, mass of the biosorbent in the reaction mixture (g); V, volume of the reaction mixture (L).

2.3. Potentiometric measurements

The pH measurements of the effluents from the reactors during the period of operation of the experimental system were performed once a day by the potentiometric method, according to APHA (1995) using a model TEC2 Tecnal pH-meter.

2.4. Determination of the metal ion concentration

The concentrations of the heavy metals in the influents and effluents were daily determined by a Coleman 395D UV-Visible spectrophotometer (Coleman Instruments, USA), using the dimethylglyoxime method for Ni(II) at 530 nm (Padmavathy et al., 2003), and the potassium dichromate method for Cr(III) at 440 nm adapted from Mendham et al. (2000).

2.5. Thermal analyses

Thermal decomposition studies of the samples were carried out by means of thermogravimetric curves, which were obtained by using a TGA-50 SHIMADZU thermobalance (Shimadzu Corp., Japan) in an air atmosphere with a constant flow rate of 20 mL min^{-1}, utilizing an alumina crucible, and a heating rate of 15 °C min^{-1}. Analyses were performed with an average mass of 8.5 ± 0.5 mg of five samples, and the temperature scanning was conducted in the range 25–950 °C for WS and 25–800 °C for WSNi (WS + Ni^{2+}) and WSCr (WS + Cr^{3+}). The data for each event were obtained by calculation using mathematical tool available in Soft TASYS for Windows furnished by manufacturer of the thermobalance.

The study of calorimetric behavior of the samples was undertaken by means of the DSC curves obtained with a SHIMADZU DSC-50 differential scanning calorimeter (Shimadzu Corp., Japan), at the temperature range 25–500 °C, using an alumina crucible and a heating rate of

15 °C min^{-1}, in a nitrogen atmosphere, with a flow rate of 50 mL min^{-1}. The crucibles, sample mass and data analysis method used were the same as utilized in the thermogravimetric analysis.

2.6. X-ray fluorescence analysis

The chemical composition of the samples WS, WSNi and WSCr was determined by using an EDX-800 SHIMADZU X-ray fluorescence analyzer (Shimadzu Corp., Japan), with a 10 mm collimator and a Ti-U detector operating at the 0–40 keV range, using an air atmosphere and an exposure time of 100 s.

3. Results and discussion

Results obtained during biosorption of nickel and chromium by the wastewater sludge are presented in Figs. 1 and 2 as a function of pH of effluent from the reactor, which show that the maximum biosorption of both the metals occurred in an alkaline pH. The removal efficiency of the metals in relation to the operation time in the reactors loaded with WS and RS was determined for evaluating the adsorption and/or complexation processes (Figs. 3 and 4), demonstrating that the higher efficiency observed occurred in the reactor loaded with WS, due to the presence of adsorption and complexation processes. The reactors loaded with RS, owing to absence of organic fraction, presented the retention of the metals only by surface adsorption phenomenon. The thermal analysis results of the samples of WS, WSNi and WSCr demonstrate displacement in thermal decomposition peaks (events) in the curves of TG/DTG and DSC (Figs. 5–7, Table 2). The results of X-ray fluorescence analysis of WS, WSNi and WSCr are presented in Table 3, which show the presence of the metals retained in the sludge after the biosorption process.
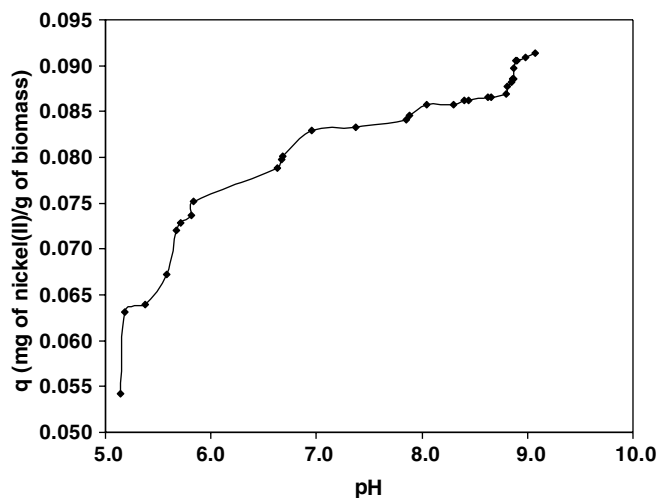

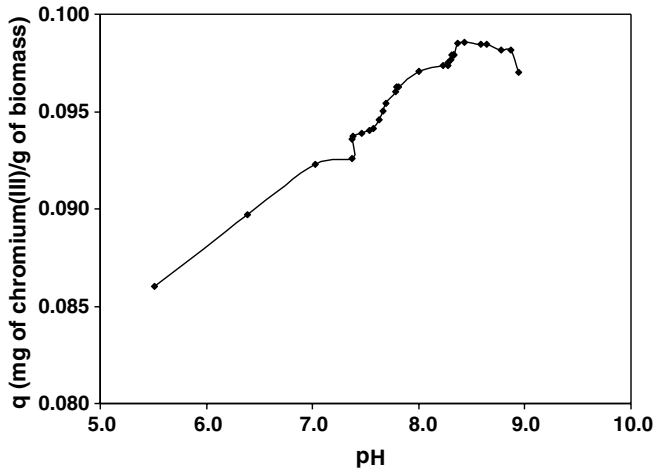Fig. 1. Biosorption of Ni(II) ion in the sludge as a function of pH.

Fig. 2. Biosorption of Cr(III) ion in the sludge as a function of pH.
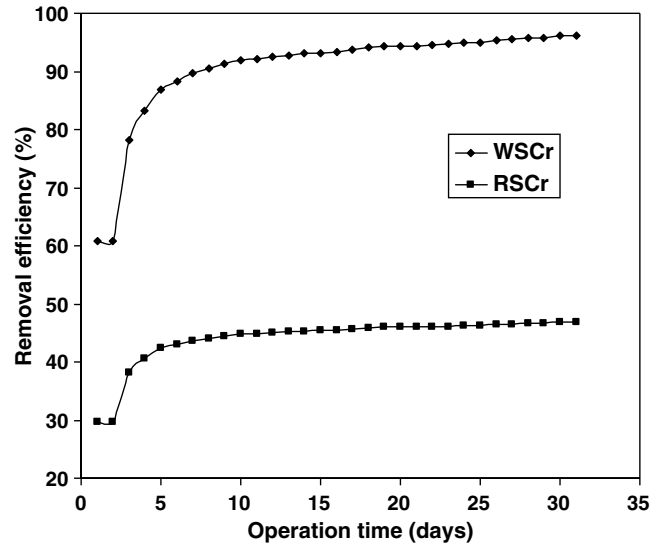

Fig. 4. Removal efficiency of Cr(III) ion in the wastewater sludge (WSCr) and screened river sand (RSCr) as a function of the operation time.
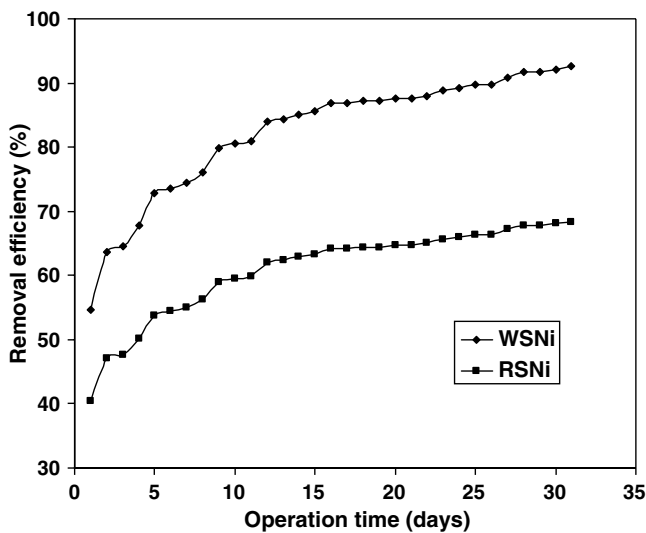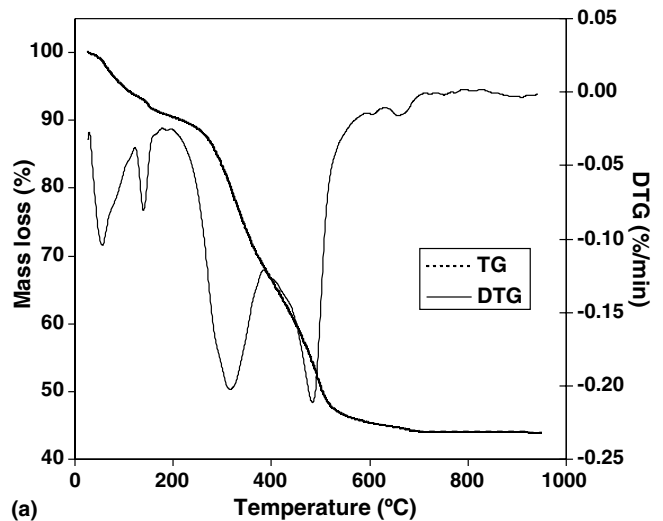

Fig. 3. Removal efficiency of Ni(II) ion in the wastewater sludge (WSNi) and screened river sand (RSNi), as a function of the operation time.
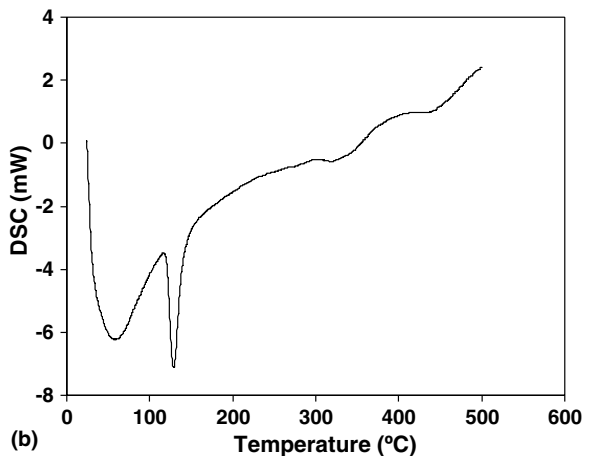

Fig. 5. Profile of the wastewater sludge (WS) curves (a) TG/DTG and (b) DSC.

The behavior of pH of the effluent liquid from the reactor in relation to the biosorption capacity (q) is presented in Fig. 1. The results demonstrate that after 30 days of contact between the WS and RS solution, the pH increased from 5.1 to 9.2 in the effluent, accompanied by an increase in biosorption capacity (q) of nickel, which varied 0.05–0.09 mg Ni^{2+} g^{-1} of WS.

The biosorption capacity profile of chromium ion by the WS, as function of the effluent liquid of the reactor is presented in Fig. 2. It showed a rising tendency both of the pH values from 5.5 to 8.9 and those of "q" from 0.08 to 0.09 mg Cr^{3+} g^{-1} of WS. Therefore, the behaviors observed for the two metals were similar nevertheless the chromium ion was adsorbed to a higher level than nickel ion.

The increase in pH can be indicative of the biosorption process involving hydrogen ions or the liberation of some ions, such as carbonate, which can cause mild alkalinity (Vilar et al., 2005). The oxides and hydroxides of metals
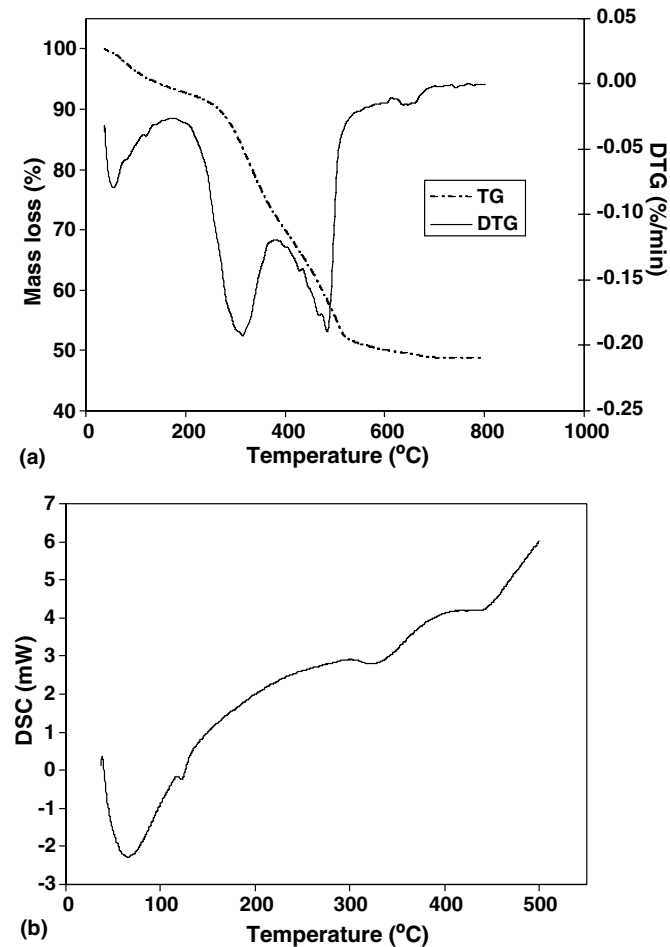
Fig. 6. Profiles of the wastewater sludge/nickel (WSNi) curves (a) TG/DTG and (b) DSC.
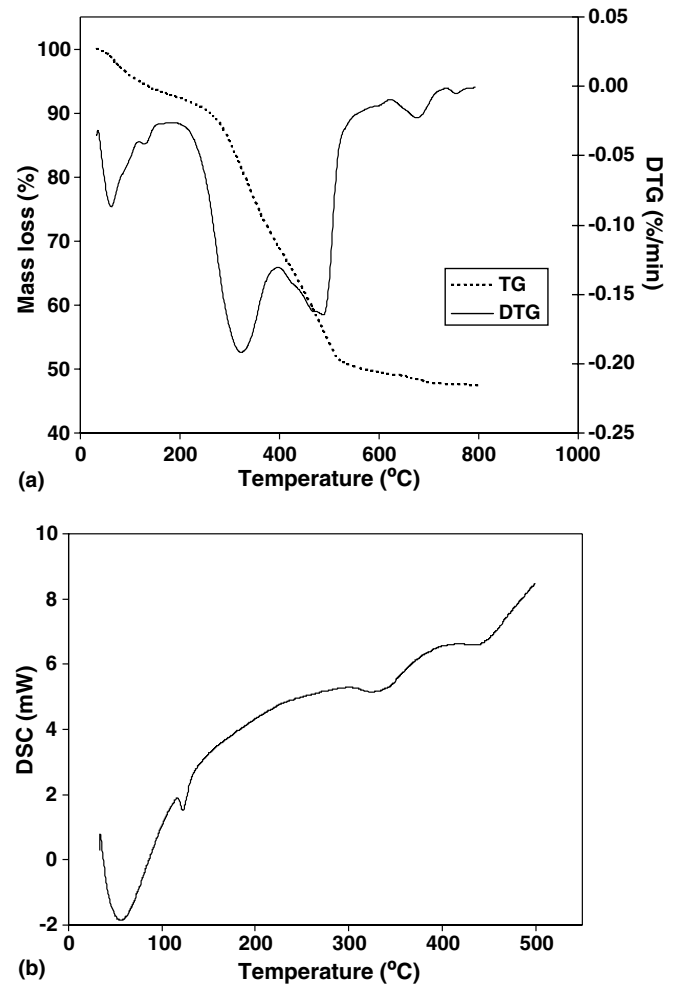

Fig. 7. Profiles of the wastewater sludge/chromium (WSCr) curves (a) TG/DTG and (b) DSC.

in natural systems coordinate with water molecules forming hydroxyl sites, acquiring very important acid-base characteristics for the processes of adsorption and complexation, where they can bond with the metal ions and other ligands in solution (Bruno, 2000).

According to Huang et al. (1988), this increase in pH occurs due to the formation of anionic ligands on the surface of the substrate used in the biosorption process, favoring the protonation of the same. Values obtained by Petroni et al. (2000), who studied the retention of zinc and cadmium in peat columns, showed similar pH changes. Other results similar to this work were obtained by Lee and Yang (1997) who utilized apple wastes for removal of copper in aqueous solution.

Barros Jr. et al. (2002), who studied the process of biosorption of cadmium by *Aspergillus niger*, obtained the maximum values of biosorption when the pH values varied between 7.0 and 9.0. According these workers the biosorption phenomenon occurs due to the increase in negative charge of the biosorbent surface, provided by the mechanism of its protonation and finally resulting in the removal of the metallic ions in solution. In other studies conducted by Eccles (1995) on dead biomass (left over of vegetable

stuff), the same mechanism was observed, strengthening the opinion sustained by Barros Jr. et al. (2002).

Arican et al. (2002), investigating the mechanism of biosorption of nickel in activated sludge also obtained similar data in relation to the variation of pH. Jordão et al. (2000), studying the biosorption of Cu(II) ions in humic yellow red oxisol, obtained a maximum biosorption at a pH of about 9.0, followed by a reduction in biosorption and they attributed this effect to the dissolution of the organic matter at this pH level, thus allowing the complexation of copper ions by the oxisol.

The removal percentages of the metals as a function of the operation time of the reactors loaded with WS and RS and fed with solutions of nickel and chromium are presented in Figs. 3 and 4, respectively. The figures show that a higher removal of the metallic ions was achieved with the sludge than with the inert material (RS) used in these reactors. The data obtained during the performance of the reactors loaded with WS varied from 54.6% to 92.5% for the reactor fed with the nickel solution, presenting an average removal of 83.4%, whereas for the reactor that received an influent flow of chromium ion, the average removal was

Table 2

Thermal analyses (DSC and TG) data obtained for the WS, WSNi and WSCr samples

Parameters	Samples											
	WS				WSNi				WSCr			
Events[a]	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th
T (°C)	60	129	320	402	65	122	322	403	56	122	324	439
ΔH (J g^{-1})	169.7	29.5	11.1	11.7	59.8	1.1	9.9	16.6	59.9	2.3	9.6	13.4
ML (%)	6.8	2.6	24.0	20.2	5.2	22.6	18.7	0.8	5.4	1.1	23.2	18.4
AC (%)		46.5				52.6				51.8		

WS—wastewater sludge; WSNi and WSCr—wastewater sludge with nickel (II) and chromium (III) after the sorption process, respectively; T—temperature; ΔH—enthalpy; ML—mass loss; AC—ash content.

[a] The term "event" in thermal analysis is used to designate the peaks resulting from the data (Figs. 5 and 6) variation in relation to loss or gain in mass observed during analysis process of samples.

Table 3

Elemental composition of the wastewater sludge before and after sorption, obtained by X-ray fluorescence

Element	Samples (wt.%)		
	WS	WSNi	WSCr
Silicon	29.28 ± 1.28	30.64 ± 1.40	31.15 ± 1.46
Iron	28.73 ± 0.12	29.34 ± 0.13	29.82 ± 0.13
Calcium	21.89 ± 0.11	20.49 ± 0.11	19.32 ± 0.11
Sulfur	11.38 ± 0.17	10.77 ± 0.17	10.48 ± 0.17
Potassium	3.52 ± 0.06	3.27 ± 0.06	3.47 ± 0.06
Titanium	2.37 ± 0.06	2.48 ± 0.06	2.39 ± 0.06
Zinc	1.56 ± 0.02	1.61 ± 0.03	1.63 ± 0.03
Copper	0.51 ± 0.01	0.52 ± 0.02	0.52 ± 0.02
Chromium	0.00	0.00	0.50 ± 0.02
Nickel	0.00	0.28 ± 0.01	0.00
Strontium	0.34 ± 0.01	0.30 ± 0.01	0.32 ± 0.01
Vanadium	0.19 ± 0.01	0.00	0.00
Zirconium	0.24 ± 0.01	0.30 ± 0.01	0.30 ± 0.01

90.4% varying from 60.8% to 96.1%. As for the reactors loaded with sand, the removal 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, presenting an average removal of 60.9% and 44.0%, respectively.

A similar behavior was observed by Petroni et al. (2000) in the studies for the removal of cadmium and zinc using peat, which absorbed about 99.0% of these two metals present in solution. Barros Jr. et al. (2002) verified that the biomass attained 84.0% of its saturation capacity right at the beginning of the biosorption process and that at the final stage of the process a mild uptake of cadmium was observed, obtaining about 94.0% of saturation capacity. The data obtained in the present work for the biosorption of chromium and nickel by WS indicate a behavior similar to the one reported by these workers. The values observed in the reactors loaded with RS presented a smaller removal, due to the absence of organic material, responsible for the complexation process of the metals. Therefore, in these reactors containing inert material the predominant process is adsorption, due to the absence of bonding sites of biological origin.

The data related to the thermogravimetric (TG/DTG) and calorimetric (DSC) studies of the samples WS, WSNi

and WSCr are presented in Table 2 and Figs. 5–7. The results obtained from the samples of WSNi and WSCr demonstrated a small displacement in the values observed from the sludge sample (WS). This fact can be verified by examining the temperature data in Table 2 and in the corresponding Figs. 5(a), 6(a) and 7(a). This displacement should have occurred due to the biosorption process of the metals that contributed in increasing the inorganic fraction of WS, caused by mineralization of the samples during the sorption process, promoting the displacement of the decomposition temperature.

The three types of samples presented a predominance of endothermic processes, as shown in the DSC curves (Figs. 5(b), 6(b) and 7(b)) and the enthalpy data (ΔH) (Table 2). It can be observed that the absorbed energy has decreased on addition of thermal energy to the samples WSNi and WSCr in relation to the sample WS, demonstrating the existence of systems with greater stability (decomposition resistance).

The WS samples presented an initial endothermic enthalpy of 169.7 J g^{-1} at a temperature of 59 °C and mass loss of 6.8% related to the first thermal event, whereas the samples of WSNi and WSCr in the same event obtained ΔH values of 59.8 J g^{-1} and 59.9 J g^{-1}, with a mass loss of 5.2% and 5.4% and decomposition temperature of 65 and 56 °C, respectively. In the second event, a decrease larger than 6 °C was observed in the decomposition temperature of samples of WSNi and WSCr in relation to the sample WS, which can be kinetically observed in the DSC curves by the reduction of the endothermic peak of the samples that assimilated the metals (Table 2 and Figs. 5(b), 6(b) and 7(b)).

The third and fourth events observed in the three samples (WS, WSNi and WSCr) presented individual characteristic and variations for each system formed by the sludge and sludge/metal, what can be seen as a thermal bimodal profile in Figs. 5(a), 6(a) and 7(a) in the DTG curves. The WS presented mass losses of 24% and 20.2%, with temperatures of the bimodal profile of the DTG curve of 320 and 402 °C with energy absorptions of 11.1 and 11.7 J g^{-1}, respectively.

The ash content of the WSNi and WSCr samples evidently increased due to the biosorption process that

occurred during the operation of the system, where the retention of the metals Ni(II) and Cr(III) occurred by means of the sorption phenomenon of these metals by the vacant sites of sludge. This affirmation can be confirmed by the increase to 52.2% and 50.6% of inorganic fraction in WSNi and WSCr samples, respectively, in relation to the sludge that contained about 46.8% of inorganic fraction, confirmed by X-ray fluorescence analysis of WSNi and WSCr samples (Table 3), which presented the insertion of the metals after the biosorption process. Consequently, the organic fraction of WS, WSNi and WSCr samples was 53.2%, 47.8% and 49.4%, respectively. According to the results obtained by FTIR in our laboratory, this organic fraction contains carboxylic groups responsible for capturing the metals on the surface (Barros et al., 2006). Bruno (2000), studying the adsorption of copper and lead in particulate material of aquatic environment also found a similar WS composition employing the fluorescence technique.

For the sample of WSNi, the decomposition temperatures of the bimodal profile (Fig. 6(a)), were 322 and 403 °C, with mass losses of 18.7% and 0.8% and ΔH of 9.9 and 16.6 J g^{-1}, respectively. The sample of WSCr showed decomposition temperatures of bimodal profile (Fig. 7(a)) of 325 and 439 °C, with enthalpies of 9.6 and 13.4 J g^{-1} and mass losses of 23.2% and 18.4%, respectively. The ash content of WS was 46.8% (Table 2), which practically corresponds to the inorganic fraction of the sludge (see Table 3).

Mercê et al. (2000) studying the utilization of solutions of a natural biopolymer (galactomannan of *Leucaena leucocephala*) as a complexing agent for metallic ions (Co^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+}) obtained TG and DSC curves, which presented final degradation temperatures higher than those observed in the curves of the pure biopolymer, a behavior similar to that obtained in our study. Otero et al. (2002) studied the thermal decomposition of different types of sludge, produced by a municipal sewage, a food industry and a milk industry treatment station, by TG/DTG and DTA curves, and observed a thermoanalytical behavior similar to that of our WS sample. Mangrich et al. (2000) reported thermal decomposition and kinetic behavior of vermi-composts, which presented thermal decomposition peaks at temperature ranges similar to those found in our work. However, the mass loss percentage of vermi-composts was considerably higher, due to a higher participation of the organic fraction in these composts.

4. Conclusion

Results of the biosorption of Ni(II) and Cr(III) by the utilization of WS in upflow reactors demonstrated an efficient removal of the metals. Higher biosorption capacity values at pH higher than 7.0 were observed. This increase in pH may be due to the hydrolytic protonation of the biomass due to the action of the metallic solution on the biosorbent.

Biosorption of the metallic ions occurred more intensely in the columns loaded with wastewater sludge in comparison to the columns with inert material. Which may be ascribed to the more effective complexation action due to presence of chemisorption and physisorption phenomena promoted by the organic and inorganic compounds existing in this type of biosolid.

The DSC and TG studies of the samples demonstrated that the shift of the final thermal decomposition peaks of the samples WSNi and WSCr in relation to the sample WS evidenced the existence of an interaction of physicochemical nature between the metals and the sewage sludge. This fact was also confirmed by the energy absorption evidenced by the endothermic behavior of the samples. The increase in ash contents that represent inorganic fraction in WSNi and WSCr samples in relation to the sludge sample indicated the presence of the metals after the biosorption process.

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