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DTG-DTA STUDY OF SEWAGE SLUDGE USED IN THE SORPTION OF Cd^{2+} AND Co^{2+}

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The present study was carried out for evaluating the retention behavior of sanitary sewage in relation to cadmium and cobalt ions in an ascendant continuous-flow reactor. It was found that the studied sludge presented a high assimilation of the metals, probably due to the presence of anionic groups, which favors adsorption and complexation processes. Thermal analyses of the samples showed a shift in the thermal decomposition 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.

Keywords: *DTA, heavy metal, sewage sludge, sorption, TG*

Introduction

At present, one of the most serious problems faced in nature is the chemical pollution with 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 and for other environmental concerns [1]. 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 milligrams or micrograms per liter) [2, 3].

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 [4–6]. As removal efficiency of a metallic species is related to the characteristics of the sorbent used in the biosorption of the metal, a high sorption capacity of the applied sorbent in this process may allow the recovery of the chemical element for its industrial reutilization [4].

Biosorption can be defined as the removal of metallic ions by means of the adsorption and/or complexation by live biomass or dead organic material [7], the 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 [8].

This objective of this study is to evaluate the thermal decomposition of the compounds formed upon the sorption of solutions of heavy metals, using as sorbents sewage sludge. Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) was used for the thermal stability evaluation.

Experimental

Samples

The sewage sludge (SS) was collected from an anaerobic blanket reactor, followed by packing in a rectangular fiberglass box for air drying. This sludge was

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turned around daily to facilitate the drying, which occurred in a period of 14 days. The dry SS was powdered and sieved through an 18 mesh (∅=4 mm) and packed in plastic bags.

The experimental system consisted of two ascendant continuous-flow fixed packed-bed reactors, each one with 3.5 L capacity, of which one reactor was fed with the flow rate of 500 mL day^{-1} of a water solution containing 50.00±0.48 ppm of cadmium (Cd^{2+}) and the other reactor with the same flow rate of a solution containing 50.00±0.48 ppm of cobalt (Co^{2+}). They were monitored for 100 days, without reaching the metal saturation of the reactors during such period of time.

The results of inorganic and organic composition of samples, performed by means of elemental and X-ray fluorescence analysis. Samples were taken from both the sewage sludge utilized in the aforementioned reactors for the metal removal are presented in Table 1. The sample SS represents the sewage sludge and the samples SSCd (SS+Cd^{2+}) and SSCo (SS+Co^{2+}) the sewage sludge after the metal uptake. The differences found in the SSM (SSCd and SSCo) samples in relation to the SS sample are resulted from the 100-day sorption process to which the absorbent was submitted.

The amount of cations present in the reactor effluent was determined by using an atomic absorption spectrophotometer Varian GBC-808 with deuterium corrector. The elemental analysis of the samples was performed by using an elemental analyzer Thermoquest CE Instruments EA 1110 CHNS-O. X-ray fluorescence analysis was performed by using an EDX-800 Shimadzu X-ray fluorescence analyzer, with a 10 mm collimator and a Ti–U detector operating at the 0 to 40 keV range, using an air atmosphere and an exposure time of 100 s.

Evolution kinetic

The sorption capacity of the sewage sludge is expressed as milligrams of biosorbed ion per gram of dry mass of the biomass (q/mg g^{-1}) and the removal efficiency of metallic ion (E/%) was calculated by Eqs (1) and (2), respectively [9].

$$q=\left(\frac{C_\mathrm{i}-C_\mathrm{f}}{m}\right)V \tag{1}$$

$$E=\left(\frac{C_\mathrm{i}-C_\mathrm{f}}{C_\mathrm{i}}\right)\cdot 100 \tag{2}$$

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

Table 1 Elemental composition of the SS and SSM samples (mass%)

Element	Sample		
	SS	SSCd	SSCo
Carbon	19.74±0.60	17.38±0.58	16.99±0.64
Hydrogen	2.83±0.50	2.71±0.48	1.95±0.47
Nitrogen	1.82±0.14	1.40±0.10	1.55±0.12
Oxygen	75.61±0.24	78.51±0.25	79.51±0.26
Cadmium		2.69±0.08	
Calcium	61.5±0.20	57.58±0.20	61.61±0.19
Cobalt			3.21±0.04
Copper	0.70±0.02	0.84±0.02	0.56±0.02
Sulfur	0.42±0.01	0.32±0.01	0.37±0.01
Strontium	0.84±0.01	0.82±0.01	0.65±0.01
Iron	32.11±0.16	32.71±0.17	25.73±0.13
Lutetium			1.96±0.05
Manganese	0.55±0.02	0.66±0.03	0.51±0.02
Potassium	2.30±0.04	2.19±0.04	1.91±0.04
Silicon	0.21±0.01	0.25±0.01	
Titanium			2.13±0.07
Zinc	1.35±0.03	1.52±0.03	1.02±0.02
Zirconium	0.44±0.01	0.43±0.01	0.34±0.01

[a]The percentage is calculated on dry basis.

Thermal analyses

The thermal decomposition studies of the samples were performed by means of TG(DTG) and DTA curves recorded using an SDT-2960 TA Instruments simultaneous TG-DTA unit, in air atmosphere at a flow rate of 110 mL min^{-1}, using alumina crucibles and a heating rate of 20 K min^{-1}. The sample mass (average) was of 10.0±0.5 mg of five parallel analyses, and the studied temperature range studied varied from room temperature up to 1273 K. The data analysis has been done by a software supplied by the producer (TA Instruments).

Results and discussion

The results on sorption capacity (q) as a function of operation time of the reactor loaded with SS and fed with Cd^{2+} and Co^{2+} solution are demonstrated in Fig. 1. It can be observed that the sorption capacity of Cd^{2+}, initially at around 0.77 mg g^{-1}, finally increased to 1.77 mg g^{-1}. The profile for sorption of Co^{2+} solution during the period of operation of the reactors was similar to that of the reactor fed with Cd^{2+} solution, showing that Co^{2+} had an initial sorption of 0.73 mg g^{-1} and a final sorption of 1.77 mg g^{-1}.

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 [10–13].

The percentages of removal of the metals as a function of operation time of the reactors loaded with SS and fed with solutions of cadmium and cobalt are presented in Fig. 2. The data obtained during operation of the reactors varied from 43.8 to 100.0% for the reactor fed with the Cd^{2+} solution, whereas for the reactor that received an affluent flow of Co^{2+} ion, the variation was from 41.1 to 99.9%. The high capacity for sorption of the cations by SS was related to its organo-mineral composition with a high proportion of bonding sites for organic and inorganic systems [14, 15].

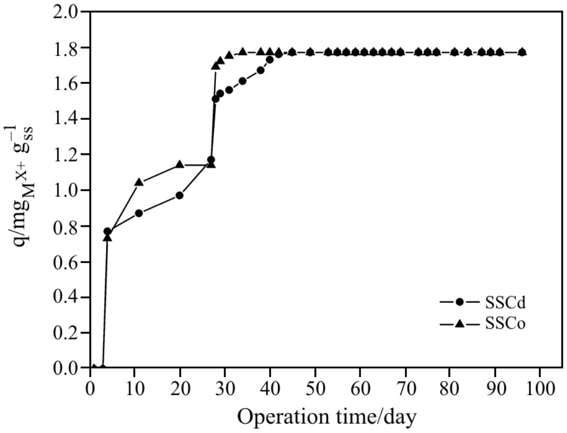

Fig. 1 Sorption of Cd^{2+} and Co^{2+} ion in SS *vs.* the operation time of reactor

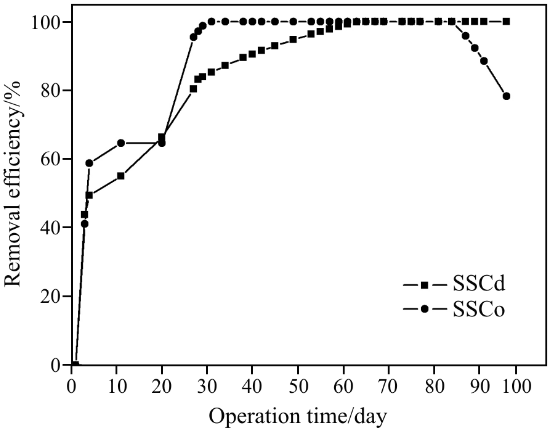

Fig. 2 Removal efficiency of Cd^{2+} and Co^{2+} ion in the SS *vs.* operation time

The data corresponding to the thermogravimetric (TG/DTG) and differential thermal analysis (DTA) studies for the samples of SS and SSM are presented in Table 2 and Figs 3–5. Table 2 shows that the TG, DTG and DTA curves of the three samples present three and four characteristic events for SSM and SS, respectively. The obtained results demonstrated that the thermal decomposition temperatures of the samples that contain metals (Cd^{2+} and Co^{2+}) shifted towards lower temperatures compared to the corresponding SS samples (Table 2).

The first event in all the samples is attributed to the water elimination. Those two samples that passed through the sorption of metals presented modifications with lower percentages of mass loss values.

Most of the decomposition of SS takes place in the second, third and fourth events, which should be mainly ascribed to the oxidative decomposition of the sorbent. The absorbent sample (SS) presented the high mass loss in the second event which may be related to the presence of long chain carbonyl organic compounds [10].

The decomposition temperature of SS for the second event is between 462 and 666 K. The samples where metal sorption took place presented dislocation

Table 2 Average data obtained from the TG/DTG and DTA curves of the samples

Sample	Stage or event	Parameter						
		TG/DTG					DTA	
		$T_{initial}$/K	T_{final}/K	T_{peak}*/K	mass loss/%	ash/%	T_{peak}/K	transition
SS	1	297.0	440.0	336.0	8.1	52.1	350.0	endo
	2	462.0	666.0	537.0	23.3		604.0	exo
	3	692.0	845.0	877.0	3.4		711.0	endo
	4	845.0	1255.0	988.0	13.1		990.0	endo
SSCd	1	298.0	425.0	419.0	7.7	59.4	348.0	endo
	2	456.0	835.0	601.0	28.0		614.0	exo
	3	845.0	1254.0	980.0	4.9		980.0	endo
SSCo	1	296.0	446.0	425.0	7.3	61.9	348.0	endo
	2	476.0	799.0	599.0	25.0		617.0	exo
	3	813.0	1253.0	980.0	5.8		982.0	endo

*Temperature of the peak related to the DTG curve

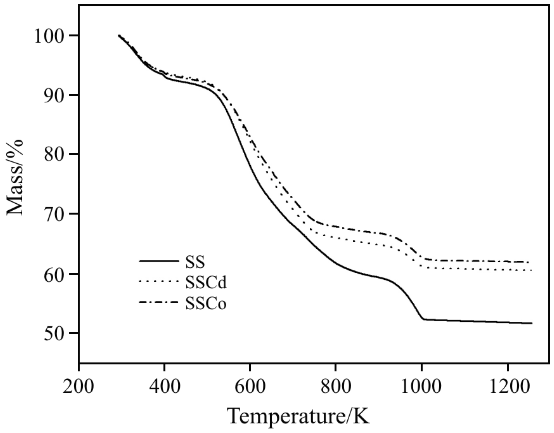

Fig. 3 TG curves of SS, SSCd and SSCo samples

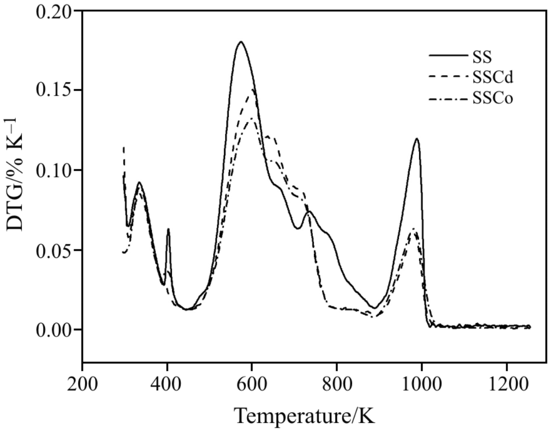

Fig. 4 DTG curves of SS, SSCd and SSCo samples

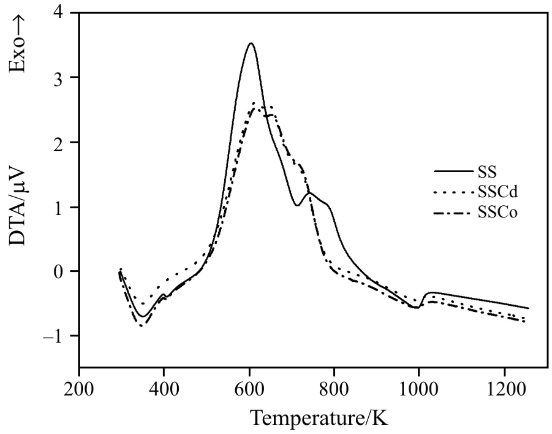

Fig. 5 DTA curves of SS, SSCd and SSCo samples

in the decomposition temperatures compared to the SS sample. This dislocation is due to the interactions that occurred between the metal and absorbent [9, 14].

Therefore the observation of the global decomposition process of the three samples, where they have been submitted to the sorption of metals presented a significant decrease of the decomposed organic fraction of absorbent (Table 1). This alteration may be attributed to the dissolution process of organic substance from SS in the form of a highly reactive hydroxide, carbonyl and phenolic compounds that can react with metallic ions forming compounds which can precipitate on the surface of the absorbent [16].

On the other hand, the loss of hydrogen ion by the absorbent surface due to the equilibrium reactions between the liquid medium and solid favors the bonding of the metallic ion and the surface, principally, favored by the higher bonding force of transition metal atoms in relation to hydrogen. In this way the presence of inorganic fraction in the samples that suffer metallic sorption increased [4].

The SSM samples presented a higher amount of inorganic compounds confirmed by X-ray fluorescence analysis (Table 1) [17]. Related to the presence of the metals sorbed by the sorbent, demonstrated by the amount of 59.4 and 61.9% of the inorganic fraction for the SSCd and SSCo samples presenting a 7.3 and 9.8% increase compared to the SS sample, respectively, when one analyses all the process of global decomposition of the TG experiments (Fig. 3).

The three samples presented a predominance of the endothermic processes; according to the DTA curves (Fig. 5), which allowed calculating the enthalpies related to each one of the events (Table 2). Such predominance of endothermic events suggests that they might be related to the breakage of organic groups [16].

The DTA curves (Fig. 5) indicate a presence of the three endothermic events and an exothermic one for the SS sample. The first characteristics event is attributed to the loss of humidity (T<398 K). The second event indicates an exothermic transition, showing the liberation of a great amount of energy during the thermal decomposition of the organic matter [18]. The third and fourth events presented endothermic change related to the decomposition or structural rearrangement of the inorganic fraction present in this sample.

The SSCd and SSCo samples presented three events in which the first and third events related to endothermic transitions and the second event related to exothermic transition. The first event observed in these two samples is related to the same process as observed in the SS sample, shifting the temperature to lower range. This was confirmed by the TG curves of the SSM samples. These two events can be related to a certain transformation (degradation and/or polymerization) of the organic compounds present in these samples [19, 20].

The intense second peak, caused by oxidative evaporation or combustion of the resulted organic compounds (e.g. decomposition of the carbonyl side chains) [14, 19].

The sorption process showed that the samples presented an increase in ash contents of the samples, which is demonstrated by the X-ray fluorescence analysis (Table 1) and in the TG/DTG curves (Figs 3 and 4) of the samples.

Conclusions

The thermal study of sewage sludge submitted to the process of sorption of the metals (Cd^{2+} and Co^{2+}) demonstrated that there exists a significant alteration in physico-chemical characteristics of the sewage, observed by the alteration of the decomposition temperatures of the biosolid used as absorbent. The profile of the TG and DTA curves presented significant qualitative and quantitative modifications of the events demonstrating that the sorption of the metals alter the absorbent properties, increasing its thermal decomposition resistance.

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