Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 2, 291–295

THERMAL DECOMPOSITION STUDY OF SEWAGE SLUDGE AND OF ORGANIC WASTE USED IN THE SORPTION OF METALS

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The conventional treatments of effluents containing heavy metals produce significant quantities of byproducts with recalcitrant characteristics, making necessary looking after alternative techniques in order to avoid the production of new contaminated residues. Sorption process of chromium and zinc in vertical columns loaded with sewage sludge and organic solid waste has been studied in this work. The data from the TG curves of the two sorbents presented significant differences when they were submitted to the metal uptake, being noticed the displacement of the thermal events towards lower temperatures for both types of sorbents studied. As it was expected, for both sorbents, an increase in the mass of samples has been observed at the completion of the thermal tests upon metal uptake. Therefore, these facts demonstrate that during the biosorption process a physico-chemical interaction took place between sorbents and metals, as it was evidenced by the more than 100 K increase in the decomposition temperatures as well as the variation of the ΔH values of the samples.

Keywords: *biosorption, DSC, heavy metal, organic solid waste, sewage sludge, TG*

Introduction

In general, the expression 'heavy metal' is used to designate the metallic chemical elements that pollute the air, water, soil, plants and foods. By definition, heavy metals are all those elements that present specific mass values larger than 5 g cm^{-3}. However, in contrast with the popular belief, these elements exert a beneficial action for microorganisms, plants and animals at assimilable concentrations by the living organisms, according to their metabolic necessities [1, 2]. Unfortunately, due to the high polluting and contaminating character of the modern society, these elements have reached high concentrations in the environment becoming harmful to the living species.

The request to develop purification technologies, which are conceived for not generating any damage to the environment reached, has distinguished importance [3]. Among these new technologies, the sorption of dissolved metals by the biochemical activity of microbial biomass or dead vegetable waste may be considered as a promising route for removal and recovery of the metals [4, 5].

Sorption includes two different processes: the first one is absorption, which involves the removal of a pollutant from a gaseous, liquid or solid phase to another phase. The second process is adsorption, which occurs by the condensation and concentration of the ions or molecules as one phase on another phase, taking place either by physisorption or chemisorption between the ions or molecules of the absorbent and of the absorbate (metallic ions) [5, 6].

Therefore, the removal efficiency of a metallic species is related to the characteristics of the absorbent used in the biosorption of the metal, and nowadays it is also related to the capacity of the applied absorbent in this process to allow the recovery of the chemical element to its industrial reutilization [7].

Many authors have published research to investigate the interaction between metal and absorbent by utilizing the thermoanalytical techniques (TG, DSC, DTA) on different biomaterials, such as sewage sludge [8], natural biopolymer [9], organic waste [10], biomass [11], and vermicomposts [12].

The aim of the present work is to study the thermal properties of the compounds formed upon the sorption process of heavy metals, using sewage sludge and organic waste (peels of green vegetables and fruits) as absorbents. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were used for thermal studies.

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Experimental

Samples

The sanitary sewage sludge (SS) was collected from a UASB (Upflow Anaerobic Sludge Blanket) reactor, followed by packing in a rectangular fiberglass box for air drying. This sludge was turned around daily to facilitate the drying, which occurred for 14 days. The dry SS was triturated and sieved through a mesh (∅=4 mm) and packed in plastic bags. The organic solid waste (OW) utilized in the experimental system consisted of samples taken at randomly from organic solid waste collected from the agricultural product supply center of Campina Grande (PB) city, which was triturated and dried in air for 10 days, then undergoing on the same procedure sieving and packing as of the SS.

The experimental system was constituted from two reactors, each one with 6L capacity. One reactor was loaded with OW and the other with SS, were fed with the flow rate of 100 mL day^{-1} of a water solution containing 50.00±0.48 mg L^{-1} of chromium and also of 50.00±0.48 mg L^{-1} of zinc. They were monitored for 60 days, without reaching the metal saturation of the reactors during this time period. The removal of metals was over 99%, thus leading to an effluent chromium and zinc concentration (both below of 0.5 mg L^{-1}).

Table 1 presents the results of physico-chemical analyses, performed by APHA standardized methods [13], of samples taken from both the organic wastes and the sewage sludge utilized in the aforementioned reactors for the metal removal. The sample OW stands for the organic wastes, before being submitted to the metal uptake, whilst the sample OWM is the former sample after sorption of metals. Similarly, sample SS represents sewage sludge and sample SSM the sewage sludge after metal uptake. The differences found in the OWM and SSM samples in relation to the other samples are resulted from the 60-day sorption process to which the absorbents were submitted.

Methods

The thermal decomposition studies of the samples have been done using SHIMADZU TGA-50 thermobalance, in air atmosphere (flow rate 20 mL min^{-1}), alumina crucibles and at a heating rate of 15 K min^{-1}. The sample mass (average) was about 8.5±0.5 mg of five analyses, and the temperature range varied between room temperature up to 1223 K. The data for each event were obtained by calculation using TASYS software for Windows provided by the manufacturer of the thermobalance.

The calorimetric studies of the samples was performed by SHIMADZU DSC-50 differential scanning calorimeter, in the 293–873 K range, at a heating rate of 15 K min^{-1}, flowing nitrogen with a rate of 50 mL min^{-1}. The sample mass and the crucibles were the same used for the thermobalance. The data related to the DSC curves were calculated by the same method as it was used for the TG curves.

Results and discussion

Tables 2 and 3 and Figs 1 to 4 present the data corresponding to the thermogravimetric (TG) and calorimetric (DSC) studies for the samples of organic wastes (OW), organic wastes+metal (OWM), sewage sludge (SS) and sewage sludge+metal (SSM).

Table 2 shows that the TG curves of the four samples present five characteristic events. The results of the measurements demonstrated that the thermal decomposition temperatures of the samples that con-

Table 1 Physico-chemical characterization of the samples OW, OWM, SS and SSM

	OW	OWM	SS	SSM
Moisture/%[a]	9.64	7.33	8.79	8.58
pH	7.90	6.70	6.60	6.20
Alkaline content/mg L^{-1}	1180	365	340	126
Total solids/%	90.36	92.67	91.21	91.43
Fixed solids/%	46.38	56.91	43.95	42.20
Volatile solids/%	43.98	35.76	47.26	49.23
Total organic carbon/%	24.43	18.87	26.26	27.36
Chemical oxygen demand/mg kg^{-1}	1386	1614	1133	1108
N_{total}/mg kg^{-1}	26.04	86.52	26.32	3.24
P_{total}/mg kg^{-1}	12.80	9.50	18.10	40.70
S_{total}/mg kg^{-1}	16.58	17.99	29.25	3.76
Fe/mg kg^{-1}	5.02	7.06	23.79	14.86

[a]The percentage is calculated on dry basis

Table 2 Data obtained from the TG curves of the samples

Samples	Parameters	Events				
		1st	2nd	3rd	4th	5th
OW	$T_{initial}$/K	301.0	449.0	683.0	863.0	1023.0
	T_{final}/K	409.0	666.0	858.0	1017.0	1222.0
	Mass loss/%	8.0	25.0	14.0	1.9	1.9
OWM	$T_{initial}$/K	302.0	394.0	533.0	835.0	869.0
	T_{final}/K	394.0	470.0	676.0	868.0	1056.0
	Mass loss/%	6.1	2.8	2.8	26.0	0.8
SS	$T_{initial}$/K	304.0	406.0	660.0	883.0	895.0
	T_{final}/K	406.0	452.0	720.0	890.0	1038.0
	Mass loss/%	8.0	27.0	18.0	2.0	0.1
SSM	$T_{initial}$/K	320.0	401.0	540.0	683.0	920.0
	T_{final}/K	398.0	422.0	675.0	835.0	1004.0
	Mass loss/%	5.4	1.0	23.0	18.0	1.4

Table 3 Data obtained by the analysis of the DSC curves

Parameters	Samples											
	OW		OWM			SS			SSM			
Events	1st	2nd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	4th
T_{peak}/K	349	606	332	454	715	333	390	702	329	395	598	712
ΔH/J g^{-1}	95.7	–5.0	54.2	4.9	–20.7	52.2	7.9	–12.4	59.9	2.3	9.6	13.4

OW – Organic Waste; *OWM* – Organic Waste + Metal; *SS* – Sewage Sludge; *SSM* – Sewage Sludge + Metal

tain metals (Cr^{3+} and Zn^{2+}) shifted towards lower temperatures, compared to the corresponding OW and SS samples (Table 2).

The first event is assigned to the water elimination of the OW, OWM, SS and SSM samples. The substances, which sorbed the metals presented lower percentages of moisture in comparison to the other two samples [9, 12].

Major part of the decomposition takes place in the second, third and fourth steps, mainly ascribed to the oxidative decomposition of the absorbents. On the other hand, the fifth event displayed a quite small mass loss for all the samples. The absorbent samples (OW and SS) presented the high mass loss values in the second and third events, which may be related to the presence of organic compounds with long carbonyl chains [14]. Their decomposition temperatures were between 394 and 720 K. From the data presented in Table 2, it can be observed that after the sorption process of the metals by the two absorbents, their characteristics are modified, since their decomposi-

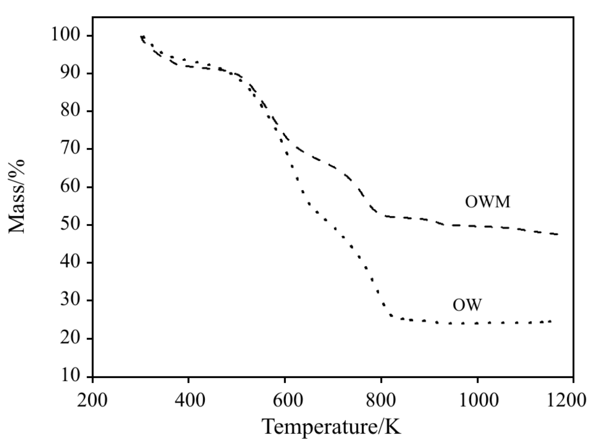

Fig. 1 TG curves of OW and OWM samples

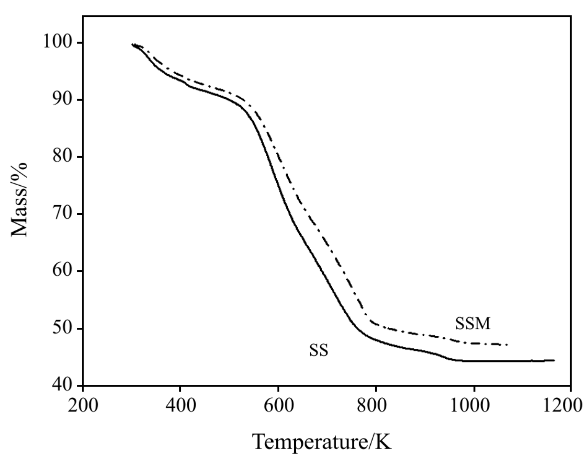

Fig. 2 TG curves of SS and SSM samples

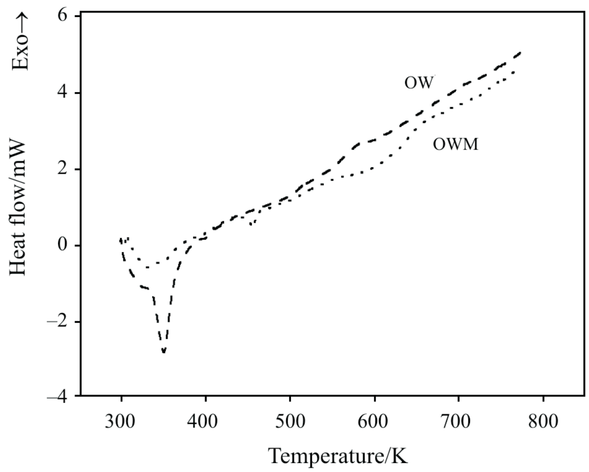

Fig. 3 DSC curves of OW and OWM samples

tion temperatures were lower compared to the samples without metals. The OWM sample in the fourth event presented the highest mass loss between 835-868 K, showing a decrease in the decomposition temperature interval compared to the OW sample, where the decomposition temperature interval was 863–1017 K. The SSM sample presented the fourth event with higher mass loss and lower temperatures than that of the SS sample, this behavior is due to the interactions occurred between the metal and absorbent [8–12].

Therefore, the observation of the total decomposition process of the four samples, where the samples were submitted to the metal sorption presented a significant decrease in the amount of the decomposed organic fraction due to mineralization of the absorbents [15].

On the other hand, the loss of hydrogen ion by the absorbent surface due to the equilibrium reactions between the liquid and solid favors the bonding of the metallic ion and the surface, principally, favored by the higher binding force of transition metal atoms with absorbent causing the liberation of hydrogen.

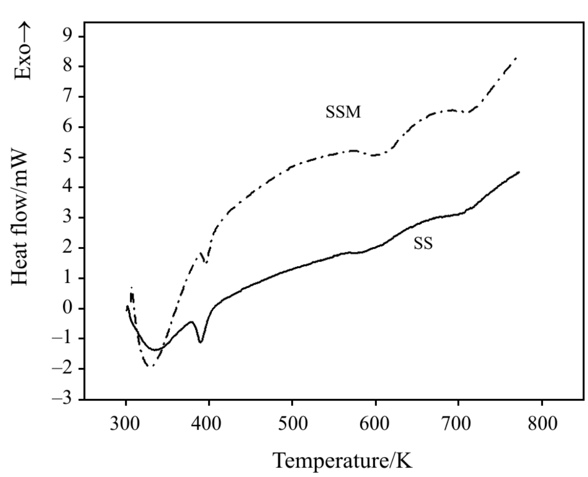

Fig. 4 DSC curves of SS and SSM samples

This behavior was evidenced by the increase in inorganic fraction in the two absorbents used in sorption of these metals (Table 2) [7].

The residue produced in TG analysis of the OW and SS samples was 49.2 and 44.9%, respectively. In case of the OWM and SSM samples the residue was 72.2 and 51.2%, respectively, thus presenting an increase of 23.0 and 6.3% in comparison to that of the OW and SS, respectively (Figs 1 and 2). This increase is due to sorption of the metals by the biosolids [8, 10, 12].

The DSC curves of the four samples indicate endothermic processes (Figs 3 and 4), allowing the calculation of the enthalpies related to each events (Table 3). According to [15], these endothermic events might be related to the cleavage of organic groups [15].

The first endotherm event in the DSC curves of the four samples can be attributed to the loss of humidity (t<398 K). The second one of the OW sample related to exothermic process (Table 3) and should be due to an intramolecular reaction, indicating the rearrangement of the molecular structure of organic part of the sample [15]. On the contrary, the second heat effect in the DSC curve of the OWM samples is endothermic, which is related to the fusion of the organo-mineral compound. According to the literature data, the third heat effect in the DSC curve of OWM can be attributed to intermolecular bonds related to organo-mineral coupling of the organic matter [9, 11, 12].

The SS and SSM samples presented the same endothermic behavior in the first and second events. An increase in temperature and enthalpy was found for SSM compared to SS. It is related to a continuous mass loss in the SSM sample suggesting the presence of strong chemical bonds.

On the other hand, such tendency in the decomposition temperature of smaller peaks was not practically observed in the DSC experiments (Table 3), however the comparison is a bit complicated because of the different number of events in the metal-free and metal-containing samples. This behavior is in agreement with the work of Otake and Walker [16], who observed that the presence of metallic cations did not affect substantially the thermogravimetric behavior of a lignite sample heat treated in nitrogen atmosphere.

Conclusions

The thermoanalytical and calorimetric properties of sewage sludge and of the organic waste were altered when these materials were submitted to biosorption of heavy metals (Cr^{3+} and Zn^{2+}). As it was expected, the metal-containing samples exhibit a higher amount of residue at the end of the TG experiments, in air. The peak temperature of the thermal decomposition events, always displayed lower temperatures for the metal-containing samples compared to the metal-free samples. On the other hand, such tendency of the lower decomposition temperature of the smaller peaks was not practically noticed in the DSC experiments, carried out in nitrogen atmosphere.

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Received: August 22, 2005
Accepted: November 5, 2005

DOI: 10.1007/s10973-005-6599-6