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THERMOGRAVIMETRIC STUDY OF AEROBIC BIODEGRADATION OF SANITARY SEWAGE SLUDGE AND LUBRICATING OIL

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The present study describes the aerobic biodegradation process of a mixture of sanitary sewage sludge and lubricating oil. TG/DTG curves confirmed that the applied aerobic biological treatment decreased the organic material content and caused significant modifications in the thermal behavior of the studied substrates after the functioning period.

Keywords: *biodegradation, lubricating oil, sludge, thermal degradation, thermogravimetry*

Introduction

Petroleum lubricating oils are derived from crude oils. In general, they consist of molecules containing 18–40 carbon atoms in three basic hydrocarbon types: paraffins, aromatics and naphthenes (cycloparaffins) [1]. These oils also contain compounds with small amount of heteroatoms, such as sulfur, nitrogen or oxygen, substituting the hydrocarbon structures [2, 3]. The lubricating oil must be viscous enough to maintain a lubricant film under operating conditions but should be as fluid as possible to conduct heat and to avoid power loss due to viscous drag. It should also be stable against heat and oxidative stress, should have low volatility and possess some ability to control friction and wear by itself [4]. They should be able to dissolve additives but to be inert toward metal surfaces, rubber seals and gaskets, too [4, 5].

Lubricating oil during its normal use becomes inadequate for its original application. Used oil contains products of partial deterioration, e.g. oxygenated and polynuclear aromatic compounds, resins, additives, metals and diverse contaminants, which might imperil the environment [1, 2, 4, 5].

Some microorganisms are able to interact chemically and physically with a large variety of natural and synthetic compounds, resulting structural change or complete degradation of the molecule. Sewage sludge is rich in nutritious organic substances and microorganisms, mainly bacteria and funguses, capable of degrading poisonous residues such as lubricating oil [6].

The aerobic metabolism is a biological process in which oxygen is introduced into the liquid substance to provide the oxidation of the organic matter by the microorganisms. As a consequence, the metabolic processes are accompanied by energy liberation [3, 4–6]. During the oxidation there is an electron transfer from the organic material (electron donors) to the oxidizer (electron acceptors) leading to the formation of CO_2 and H_2O. Thermogravimetric analysis (TG) provides information concerning to the mass changes of the sample upon heat treatment under controlled experimental conditions. However, no information is given on the composition of the gases evolved during the thermal decomposition. In many cases this missing information could be very valuable, especially when mixture of gases (water vapour, methane, formaldehyde, oxides of carbon, etc.) is simultaneously evolved during the mass loss [7].

The aim of this study is to evaluate the efficiency of the aerobic biodegradation of mixture of sanitary sewage sludge and lubricating oil using thermal analysis (TG/DTG).

Experimental

Mounting the experimental system

The experimental work was developed in the Experimental Station for Biological Treatment of Sanitary Sewage (EXTRABES), located in the district of Tambor in the city of Campina Grande (Paraíba, Northeast of Brazil). To accomplish the biodegradation runs, reactors

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were constructed together with some complementary devices. The reactors were built using PVC tubes with an internal diameter of 100 mm and height of 1 m. The capacity of each reactor was of approximately 8 L. The agitation system was set up in series and the respiration system was composed using an air compressor.

Loading of the reactors

The reactors were marked as R1, R2 and R3. Each of them was loaded with a weighed amount of sanitary sewage sludge. After it, different amounts of used lubricating oil were added and then the remaining volume of the reactor was completed with distilled water. The amount of different components used in each reactor is summarized in Table 1.

Table 1 Amounts of each component used for loading the reactors

Reactor	Composition		
	Sludge/g	Oil/g	Distilled water/L
R1	1940.0	17.6	2.0
R2	1940.0	35.2	2.0
R3	1940.0	52.8	2.0

Operation of the reactors

The mixture contained in the three reactors was called to substratum. A diaphragm compressor (Jet Master 1/3 hp) was used as respiration system to maintain the aerobic biodegradation process of the mixture present in the reactors. The air was introduced through hoses installed in the inferior part of the reactor, providing ascendant flow. Air input was maintained for 15 h day^{-1} by a digital controller providing at least 6 mg L^{-1} of dissolved oxygen in the mixture. The homogenization of the substratum was maintained by using an agitation rate of 90 rpm, during 24 h day^{-1}. Samples from the substratum were collected twice a week. The three reactors were monitored for 65 days.

Elemental analysis

The elementary composition of substratum was determined by using a Carlo Erba EA 1110 elemental analyzer.

Thermal analysis

The dynamic TG/DTG curves were recorded in the 25–1000°C temperature range using Shimadzu TGA-50 thermobalance in nitrogen at flow rate of 20 mL min^{-1}, using alumina crucibles. The applied heating rate was 25°C min^{-1}, the initial sample masses were 10.0±0.5 mg.

Results and discussion

Elemental analysis

The results of the elemental analysis of the sludge, oil, substratum and partially biodegraded residue obtained after the biological treatment are presented in Table 2.

The results of the elemental analysis confirmed the presence of carbon, nitrogen, hydrogen and sulfur in all the substrata and residues. Carbon was the most abundant element in all of samples, which is originated from the constituents of the sanitary sewage sludge and the used lubricating oil. On the contrary, nitrogen and sulfur is originated from the sanitary sewage sludge.

After 65 days from the beginning of the biological treatment, due to the microbial activity, the amount of C, N, H and S have decreased.

Thermal analysis

Thermal stability of the sanitary sewage sludge, lubricating oil and their mixture was followed by thermogravimetry. The representative data of the thermogravimetric experimetns are summarized in Table 3.

TG/DTG curves of the sanitary sewage sludge and lubricating oil samples are presented in Fig. 1.

TG/DTG curves (Fig. 1) indicate that the first stage of decomposition of the sewage sludge took place between 63–138°C. The mass loss in the first stage was due to the loss of humidity and of organic material with low boiling point. The highest mass loss was observed in the second stage, which corresponds to the degradation of organic part of higher molecular mass in the temperature range of 282–435°C. The observed mass losses in the third, fourth and fifth stages are representative for the degradation of inorganic constituents in the 580–740, 740–869 and 869–968°C temperature ranges, respectively. According to [8], the

Table 2 Results of the elemental analysis of the substratum in reactors R1, R2 and R3

Element	Sludge	Oil	R1		R2		R3	
			substratum	residue	substratum	residue	substratum	residue
N/%	3.05	0.00	2.54	2.09	2.14	2.04	2.20	2.06
C/%	31.55	85.00	24.82	24.06	26.21	23.36	27.17	25.75
H/%	4.91	13.60	4.86	4.36	4.79	4.04	5.08	4.81
S/%	1.39	0.00	4.44	1.69	4.14	3.16	5.31	4.63

Table 3 Thermoanalytical data of the sanitary sewage sludge and lubricating oil

Sample	Parameter	Stage					
		1st	2nd	3rd	4th	5th	mineralized product
Sanitary sewage sludge	T_i*/°C	63	282	580	740	869	>968
	T_f**/°C	138	435	740	869	968	–
	P_m***/%	7.16	41.33	3.79	4.45	3.19	40.80
Lubricating oil	T_i*/°C	290	–	–	–	–	>514
	T_f**/°C	401	–	–	–	–	–
	P_m***/%	99.99	–	–	–	–	0.01

*T_i – initial temperature, **T_f – final temperature, ***P_m – mass loss

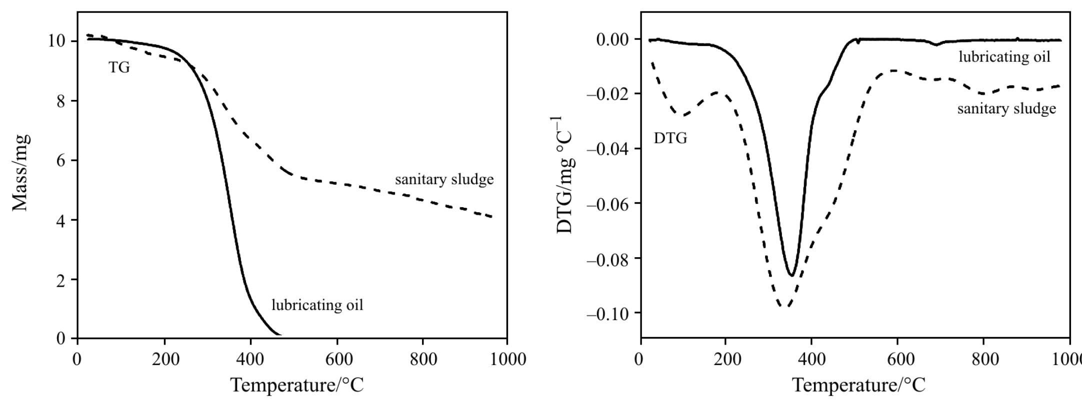

Fig. 1 TG/DTG curves of sanitary sewage sludge and lubricating oil

inorganic part of the sewage sludge contains several, e.g. as of silica-, calcium-, iron-, magnesium-, sodium-, potassium- and sulfur oxides. The sewage sludge sample used as inoculate, presented a high amount of mineralized material basically constituted of oxides, with higher decomposition temperatures than 968°C.

In the TG curve of the lubricating oil a single mass loss step was observed in the 290–401°C range (Table 3). Practically total (100%) mass loss was measured. The degraded organic matter corresponds to the high concentration of organic carbon of compounds with high molecular mass and long chains present in the sample [9].

Table 4 Thermal decomposition data of the substrata before and after the aerobic biological treatment of R1, R2 and R3 (at 10°C min^{-1} heating rate)

Reactor	Sample	Parameter	Stage			
			1st	2nd	3rd	residue
R1	before	T_i*/°C	27	143	422	>678
		T_f**/°C	143	422	678	
		P_m***/%	9.33	44.40	12.37	33.90
	after	T_i*/°C	33	169	391	>618
		T_f**/°C	169	391	618	
		P_m***/%	9.26	32.76	20.93	37.05
R2	before	T_i*/°C	28	138	441	>691
		T_f**/°C	138	441	691	
		P_m***/%	11.46	47.30	9.42	31.82
	after	T_i*/°C	37	177	374	>679
		T_f**/°C	177	374	679	
		P_m***/%	9.93	30.48	24.75	34.84
R3	before	T_i*/°C	25	147	435	>701
		T_f**/°C	147	435	701	
		P_m***/%	6.23	48.89	11.29	33.59
	after	T_i*/°C	25	195	371	>625
		T_f**/°C	195	371	625	
		P_m***/%	10.47	29.04	23.78	36.71

*T_i – initial temperature, **T_f – final temperature, ***P_m – mass loss

Thermogravimetric analysis on virgin lubricating oil samples in nitrogen also showed a single decomposition stage in the 170–470°C temperature range [10]. The differences between the degradation temperatures of the lubricating oil and the virgin oil can be attributed to the increase of the thermal stability caused by the natural degradation during their use in the engines.

Thermogravimetric study of the substrata and of the residues formed after the biological treatment aimed to check how the thermal stability caused by biodegradation of the organic material changed [11, 12].

Table 4 shows the thermal decomposition data taken from the TG curves of substrata in reactors R1, R2 and R3 before and after the aerobic biological treatment.

TG curves of the substratum and of the residue present in the reactors R1, R2 and R3 are shown in Fig. 2.

According to the TG curves, the substrata of reactors R1, R2 and R3 show three thermal decomposition events.

From the data of Table 4 it can be concluded that the second decomposition of the substrata of reactors R1, R2 and R3 before the biological treatment exhibited the highest mass loss which is due to the addition of different amounts of lubricating oil.

The applied biological treatment of the substrata in the reactors R1, R2 and R3 led to changes mainly in the second mass loss step, caused by decrease of the organic matter (Fig. 2). In the substratum of reactor R1 a decrease from 44.40 to 32.76%, in the substra-

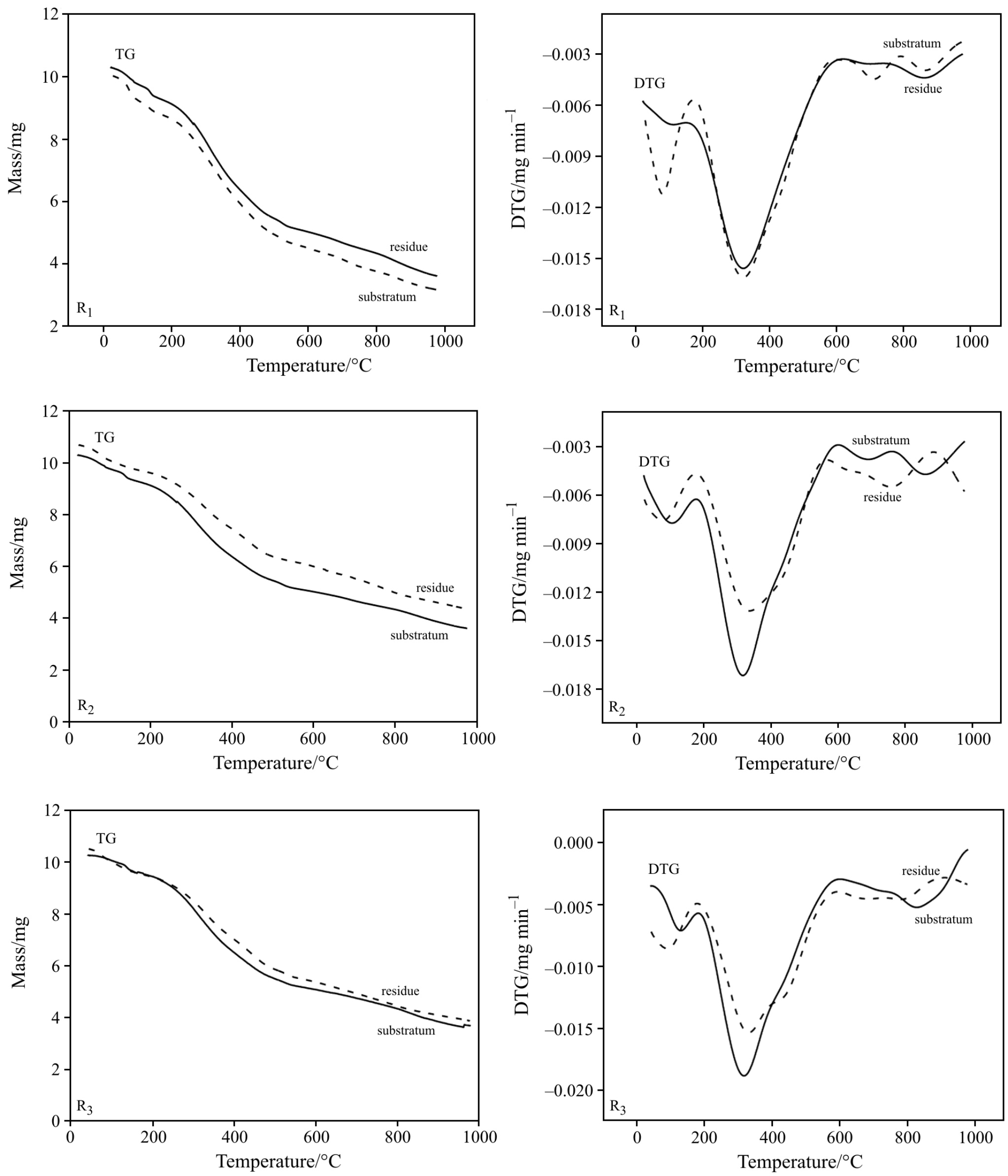

Fig. 2 TG/DTG curves of substrata and residues present in the reactors R1, R2 and R3

tum of the reactor R2 decrease from 47.30 to 30.48% and in the substratum of the reactor R3 decrease from 48.89 to 29.04% was observed, respectively. The biological treatment increased the initial decomposition temperatures and decreased the final temperatures for all substrata analyzed in the second event. The changes in the initial and final temperature ranges observed for the substrata before and after the treatment in the R1, R2 and R3 reactors were from 143–422 to 169–391, from 138–441 to 177–374 and from 147–435 to 195–371°C, respectively.

Conclusions

The results of the experiments proved that the degradation of lubricating oil may occur together with the sanitary sewage sludge in aerobic reactors. The results of the elemental analysis and the thermogravimetric experiments verified the biodegradation of the organic content of the oil and sludge. The treatment resulted significant modifications in the chemical composition of the organic substances and cleavage of the carbon chains to smaller ones rendering them to higher thermal stability. This phenomenon was proved by the shift in the ranges of the initial and final temperatures of thermal decomposition and by the decrease of the mass loss in the second step, which was representative to all of the substrata after the biological treatment in reactors R1, R2 and R3.

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