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Sewage sludge coke estimation using thermal analysis

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Abstract The imposition of more stringent legislation by CETESB in the State of São Paulo (Brazil) governing the disposal and utilization of sewage sludge, coupled with the growth in its generation has prompted a drive for alternative uses of sewage sludge. One option that is especially promising, due to its potential to valorize sludge, is its conversion into carbonaceous adsorbents or coke for industrial effluents treatment. Thus, a methodology is presented to estimate the coke produced from the sludge of a sewage treatment station using thermal analysis. The used sewage sludge, which comes from aerobic treatment, was collected in the wastewater treatment station of Barueri, one of the largest of the São Paulo metropolitan area. The sludge samples were collected, dried, ground, and milled until they passed an ABNT 200 sieve. The inert ambient used during its thermal treatment produces inorganic matter and coke as residual materials. Coke formation occurs in the 200–500 °C range and, between 500 and 900 °C, its thermal decomposition occurs. The highest formation of coke occurs at 500 °C.

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Introduction

The requirements of governmental legislation for the disposal and use of sewage sludge coupled with the increase of their generation and decreasing acceptance of traditional routes for their disposal have led to a search for new alternative uses for sewage sludge [1].

The most common methods for disposal or treatment of sewage sludge are landfilling, agricultural application, and incineration, none of which are exempt of environmental problems [2]. The presence of heavy metals in wastewater sludge, with the risk of proliferation of disease-carrying insects limits its use in agricultural application as a fertilizer [3, 4].

Disposal of sewage sludge through landfilling should be avoided as it does not allow the use of soil for agricultural use and decreases landfills service life. Incineration reduces the volume of sludge but it is costly and generates emissions into air, soil, and water [5].

As the generation of sewage sludge increases yearly and nature can not eliminate this pollution, many rivers have become open sewers, such as Tietê, Piracicaba and many others in Brazil. Therefore, the largest urban centers established sewage treatment stations to solve such problems. However, the treatment ends up causing another problem to society and the environment: the huge amount of originated sludge [6].

For the metropolitan region of Sao Paulo for 2013, a production of 890 tons per day of sludge is estimated [7]. For the final disposal of this sludge, the wastewater treatment station from the metropolitan region of Sao Paulo recommended sending the sludge to landfills, areas of reforestation, fertilization in agriculture, and its incineration, producing biogas.

Although, these sludge disposal solutions may provide a momentary tranquility feeling, they might afterward cause severe environmental problems; hence, whenever possible, the use of this waste material properties and characteristics must be attempted to turn it into a resource [8].

Recycling is the best way, from the economical and environmental point of view, among the present solutions. As ways to reuse the residue, it is possible to highlight agricultural fertilizer in accordance with existing laws, as raw material component in cement production and ceramic industry (bricks, tiles, and pavement) and the use of its organic content calorific power [9, 10].

Recently, another potential alternative, due to its ability to valorize the sludge, is the conversion of this residue into a coke adsorbent material [11]. Coke sludge results from thermal decomposition of its organic part and is produced by heat treatment of sewage sludge in inert atmospheres at temperatures above 300 °C [12].

The solid residue of pyrolysis (coke) contains carbonaceous material as the product of the cracking reactions that take place during thermal treatment in inert atmosphere [13]. The coke produced can be used as adsorbent material for liquid and gaseous pollutants [14]. As there is currently a growing interest not only in using low-cost materials with adsorptive properties but there is also a growing concern about the reuse or recycling of waste and other such materials, the production of coke adsorbents from sewage sludge combine these two purposes of environmental research [15].

A methodology is presented in this article to quantitatively estimate the produced sewage sludge coke, by using thermal analysis. The sewage sludge used in this study comes from aerobic treatment and was collected in the treatment station of Barueri, one of the largest in the São Paulo metropolitan area.

Materials and methods

Sample preparation

The sludge samples were collected, dried at 110 °C to constant weight, ground, and milled before analysis. Figure 1 shows the sewage sludge before preparation (SSBP), collected from the sewage treatment plant of Barueri, and after the preparation (SSAP), from which the samples were used in thermal analysis.

As sewage sludge is a very heterogeneous material, it was ground and milled, passed an ABNT 200 sieve to decrease the size of its particles and increase their contact surface, making the sample more homogeneous and thus more representative [16].

Thermal analysis

The analyses were performed in a simultaneous TG-DTA equipment, TA Instruments, model SDT Q600, with a 10 °C min^{-1} constant heating rate from 25 to 1,000 °C. Air or nitrogen was used as purge gas at a 100 mL min^{-1} flow rate. About 6.5 mg of SSAP were used in platinum pans in each analysis. The TA Instruments software provides the TG, derivative thermogravimetry (DTG), and differential thermal analysis (DTA) curves.

Sewage sludge coke estimation

Three runs were performed in air atmosphere and three in nitrogen atmosphere. To estimate the amount of coke, we started from the assumption that at a given temperature "*T*", the SSAP analyzed in air loses the residual water and other products arising from the decomposition of inorganic materials, the decomposition and burnout of organic matter is complete and only the inorganic oxides remain in the residual mass at the end of the thermal analysis [17, 18].

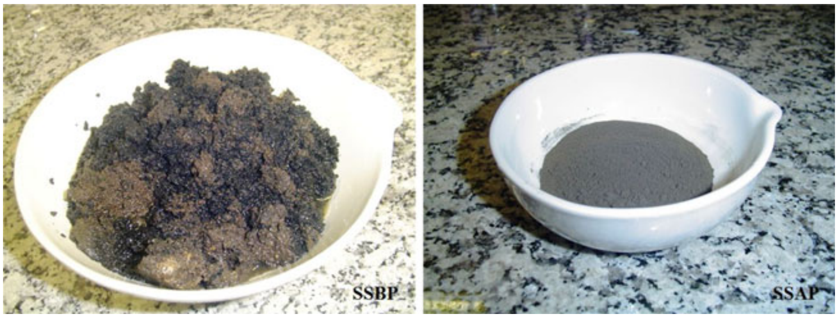


Fig. 1 Sewage sludge samples before preparation (SSBP) and after preparation (SSAP)

The SSAP analyzed in nitrogen atmosphere loses the same products as the previous case for the inorganic contents, but the organics are pyrolysed this time, forming coke as residual carbonaceous matter. The coke formed at a given temperature "*T*" is estimated by the difference of respective residual masses in air and nitrogen at *T*.

Characterization by elemental analysis

The carbon, hydrogen, and nitrogen contents were determined by elemental analysis using a LECO equipment, model CHN 1000 with automatic sampler.

The analyses were performed using two sewage sludge samples: the first was SSAP, and the second was the same sewage sludge but after submitted to pyrolysis up to 500 °C (SSAPP).

X-ray diffraction characterization

These analyses were performed by the powder method, through the use of a PANalytical X-ray diffractometer, model X′Pert PRO with X′Celerator detector. The analysis operating conditions were: Cu as the source of X-rays, energy 45 Kv × 40 mA and the measurements were done within the range of 2θ from 4° to 70°.

The identification of crystalline phases was obtained by comparing the diffractograms of the sample with the databases of PDF2 ICDD-International Centre for Diffraction Data 2003 and PAN-ICSD-Inorganic Crystal Structure Database PANalytical 2007.

Results and discussion

Thermal analysis

Figures 2 and 3, respectively, show the TG, DTG and DTA curves of SSAP sewage for the three runs in air and nitrogen.

Taking as reference the initial respective SSAP mass, mass losses up to 1,000 °C were estimated for samples in air and in nitrogen. Table 1 presents the calculated values.

As can be seen the average total weight losses up to 1,000 °C in air and in nitrogen are similar, indicating that the coke was decomposed in both atmospheres. Thus, when the sludge is analyzed in air or nitrogen up to 1,000 °C, the loss of its organic part occurs, and inorganic oxides remain.

To better understand how coke formation occurs, several temperatures were used to determine the residual mass in nitrogen and air atmospheres to estimate, by their difference, the amount of coke formed at each temperature in the former case.

Sewage sludge coke estimative

Figure 4 shows comparisons of TG curve of the SSAP in nitrogen and air for all three runs.

From TG curves of the three run presented in Fig. 4, it can be seen that the residual mass of SSAP at 1,000 °C in air and nitrogen are nearly equal and, checking other temperatures, the thermal degradation of SSAP is verified to occur more rapidly in air. The residual masses in air and nitrogen for three runs for some temperatures were obtained

Fig. 2 TG, DTG, and DTA curves of SSAP for the three runs in air

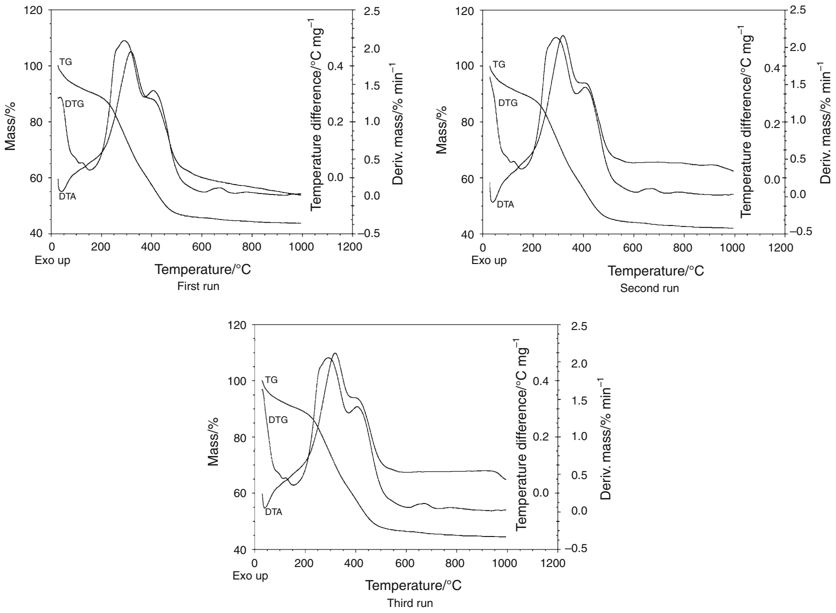


Fig. 3 TG, DTG, and DTA curves of SSAP for the three runs in nitrogen

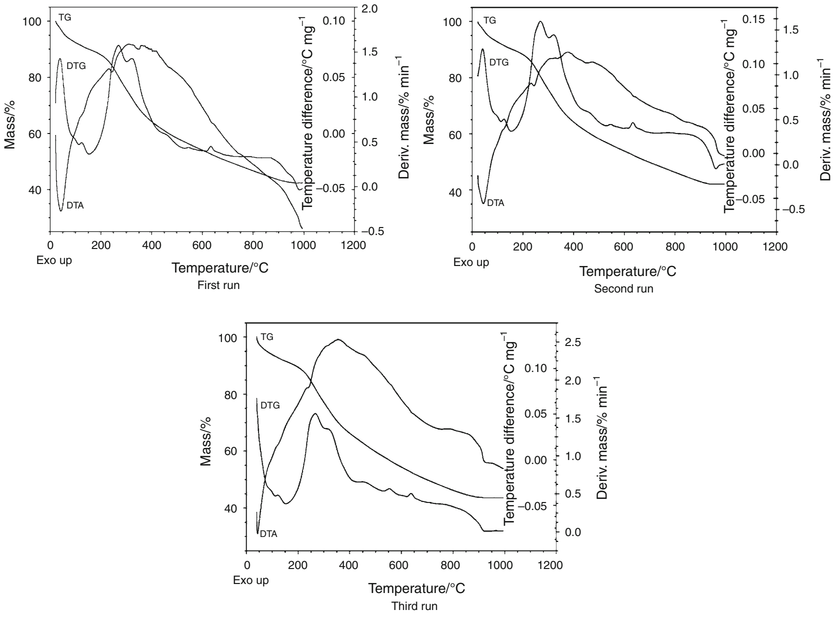
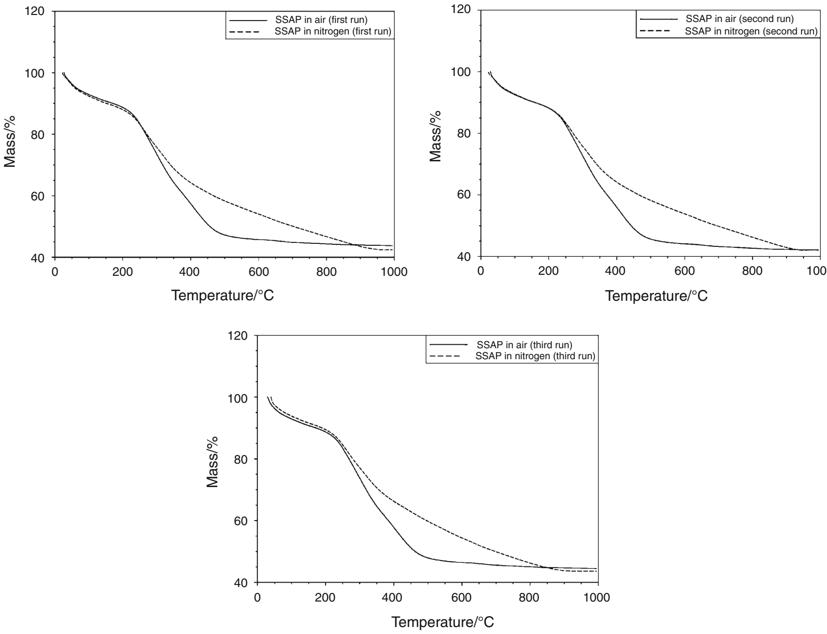


Table 1 Mass loss up to 1,000 °C for SSAP in air and nitrogen

	SSAP in air (first run)	SSAP in air (second run)	SSAP in air (third run)	SSAP in nitrogen (first run)	SSAP in nitrogen (second run)	SSAP in nitrogen (third run)
Mass loss/% up to 1,000 °C	56.21	58.11	55.79	56.79	57.04	56.60
Average mass loss/% up to 1,000 °C		56.70			56.81	

Fig. 4 Comparisons of TG curves of SSAP in nitrogen and air for the three runs



from their respective TG curves. Table 2 presents an illustration, for the first run, of how the coke formed at these temperatures can be estimated, by the difference of respective residual masses of SSAP in air and in nitrogen.

By using the Universal Analysis 2000 software, version 4.7a, supplied by TA Instruments, estimates of the formed coke for all analysis temperatures for the three tests were done by subtracting their respective TG curves in air from

Table 2 Coke estimation by the difference between the residual mass (*M*) of SSAP in nitrogen and air at a determined temperature (data from the first run)

	$M_{300\ ^\circ\mathrm{C}}$	$M_{350\ ^\circ\mathrm{C}}$	$M_{400\ ^\circ\mathrm{C}}$	$M_{450\ ^\circ\mathrm{C}}$	$M_{500\ ^\circ\mathrm{C}}$	$M_{550\ ^\circ\mathrm{C}}$	$M_{600\ ^\circ\mathrm{C}}$	$M_{650\ ^\circ\mathrm{C}}$	$M_{700\ ^\circ\mathrm{C}}$	$M_{750\ ^\circ\mathrm{C}}$	$M_{800\ ^\circ\mathrm{C}}$
SSAP residual mass/% in air	73.45	64.25	57.38	50.72	47.26	46.24	45.82	45.45	44.95	44.73	44.50
SSAP residual mass/% in nitrogen	75.56	68.70	64.10	60.88	58.19	55.98	53.91	51.85	50.01	48.30	46.60
Coke/%	2.11	4.45	6.72	10.16	10.93	9.74	8.09	6.40	5.06	3.57	2.10

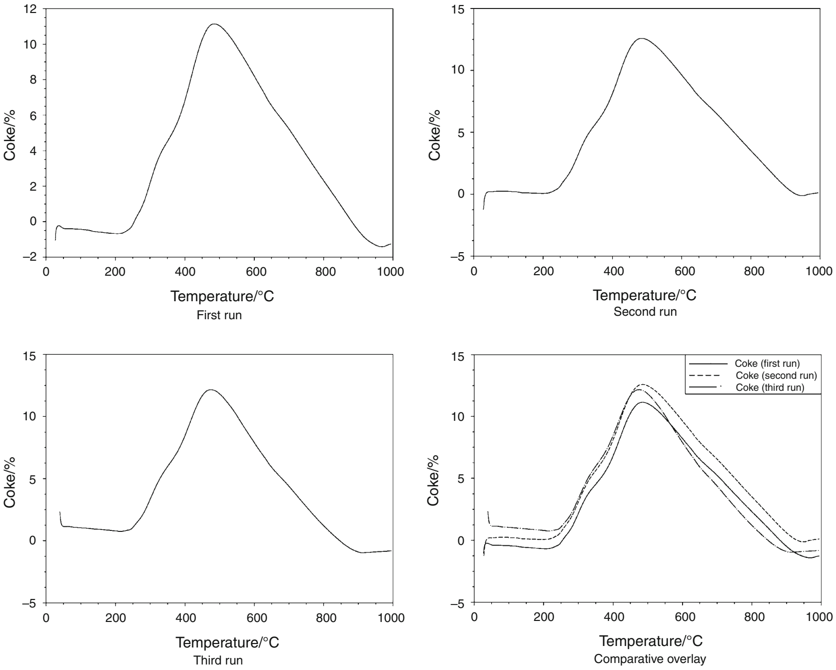


Fig. 5 Curves of formation and decomposition of coke for the three runs and their comparative overlay

those obtained in nitrogen flow. Thus, curves of coke formation and decomposition as a function of temperature were obtained for the three runs, which are shown in Fig. 5.

The curves in Fig. 5 show that the coke formation occurs in the 200–500 °C range and from 500 to 900 °C occurs its thermal decomposition. The highest coke formation occurs at 500 °C. These characteristics can be better visualized in the comparative overlay of the three difference TG curves, which indicates that in all three runs, practically occurred the same behavior.

Characterization by elemental analysis

Table 3 shows the carbon, hydrogen, and nitrogen contents determined by elemental analysis for SSAP and SSAPP.

Table 3 Carbon, hydrogen, and nitrogen contents in SSAP and SSAPP

Sample	C/%	H/%	N/%
SSAP	25.6	4.3	3.7
SSAPP	15.9	1.0	2.5

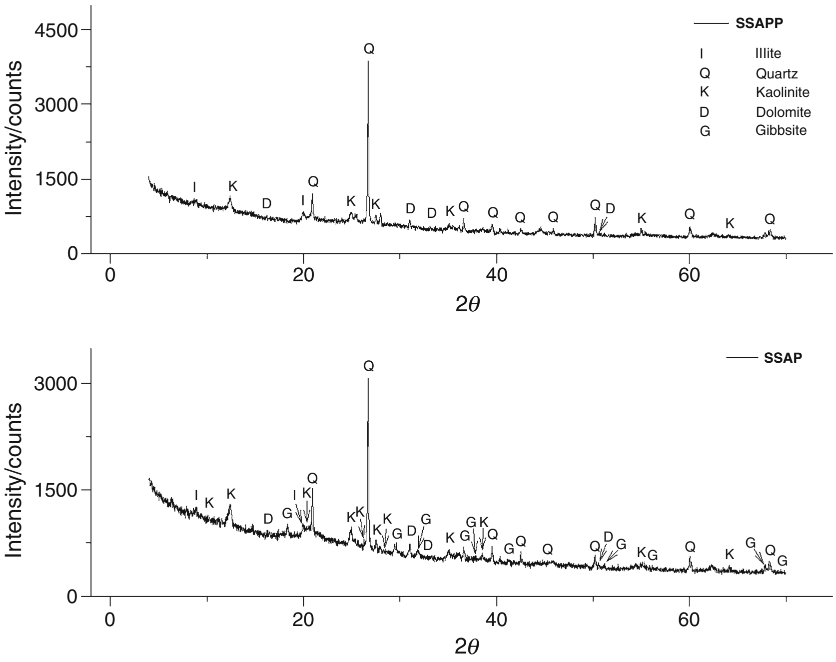
The SSAP, when pyrolized up to 500 °C, forming the SSAPP, loses part of its organic matter, in this case the most volatile, leaving coke as the organic residue plus inorganic solids in the residual material [17]. From Fig. 3 and considering the mean value of the three runs in nitrogen, the residual mass at 500 °C represents 59.21% of the initial mass of SSAP. Thus, according to the elemental analysis data, SSAPP has only $59.21 \times 0.159 = 9.41\%$ of carbon, when referred to initial mass of SSAP. This means that actually SSAP loses 63.23% of its carbon content when pyrolized up to 500 °C, but producing SSAPP with the highest content of residual coke, as previously seen from Fig. 5.

X-ray diffraction characterization

Figure 6 shows the X-ray diffraction patterns of SSAP and SSAPP.

From Fig. 6 it can be seen that when the SSAP was pyrolysed at 500 °C, forming the SSAPP, as its organic fraction has decreased, some inorganic crystalline phases were concentrated and others were total or partially dehydrated.

Fig. 6 SSAP and SSAPP X-ray diffraction patterns



For SSAP, the identified crystalline phases were quartz, kaolinite, dolomite, illite, and gibbsite. For SSAPP, there is no gibbsite because it was thermally decomposed [19] and partial dehydroxylation of kaolinite and illite is noticed from the relative decrease of respective XRD peaks.

The dolomite when treated in inert atmosphere at 900 °C decomposes via a single stage into CaO and MgO separate phases [20, 21]. Then, as the SSAPP was submitted to the temperature of 500 °C, the decomposition of dolomite has not started, and respective XRD peaks are the same as those identified for SSAP.

Conclusions

- Thermogravimetry is an efficient technique to estimate the amount of coke produced from the pyrolysis of the sludge of sewage treatment plants
- The method is based on obtaining a thermogravimetric difference curve from the difference between TG curves of the sludge in nitrogen and air
- The analyses, done in triplicate, indicate that for all cases, the maximum coke formation occurs at 500 °C.
- This method allows one to know the temperature ranges of coke formation and decomposition for a specific type of sewage sludge and to optimize the production of coke adsorbents there from.

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References

1. Rio S, Faur-Brasquet L, Coq L, Cloirec LP. Structure characterization and adsorption properties of pyrolized sewage sludge. Environ Sci Technol. 2005;39(11):4249–57.
2. Shen W, Guo Q, Wang H, Yang X, Liu Y, Zhang Y. Product composition of pyrolized sewage sludge and adsorption of methylene blue by porous material derived from it. Environ Eng Sci. 2008;25(1):99–105.
3. Dweck J, Morais LC, Fonseca MVA, Campos V, Buchler PM. Calcined sludge sintering evaluation by heating microscopy thermal analysis. J Therm Anal Calorim. 2009;95:985–9.
4. Vogel C, Adam C, Unger M. Heavy metal removal from sewage sludge ash analyzed by thermogravimetry. J Therm Anal Calorim. 2010. doi:10.1007/s10973-010-0966-7.
5. Hossain MK, Strezov V, Nelson PF. Thermal characterization of the products of wastewater sludge pyrolysis. J Anal Appl Pyrolysis. 2009;85:442–6.
6. Capana AS, Martins QV, Crespi MS, Ribeiro CA, Barud HS. Thermal behavior of residues (sludge) originated from Araraquara water and sewage treatment station. J Therm Anal Calorim. 2009;97:601–4.
7. Gonçalves MC. The question of sludge produced in sewage treatment plants in the metropolitan area of São Paulo, 2007. http://www.cetesb.sp.gov.br/noticentro/2007/10/sabesp.pdf. Accessed 21 Jan 2010.
8. Otero M, Gómez X, Garcia AI, Morán A. Non-isothermal thermogravimetric analysis of the combustion of two different carbonaceous materials: coal and sewage sludge. J Therm Anal Calorim. 2008;93:619–26.
9. Ischiam M, Perazolli C, Maschio R, Campostrini R. Pyrolysis study of sewage by TG-MS and TG-GC-MS coupled analyses. J Therm Anal Calorim. 2007;87:567–74.

10. Otero M, Sanchez ME, Garcia AI, Morán A. Simultaneous thermogravimetric–mass spectrometric study on the combustion of coal and sewage sludges. J Therm Anal Calorim. 2006;86:489–95.
11. Ferreras JF, Posadas HG, Gutierrez JLR, Omaechevarría JR. Use of ash from sewage sludge in the preparation of desulfurant sorbents. J Chem Reac Eng. 2010;8:1–10.
12. Mocelin C. Sewage sludge pyrolysis: Production of adsorbent and fuel oils, MSc Dissertation-Post-graduate in Mechanical Engineering and Materials, Federal Technological University of Parana, Curitiba, Brazil, 2007.
13. Ischia M, Maschio R, Grigiante M, Baratieri M. Clay-sewage sludge co-pyrolysis. A TG-MS study on potential advantages afforded by the presence of clay in the pyrolysis of wastewater sewage sludge. Waste Manag. 2011;31:71–7.
14. Martín MJ, Serra E, Ros A, Balaguer MD, Rigola M. Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions. J Chem Eng. 2003;94(3):231–9.
15. Otero M, Rozada F, Morán A, Calvo LF, García AI. Removal of heavy metals from aqueous solution by sewage sludge based sorbents: competitive effects. Desalination. 2009;239:46–57.
16. Brown ME, Gallagher PK. Handbook of thermal analysis and calorimetry. Principles and practice. V. 1. Amsterdam: Elsevier Science; 1998.
17. Dweck J, Morais LC, Menezes JC, Buchler PM. Thermal analysis of municipal sludge waste combustion. Mater Sci Forum. 2006; 530–531:740–6.
18. Morais LC, Dweck J, Gonçalves EM, Buchler PM. A case study of the ceramic matrix sintering of sewage sludge when fired at high temperatures. Mater Sci Forum. 2006;530–531:734–9.
19. Dweck J. Qualitative and quantitative characterization of Brazilian natural and organophilic clays by thermal analysis. J Therm Anal Calorim. 2008;92(1):129–35.
20. Kok MV, Kloss-Smykatz W. Thermal characterization of dolomites. J Therm Anal Calorim. 2001;64:1271–5.
21. Samtani M, Dollimore D, Alexander KS. Comparison of dolomite decomposition kinetics with related carbonates and the effect of procedural variables on its kinetic parameters. Therm Acta. 2002;392–393:135–45.