

## Preparation of carbon-based adsorbents from pyrolysis and air activation of sewage sludges

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### Abstract

The pyrolysis of 10 sewage sludges (5 anaerobic and 5 aerobic) from the Madrid region (Spain) was carried out at 450 °C during 1 h in a vertical glass-furnace. A thorough characterisation of sewage sludges was performed in order to study the influence of their properties on the pyrolysis process. Both anaerobically and aerobically stabilized sewage sludges that lead to pyrolysed materials with higher carbon content (38.6 and 43.4 wt.%, respectively) were selected for the preparation of carbon-based adsorbents. These two materials were air-activated at 275 °C during 4 h in order to improve their properties. After that, the BET surface area of carbon-based materials increased from 16 to 102 m<sup>2</sup>/g for the aerobic sludge and from 81 to 105 m<sup>2</sup>/g for the anaerobic one. These results showed that pyrolysis of sewage sludges using lower pyrolysis temperatures and air activation could be an interesting alternative route for the inexpensive and environmentally acceptable synthesis of carbon-based adsorbents.

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### 1. Introduction

Sewage sludges are inevitable by-products of wastewater purification. In the last decades, wastewater treatment plants have produced an important increment on sewage sludge production due to the major limitations in water disposal and the increase in the percentage of households connected to central treatment plants. Consequently, the world is currently undergoing a rapid increase in sludge production that is expected to continue up during the next years.

Sludges resulting from wastewater treatment operations are usually in the form of very dilute suspensions which typ-

ically contain from 0.25 to 12 wt.% of solids. On the other hand, sewage sludges are composed largely of the substances responsible for the offensive, pathogenic and toxic characteristics of the untreated wastewater [1]. Therefore, sludges processing should be intended to reduce smell and quantity of organic volatiles, eliminate disease-causing bacteria, reduce water content through dehydration and to produce the sludge stabilization [2]. Generally, three stabilization methods have been used: thermal [3,4], chemical and biological [5]. The last method is the most extensively used in the European countries and consequently, in Spain. Biological stabilization involves partial transformation of organic matter into a gas and the production of a stabilized residue with the help of bacteria either in the absence or presence of oxygen leading to anaerobically or aerobically stabilized sewage sludge, respectively [5].

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At the moment, the conventional uses of sewage sludges include industrial utilization, landfilling, individual combustion [6] or with coal [7] and composting for farmland utilization [8]. Direct farmland application is limited by the potential pollution by the metals present in the sewage sludges [8]. Landfilling has been a major option in disposal of sewage sludge for a long time, but it will not be sustainable due to the increasing competition for landfill space, higher costs and more stringent environmental standards applied, especially in the European countries. Also, combustion of sewage sludges needs rigid control of the volatile pollutants generated during the process [6,7]. In recent years, a growing research interest has been focused on the production of carbon-based adsorbents from a wide range of residues, such as forest and agricultural wastes [9], sewage sludges [10] and other waste materials [11,12]. Pyrolysis of sewage sludges leads to three fractions: liquid, solid and gaseous [13,14]. The solid fraction obtained could be incinerated, disposed on landfill or used as cheap carbon-based adsorbent [15,16]. Activated carbons are highly effective adsorbent materials that were extensively used for air and water purification due to their elevated surface area (about  $1500 \text{ m}^2 \text{ g}^{-1}$ ) [17]. Despite their interesting properties, activated carbons are expensive materials and this fact could limit their interesting uses. Generally, the activated carbons produced from pyrolysis of sewage sludges have a surface area of  $100\text{--}400 \text{ m}^2 \text{ g}^{-1}$  and could be used as cheaper adsorbents in conventional applications [15,16]. Generally, chemical activation using  $\text{H}_2\text{SO}_4$  (in 1:1 weight relation) and other mineral acids ( $\text{ZnCl}_2$ ) is used in order to increase the surface area of carbon materials [15,16]. Usually, temperatures from  $650$  to  $950^\circ\text{C}$  were used [15,16]. Nevertheless, these methods can produce a high quantity of acid wastes (sulfur and metal compounds) that are not environmentally acceptable due to the potential risk of water and air pollution. Therefore, the use of mineral acids is not attractive. In this work, physical activation using air at low temperatures was performed. Several works have studied the removal of different water organic compounds like dyes [18], phenol or carmine [19] using carbon-based adsorbents obtained from sewage sludge, but there are not enough works that study metal adsorption by these cheap materials.

The main objective of this work was to prepare carbon-based adsorbents from sewage sludge using low pyrolysis temperatures and activation with air. Pyrolysis of 10 sewage sludges (5 anaerobic and 5 aerobic) was performed at  $450^\circ\text{C}$  during 1 h. Then, the two pyrolysed materials with the highest carbon content from anaerobic and aerobic sludges were selected for air activation at  $275^\circ\text{C}$  and use for the  $\text{Fe}^{3+}$  removal.

## 2. Experimental

### 2.1. Sewage sludge characterisation

Five anaerobic and five aerobic sewage sludges from different wastewater treatment plants of Madrid region (Spain)

were used for the production of carbon-based materials. First, samples of sewage sludges were air-dried, crushed and sieved through 2 mm mesh. Then, sludges were characterised according to their total humified substances (HA + FA), humic acids (HA), fulvic acids (FA) and pH. A subsamples of the sewage sludges for determination of the total carbon content (TC), the total content of Cr, Ni, Cu, Zn, Cd and Pb (T) and for sequential extraction to measure organically bound metal fractions were crushed and sieved through 0.074 mm mesh [20].

Total organic matter (TOM) of sewage sludges was determined by burning at  $540^\circ\text{C}$  [21]. Total carbon (TC) was calculated from the weight of sample before and after its oxidation at  $950^\circ\text{C}$ . Total humic substances (THS) were extracted with a mixture of 1 M  $\text{Na}_4\text{P}_2\text{O}_7$  and 0.1 M NaOH, centrifuged at 3000 rpm and filtered using Whatman No. 42 filters [22]. An aliquot of this extract was acidified with concentrated  $\text{H}_2\text{SO}_4$  to pH 1, centrifuged to separate coagulated humic acids (HA) and then, the HA were re-dissolved with 0.1 M NaOH [23]. The non-coagulated fraction with  $\text{H}_2\text{SO}_4$  is referred to as fulvic acids (FA) and it was calculated as the difference between THS and HA. The C contents of the THS and HA were determined by the Walkley–Black method [24] after being dried in a thermostatic bath at  $60^\circ\text{C}$ . pH was measured after stirring a mixture of sewage sludge and distilled water (4 g/L) for 2 h.

Total sewage sludges content in Cr, Ni, Cu, Zn, Cd, Pb were extracted with HCl and  $\text{HNO}_3$  following 3051a USEPA method [25]. Metals bound to organic matter ( $M_{\text{OM}}$ ) were determined by Tessier method [26].  $M_{\text{OM}}$  were released with 30%  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$ , pH 2.0 at  $85^\circ\text{C}$ . After cooling, 3.2 M  $\text{NH}_4\text{OAc}$  in 20% (v/v)  $\text{HNO}_3$  was added to prevent adsorption of extracted metals onto the oxidized sediment [26]. Metals in extracts were measured by Perkin Elmer 403 atomic absorption spectrophotometer.

Three replicates for each determination were performed. The statistical significance of the results obtained was assessed by multiple ANOVA (Duncan's multiple range tests) with a probability level of 95%.

### 2.2. Thermogravimetric analysis of sewage sludges

Thermogravimetric analysis at  $950^\circ\text{C}$  was achieved in a thermogravimetric equipment Mettler TA 4000 thermal analyser under nitrogen atmosphere. Thirty mg samples were heated at  $10^\circ\text{C min}^{-1}$  up to  $950^\circ\text{C}$  using a nitrogen flow rate of  $25 \text{ mL min}^{-1}$ . Carbon yield was calculated from the weight of carbonised residue after pyrolysis at  $950^\circ\text{C}$ . Weight loss of sewage sludge at intermediate carbonization temperatures (300, 450 and  $900^\circ\text{C}$ ) was calculated. Two replicates of the thermogravimetric analysis were performed.

### 2.3. Preparation of pyrolysed materials

Pyrolysis at  $450^\circ\text{C}$  was performed in a vertical furnace. Ten grams of sample was put in a glass reactor in the middle

of the vertical electric furnace and heated at  $10\text{ }^{\circ}\text{C min}^{-1}$  up to  $450\text{ }^{\circ}\text{C}$ . This temperature was maintained for 1 h using a nitrogen flow rate of  $150\text{ mL min}^{-1}$  during all the experiment. Pyrolysis yield (PY) was calculated from the sample weight before and after heat treatment at  $450\text{ }^{\circ}\text{C}$ . Two replicates of the sewage sludges pyrolysis were performed.

#### 2.4. Characterisation of pyrolysed materials

Carbon residues obtained after pyrolysis of sewage sludges at  $450\text{ }^{\circ}\text{C}$  were characterised according to their pH (Section 2.1) and total carbon content (TCp). TCp was calculated from the weight of sample before and after their oxidation at  $950\text{ }^{\circ}\text{C}$ . The ratio  $D$  (%) between total carbon content of corresponding pyrolysed materials (TCp) and total carbon of sewage sludges (TC) would be indicative of the carbon enrichment during pyrolysis. The ratio  $D$  (%) was calculated as follows:

$$D(\%) = (\text{TC}_{Pi}/\text{TC}_i) \times 100$$

where  $\text{TC}_{Pi}$  is the total carbon content of carbon-based material obtained from pyrolysis, of sewage sludge  $i$  and  $\text{TC}_i$  the total carbon content of sewage sludge  $i$ .

The two pyrolysed samples with the highest TCp content from the aerobically and anaerobically stabilized sewage sludges were selected for further characterisation (surface area and infrared analysis). The textural characterisation of the pyrolysed materials was based on  $\text{N}_2$  adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. The micropore volumes ( $W_0$ ) and mesopore surface areas ( $S_{\text{meso}}$ ) were determined by the  $t$ -method using a standard isotherm for carbon materials. The DRIFTS spectra were obtained without sample dilution in a Nicolet 510P spectrophotometer equipped with a diffuse reflectance attachment. The samples were finely ground in a mortar prior this analysis.

#### 2.5. Air-activation of pyrolysed materials

The two pyrolysed materials with the highest carbon content from anaerobic and aerobic sludges were selected for air activation. Due to the low temperatures used during pyrolysis of sewage sludges ( $450\text{ }^{\circ}\text{C}$ ), the activation of corresponding pyrolysed materials was performed at lower temperatures using air as physical activator. Carbon-based materials obtained after pyrolysis of sewage sludges were put in a glass reactor and heated at  $10\text{ }^{\circ}\text{C min}^{-1}$  up to  $275\text{ }^{\circ}\text{C}$ . This temperature was maintained for 4 h. The  $\text{O}_2$  flow rate used during the activation was  $5\text{ mL min}^{-1}$ , using a total flow rate of  $150\text{ mL min}^{-1}$  of  $\text{N}_2/\text{O}_2$ .

#### 2.6. Characterisation of air-activated carbon-based materials

Carbon-based adsorbents prepared from air activation of pyrolysed materials were characterised according to their pH,

total carbon content and surface area following the methodology described in Section 2.4. Infrared analysis was performed in order to characterise the status of the surface groups after air activation. The DRIFTS spectra were obtained without sample dilution in a Nicolet 510P spectrophotometer equipped with a diffuse reflectance attachment. The samples were finely ground in a mortar prior this analysis.

#### 2.7. Metal removal

The two air-activated carbon-based adsorbents were used for the removal of  $\text{Fe}^{3+}$ . Standard solution of  $100\text{ mg L}^{-1}$  of  $\text{Fe}^{3+}$  was prepared using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Panreac). The pH of solution was adjusted with HCl to pH 2 in order to avoid metal precipitation. To evaluate metal adsorption, 100 mL of the solution was mixed with 0.5 g of each carbon-based adsorbents and agitated during 1 h at 300 rpm. After this time, solutions were filtered to remove suspension particles and the metal final concentrations were evaluated by atomic absorption using a Perkin Elmer 2280 atomic absorption spectrophotometer.

Also, content in Cd, Zn, Cu, Pb, Ni, Cr and Fe of the filtrated solutions was determined by Perkin Elmer 2280 atomic absorption spectrophotometer and the organic matter of the filtrated solutions was analysed by Walkley–Black method [24].

### 3. Results and discussion

#### 3.1. Characterisation of sewage sludges

Table 1 shows the main characteristics of 10 sewage sludges used in this work.

##### 3.1.1. Organic matter

The total organic matter content (TOM) of sewage sludges was obtained by burning of samples at  $540\text{ }^{\circ}\text{C}$ . Organic mat-

Table 1  
Basic characteristics of sewage sludges<sup>a</sup>

Sewage sludge	Stabilization treatment	H (%) <sup>b</sup>	TOM (%) <sup>c</sup>	TC (%) <sup>d</sup>	pH
1	Aerobic	11.5 c	48.4 e	58.0 e	6.7 b
2		12.9 c	72.4 a	76.0 a	6.4 d
3		4.4 a	39.3 f	63.0 cd	6.7 b
4		6.5 a	59.8 b	65.0 c	6.5 c
5		5.5 a	46.5 e	52.0 f	6.5 c
6	Anaerobic	23.2 e	54.4 c	64.8 c	6.2 e
7		28.6 f	58.0 b	61.8 d	6.3 e
8		9.9 b	60.4 b	67.2 b	7.0 a
9		16.5 d	60.4 b	67.0 b	5.7 f
10		17.0 d	51.6 d	59.0 e	6.6 b

<sup>a</sup> Values in a given column followed by the same letter are not significantly different ( $P=0.05$ ) using Duncan's test.

<sup>b</sup> Moisture content.

<sup>c</sup> Total organic matter content (%).

<sup>d</sup> Total carbon (%).

ter is expected to play an important role in the pyrolysis of sewage sludges because organic matter undergoes physical and chemical transformations during thermal treatment. The TOM of anaerobically stabilized sludges ranged from 51.6 to 60.4 wt.%, whereas higher differences were found within aerobically stabilized group of sludges. Their TOM ranged from 39.3 (sludge 3) to 72.4 wt.% (sludge 2). In case of sewage sludge 3, its lower organic matter value (39.3 wt.%) led to the lower water content (4.4 wt.%). Generally, it is accepted that organic matter has a high influence on water retention and consequently, sewage sludges with high organic matter lead to higher water adsorption. Indeed, organic matter can directly affect water retention because of its ability to absorb up to 20 times its mass of water [27]. This direct effect depends on the quantity present and morphological structure of the organic materials [28,29]. However, there are other factors like silica or alumina content that can affect the water adsorption of sewage sludges.

### 3.1.2. pH

pH of solid compounds is related to the presence of surface functional groups, specially carboxylic acids, and the ash content. Table 1 shows the pH of the different sludges. According to these data, the lowest pH value corresponded to sewage sludge 9 (pH 5.7), whereas sludge 8 showed the highest pH (pH 7.0).

### 3.1.3. Fulvic and humic acids

Table 2 shows the fulvic (FA) and humic (HA) acids contents of all sludges. Fulvic acids are the low-molecular-weight fraction that contains the highest amount of oxygen in the form of carboxylic acids, ketone and hydroxyl groups, but lower carbon content [30]. These compounds are soluble in acid solutions [22]. On the other hand, the humic acids consist of micelles of a polymeric nature with aromatic groups and less carboxylic groups than fulvic acids [30]. Therefore, fulvic acids are less evolutioned than humic acids [23] and it can be expected that fulvic acids will be more reactive dur-

ing pyrolysis treatment of sewage sludges due to their higher content of oxygenated functional groups [30]. The FA content was higher than HA for all sewage sludges used in this work (Table 2). The highest FA content for the aerobically and anaerobically stabilized sludges correspond to sewage sludge 2 (SL-2) and sewage sludge 8 (SL-8), respectively (11340 and 7603 mg C/g). The HA/FA ratio is a measure of the evolution and polymerisation degree of sewage sludges and will be named as polymerisation index. In general, the value of polymerisation index (HA/FA) for all sludges was normal for this type of residues [31]. The highest FA + HA value corresponded to SL-2 (14465 mg C/100 g), whereas the lowest content was obtained in case of SL-7 (4990 mg C/100 g). Similar FA + HA values were obtained for SL-6 and SL-10 (6440 and 6620 mg C/100 g, respectively) but the polymerisation index of both sludges was very different (0.53 and 0.32, respectively).

### 3.1.4. Metals

The differences in the organic composition of aerobic and anaerobic sewage sludges discussed above were expected to play an important role in their pyrolysis behaviour. However, it is interesting to study other factors such as the metal content of sludges. It is accepted that some additive metals have a high influence on the pyrolysis behaviour of organic matter. Previous works have shown that the presence of metals can decrease the evolution of volatiles in the pyrolysis of organic polymers [32]. Therefore, it could be interesting to study the heavy metals bound to organic matter. This fraction was expected to have a higher influence on the pyrolysis of sewage sludges than the fraction bound to the inorganic salts. Table 3 summarises total content on Cr, Ni, Cu, Zn, Cd, Pb and their fractions bound to organic matter ( $M_{OM}$ ).

Generally, the most abundant metal was Zn with values ranging from 764.3 (SL-8) to 1274.4 mg/kg (SL-5), except for the SL-7 that had a high Cu content (1509.1 mg/kg). On the other hand, the less abundant metal was Cd with values from 1.28 to 1.8 mg/kg for SL-9 and SL-7, respectively. The metals contents did not exceed limit values for concentrations of metals in sludges fixed by European Regulations [33]. In general, the percentage of metals bound to organic matter with respect to the total metal content is according to stability order of organic-heavy metal complexes described previously by others authors [34,35]. The results show that the percentages of metals bound to organic matter are low, except for Cu and Cr (Table 3). These two metals were mostly bound to organic matter.

### 3.2. Thermogravimetric characterisation of sewage sludges

Previous works have shown that pyrolysis of sewage sludges leads to carbonaceous residues that can be used as cheap carbon-based adsorbents [18,19]. The properties of the final residue depend on the experimental conditions and the characteristics of raw materials used. During the heat treat-

Table 2  
Humic and fulvic acids contents in sewage sludges<sup>a</sup>

Sewage sludge	HA <sup>b</sup> (mg C/100 g)	FA <sup>c</sup> (mg C/100 g)	HA/FA <sup>d</sup>
1	2775 b	3579 f	0.77 a
2	3125 a	11340 a	0.28 f
3	2850 b	8130 b	0.35 e
4	1613 d	7920 b	0.21 g
5	2775 b	4240 e	0.65 b
6	2250 c	4190 e	0.53 c
7	1200 e	3790 f	0.32 e
8	2775 b	7603 c	0.36 e
9	2250 c	5262 d	0.43 d
10	1588 d	5032 d	0.32 e

<sup>a</sup> Values in a given column followed by the same letter are not significantly different ( $P = 0.05$ ) using Duncan's test.

<sup>b</sup> Humic acid content.

<sup>c</sup> Fulvic acid content.

<sup>d</sup> Polymerisation index.



Table 3  
Total metals content and fraction bound to organic matter

Sewage sludge	Cd		Zn		Pb		Cu		Ni		Cr	
	$T^a$ (mg/kg)	$M_{OM}^b$ (mg/kg)	$T$ (mg/kg)	$M_{OM}$ (mg/kg)	$T$ (mg/kg)	$M_{OM}$ (mg/kg)	$T$ (mg/kg)	$M_{OM}$ (mg/kg)	$T$ (mg/kg)	$M_{OM}$ (mg/kg)	$T$ (mg/kg)	$M_{OM}$ (mg/kg)
1	1.98 ± 0.01	<0.01 <sup>c</sup>	827.9 ± 5.3	35.2 ± 3.4	142.9 ± 8.5	<0.1	212.7 ± 10.2	126.9 ± 9.8	28.7 ± 3.2	0.10 ± 0.01	63.7 ± 6.7	18.1 ± 2.4
2	1.63 ± 0.02	<0.01	1185.3 ± 12.4	39.7 ± 4.0	48.6 ± 3.2	1.1 ± 0.1	199.4 ± 10.0	139.5 ± 8.7	24.7 ± 2.0	0.12 ± 0.01	28.2 ± 3.2	18.9 ± 2.1
3	1.88 ± 0.02	<0.01	1140.0 ± 11.2	127.5 ± 11.2	250.1 ± 10.0	0.8 ± 0.1	267.2 ± 11.4	248.1 ± 10.1	49.6 ± 4.0	0.21 ± 0.02	31.8 ± 4.1	14.9 ± 1.8
4	1.98 ± 0.01	0.03	1159.1 ± 10.0	77.4 ± 8.7	175.4 ± 9.7	<0.1	280.5 ± 11.0	231.0 ± 9.6	30.5 ± 2.7	<0.01	255.1 ± 10.1	195.4 ± 8.9
5	2.33 ± 0.03	<0.01	1279.4 ± 12.6	124.0 ± 11.3	128.6 ± 7.5	<0.1	425.5 ± 15.2	366.6 ± 10.0	74.4 ± 3.9	0.33 ± 0.01	414.6 ± 13.2	288.9 ± 9.6
6	2.33 ± 0.03	<0.01	1188.9 ± 10.9	75.4 ± 7.6	139.6 ± 7.2	<0.1	465.4 ± 16.0	374.6 ± 9.9	24.7 ± 2.0	<0.01	22.2 ± 2.6	11.0 ± 1.0
7	1.108 ± 0.06	0.29 ± 0.01	791.9 ± 10.0	47.1 ± 4.3	974.9 ± 13.2	1.5 ± 0.1	1509.1 ± 19.8	1094.4 ± 12.7	393.3 ± 9.6	<0.01	637.9 ± 11.0	184.1 ± 10.1
8	1.98 ± 0.01	0.05 ± 0.01	764.3 ± 9.4	115.6 ± 9.8	165.6 ± 10.2	0.4 ± 0.1	259.2 ± 11.0	243.5 ± 11.0	36.3 ± 4.1	<0.01	70.1 ± 4.3	51.5 ± 5.3
9	1.28 ± 0.01	<0.01	899.9 ± 8.6	45.7 ± 4.3	136.4 ± 8.5	2.3 ± 0.1	150.8 ± 12.3	98.5 ± 7.4	24.7 ± 1.8	<0.01	19.0 ± 1.8	9.6 ± 0.9
10	1.63 ± 0.02	0.06 ± 0.01	784.7 ± 11.8	63.5 ± 6.5	113.6 ± 7.6	<0.1	224.7 ± 10.1	188.5 ± 6.8	30.2 ± 2.4	<0.01	31.8 ± 4.3	15.0 ± 1.2

Mean values ± standard deviation.

<sup>a</sup> Total metals content in sewage sludges.

<sup>b</sup> Content of metals fraction bound to organic matter.

<sup>c</sup> Concentration below detection level.

ment under inert atmosphere, the organic matter of sewage sludges undergo important physical and chemical transformations. Consequently, important weight variations were produced due to the distillation of light compounds and the polymerization/condensation reactions. Thermogravimetric analysis has been an interesting and useful analytical technique for the characterisation of different organic products such as pitches [36,37], sewage sludges [38] and other waste materials [39].

Previous works have shown that there are three fractions in the sewage sludges [40]. A small fraction composed of the biodegradable material that decomposes at temperatures lower than 300 °C. A large intermediate fraction corresponding to the organic polymers present in the cells and the polymers proceeding from the biological stabilization of sludges that decomposes between 300 and 450 °C. Finally, the third fraction decomposes above 450 °C and corresponds to the non-degradable material. Table 4 shows the weight loss of sewage sludges used at intermediate carbonization temperatures of 300, 450 and 900 °C. Generally, it can be observed that the weight loss of aerobic sewage sludges at temperatures lower than 300 °C is higher than in case of anaerobic. Consequently, aerobic sludges have more biodegradable compounds than anaerobic [40]. Another interesting result was the relation between the FA content and the weight loss produced at temperatures lower than 300 °C. The highest the FA content, the highest is the weight loss at lower temperatures. This fact shows that thermogravimetry is an interesting analytical technique to study the evolution and polymerisation degree of sewage sludges. According to previous works [38], the most important weight loss is produced at temperatures ranging from 300 to 450 °C, in all cases.

Figs. 1 and 2 show the thermogravimetric TG (a) and derivate thermogravimetric DTG (b) curves of aerobically and anaerobically stabilized sewage sludges, respectively. Comparison of Figs. 1 and 2 shows an interesting fact: sewage sludges representing anaerobic stabilization with less differences in their organic composition (Tables 1 and 2) had similar TG and DTG curves (Fig. 2a and b, respectively), whereas aerobically stabilized sludges showed important differences

Table 4  
Weight loss of sewage sludges at intermediate carbonization temperatures

Sewage sludge	WL <sup>a</sup> (%)		
	25–300 °C	300–450 °C	450–900 °C
1	15.7	17.2	12.2
2	19.2	24.4	12.4
3	15.2	25.1	13.5
4	18.6	22.7	13.7
5	14.7	17.5	11.9
6	7.0	18.5	9.7
7	0.3	21.0	10.7
8	13.7	21.1	13.8
9	10.1	22.4	12.8
10	5.5	19.5	13.2

<sup>a</sup> Weight loss at intermediate pyrolysis temperatures (%).

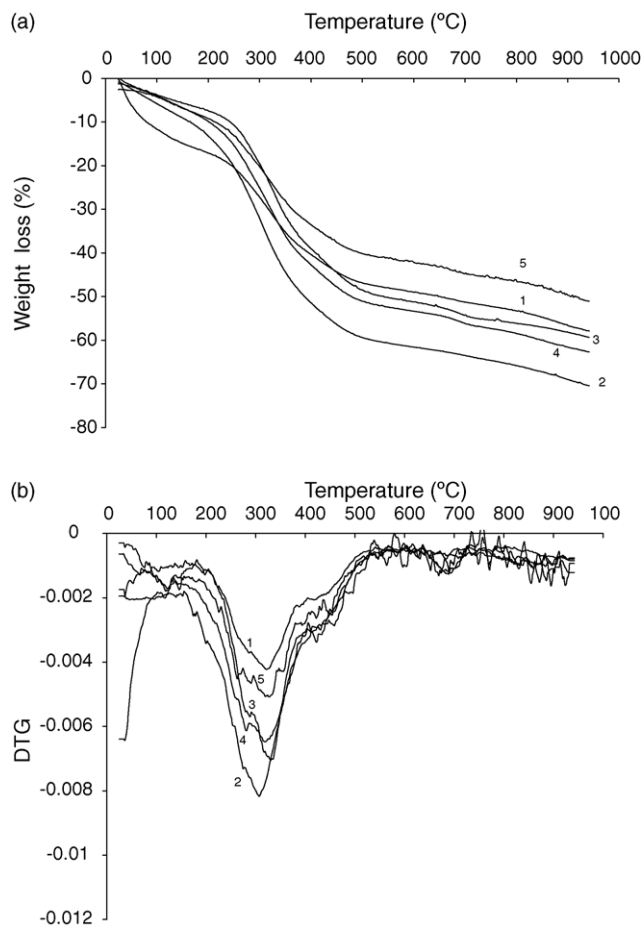


Fig. 1. TG (a) and DTG (b) analysis of aerobically stabilized sewage sludges.

in their organic composition and thermal behaviour (Fig. 1a and b).

Finally, Table 3 was compared with TG and DTG curves (Figs. 1 and 2) in order to study the possible influence of the metals in the pyrolysis of sewage sludges. It is necessary to note that no significant relation was found between total metals content (T) or metals bound to the organic fraction ( $M_{OM}$ ) with pyrolysis of sewage sludges. Previous works have shown that metals play an important role on the pyrolysis of sewage sludges [38]. After extraction of metals with acid solutions of pH 1–2, these authors found that in some cases, weight loss was retarded. Under experimental conditions used in these works, fulvic acids can be dissolved [22,23], so differences found in the pyrolysis after extraction of acids could be attributed to the extraction of fulvic acids too [41].

### 3.3. Preparation of carbon-based materials

Anaerobic and aerobic sewage sludges were pyrolysed in a vertical furnace at 450 °C during 1 h, in order to produce carbon-based materials. This temperature was selected according to previous results (Section 3.2). At 450 °C, the main important weight changes had been produced due to the light compounds volatilization and pyrolysis transforma-

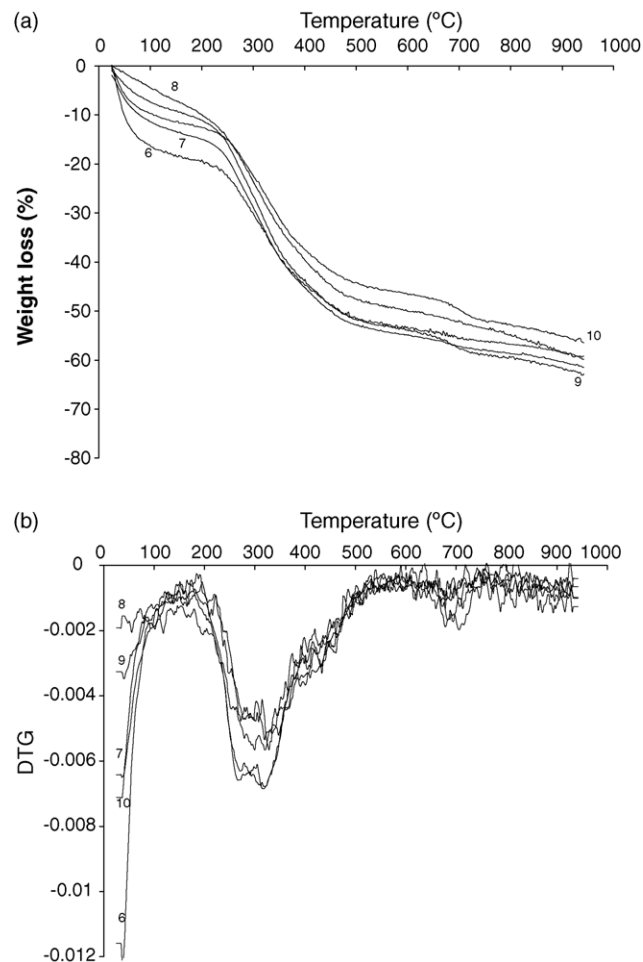


Fig. 2. TG (a) and DTG (b) analysis of anaerobically stabilized sewage sludges.

tions. Previous studies have shown that carbon content of carbon-based materials obtained from pyrolysis of sewage sludges and other organic precursors significantly decrease with the reaction temperature from 450 to 950 °C [13]. Therefore, economical and manufacturing factors recommend the use of lower pyrolysis temperatures.

Table 5 shows the pyrolysis yield (PY) and total carbon content (TCP) of pyrolysed materials. Pyrolysis yield varied from 39.4 (SL-2) to 59.2 wt.% (SL-5). Materials prepared from SL-2 and SL-8 had the highest TCP of aerobic (43.4 wt.%) and anaerobic (38.6 wt.%) sludges, respectively. It could be expected that sewage sludges with highest TOM (Table 1) lead to lower pyrolysis yields. Comparison between the TC of sewage sludges (Table 1) and the TCP of corresponding pyrolysed materials (Table 5) could give information about the different pyrolysis behaviours. Table 6 shows the ratio  $D$  (in %) calculated as shown in Section 2.3. Similar values were obtained for all sewage sludges (from 45.2 to 57.1 wt.%). The highest values of  $D$  (%) for aerobic and anaerobic sewage sludges corresponded to SL-2 (57.1%) and SL-8 (57.4%), respectively. These sludges had the highest FA of aerobic and anaerobic sludges, respectively (Table 2). Previ-

Table 5  
Pyrolysis yield (PY) and total carbon content (TC<sub>P</sub>) of pyrolysed materials<sup>a</sup>

Pyrolysed material	PY <sup>b</sup> (wt.%)	TC <sub>P</sub> <sup>c</sup> (wt.%)
P1	52.9 c	26.2 e
P2	39.4 f	43.4 a
P3	52.4 c	35.2 c
P4	49.4 d	34.8 c
P5	59.2 a	23.9 f
P6	45.9 e	30.5 d
P7	52.1 c	28.7 de
P8	47.8 d	38.6 b
P9	57.0 ab	35.6 c
P10	55.2 b	31.8 d

<sup>a</sup> Values in a given column followed by the same letter are not significantly different ( $P=0.05$ ) using Duncan's test.

<sup>b</sup> Pyrolysis yield of sewage sludges (wt.%).

<sup>c</sup> Total carbon content of pyrolysed materials (wt.%).

ous works carried out by our research group have shown this relation in case of anaerobic sewage sludges [41]. It must be pointed that the  $D$  (in %) clearly increased with the percentage of fulvic acids on aerobic (Fig. 3a) and anaerobic sewage sludges (Fig. 3b).  $D$  (in %) ratio correlated moderately well with the FA content ( $R^2 = 0.96$  and  $0.89$  for aerobic and anaerobic sewage sludges, respectively). This interesting result shows that FA could play an important role during pyrolysis of sewage sludges [41]. The highest amount of functional groups in the fulvic acids could make this fraction more reactive through pyrolysis treatment leading to higher carbon enrichment. These results could be of great importance for the preparation of carbon-based materials. In this way, it would be more interesting to choose less evolved sewage sludges with higher fulvic acids ratios.

Table 6 shows the pH of carbon-based materials. All values were higher than 6.5 (distilled water) and consequently, carbon-based materials were basic. Previous works have shown that independently of the pyrolysis conditions, all the solid carbonaceous residues have basic nature [13]. The increment of the pH with respect to raw sewage sludges (Table 1) was indicative of dehydrogenative polymerization and polycondensation reactions with significant loss of

Table 6  
Carbon enrichment of sewage sludges ( $D$ , %) and pH of carbon-based materials<sup>a</sup>

Sewage sludge	$D$ <sup>b</sup> (%)	pH
1	45.2 d	7.1 e
2	57.1 a	7.9 b
3	55.9 b	7.8 bc
4	53.6 c	7.6 cd
5	46.0 d	7.7 c
6	47.1 d	7.9 b
7	46.4 d	7.9 b
8	57.4 a	8.1 a
9	53.1 c	7.9 b
10	53.9 c	7.8 bc

<sup>a</sup> Values in a given column followed by the same letter are not significantly different ( $P=0.05$ ) using Duncan's test.

<sup>b</sup> Carbon enrichment ratio of sewage sludges during pyrolysis.

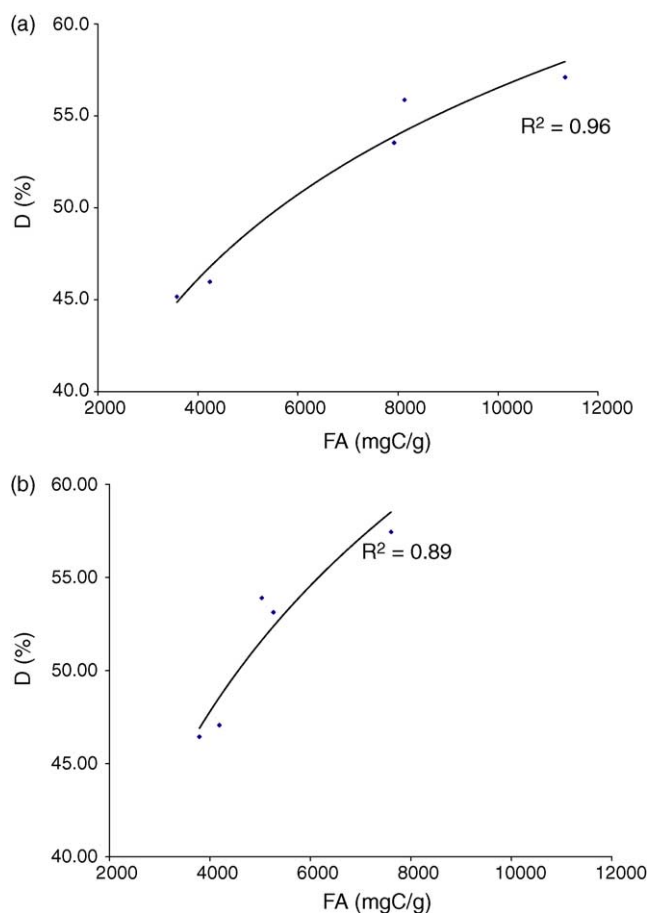


Fig. 3. Carbon enrichment ratio ( $D$ ) vs. FA content for aerobically (a) and anaerobically stabilized (b) sewage sludges.

oxygen-containing structures and is related with the increment in ash content.

Sludges 2 and 8 are the most interesting for the preparation of carbon-based materials according to results shown above and were selected for subsequent air activation and characterisation. The surface chemistry of the carbon-based materials P2 and P8 obtained from pyrolysis of sewage 2 and 8, respectively, was also studied by FTIR spectroscopy. The absorption bands and peaks provided the evidence of some surface functional groups. Experimental results are presented in Fig. 4. Inspection of Fig. 4 shows that there are three bands of interest: one broad band at  $980\text{--}1450\text{ cm}^{-1}$  associated with C–O stretching in ethers, phenols, lactones, carboxylic acids and carboxylic anhydrides, one at  $1500\text{ cm}^{-1}$  associated with C=C stretching in aromatic rings, quinones and keto-enols and one band at  $1700\text{ cm}^{-1}$  associated with C=O stretching in lactones and carboxylic anhydrides [42,43].

### 3.4. Activation of carbon-based materials

Carbon-based materials obtained from pyrolysis of sewage sludges could be used as cheap adsorbents. In order to achieve that, it is necessary to improve the porosity of the materials. Physical activation with air is proposed in this work.

Table 7  
Total carbon content (TC), pH and surface area of carbon-based materials P2 and P8 with corresponding activated adsorbents P2A4 and P8A4<sup>a</sup>

Carbon-based material	TC (wt.%)	pH	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$W_0$ (cm <sup>3</sup> /g)	$S_{\text{meso}}$ (m <sup>2</sup> /g)
P2	43.4 a	7.9 a	16 c	0.004 c	6 a
P2A4	39.2 b	7.8 ab	102 a	0.040 a	19 b
P8	38.6 b	8.0 a	81 b	0.024 c	26 c
P8A4	37.7 b	7.7 b	105 a	0.040 a	13 d

<sup>a</sup> Values in a given column followed by the same letter are not significantly different ( $P=0.05$ ) using Duncan's test.

This method is cheaper and more environmentally acceptable than chemical activations. Activation of both materials (P2 and P8) was performed in a vertical furnace using 5 mL/min of O<sub>2</sub> and 145 mL/min of N<sub>2</sub>. The activation temperature was 275 °C which was maintained for 4 h, leading to P2A4 and P8A4 materials, respectively. Table 7 shows the pH, total carbon (TC), BET surface area, micropore volume ( $W_0$ ) and meso- and macropore surface area ( $S_{\text{meso}}$ ) of carbon-based materials P2 and P8 and the corresponding activated carbon-based adsorbents (P2A4 and P8A4). The pH decreased with activation as a consequence of the introduction of oxygen functional groups. This was in agreement with DRIFTS spectra shown in Fig. 4. During air activation at 275 °C, oxygen functional groups such as carboxylic acids and anhydrides, lactones, phenols, ethers, quinines and keto-enols were introduced as shown by the increase in intensity of the characteristic DRIFTS bands.

It was also interesting to compare the carbon content of carbon-based materials P2 and P8 with the corresponding activated adsorbents. The total carbon content (TC) decreased due to their activation with air, especially for material P2 (from 43.4 to 39.2 wt.%). This result could indicate that oxidation with air was more effective in case of carbon-based

Table 8  
Percentage of Fe<sup>3+</sup> adsorption<sup>a</sup>

Carbon-based material	Initial concentration (mg L <sup>-1</sup> )	Final concentration (mg L <sup>-1</sup> )	Fe retention (%)
P2A4	100	35.0 a	65.00 a
P8A4	100	0.3 b	99.70 b

<sup>a</sup> Values in a given column followed by the same letter are not significantly different ( $P=0.05$ ) using Duncan's test.

material obtained from sludge 2. So, a higher increment in the BET surface area was produced with activation of P2 with air during 4 h, raising the surface area from 16 to 102 m<sup>2</sup>/g.

The activation process increases the micropore volume and the mesopore surface area, as we can observe in Table 7, except for sample P8A4, where a decrease in  $S_{\text{meso}}$  was observed. This decrease is explained by the collapse of some mesopores with burn-off. We also can say that the increase in surface area is a consequence of the formation of new micropores in the activation process.

### 3.5. Iron removal

Previous works carried out by our group have shown that carbon-based materials obtained from sewage sludges pyrolysis could be used for the Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> removal [41]. In this work, P8A4 and P2A4 materials were used for the removal of Fe<sup>3+</sup>. Higher removal value was obtained using P8A4 than P2A4 (Table 8). This fact demonstrate that these materials can be used as cheap adsorbents to eliminate metals in water. Also, it is necessary to note that these carbon-based adsorbents were not soluble in water and no metal lixiviation was observed according to previous works [44].

## 4. Conclusion

Pyrolysis of sewage sludges and air activation of pyrolysed materials using low temperatures (450 and 275 °C, respectively), is an inexpensive and environmentally alternative to the production of carbon-based adsorbents with BET surfaces areas >100 m<sup>2</sup>/g. However, a more detailed study of this method would be necessary in order to improve the properties of final carbon-based materials.

Carbon-based adsorbents with higher carbon content were obtained from pyrolysis of sewage sludges of higher fulvic acid content. The fulvic acids fraction seems to play an important role in the production of carbon-based adsorbents from sewage sludges.

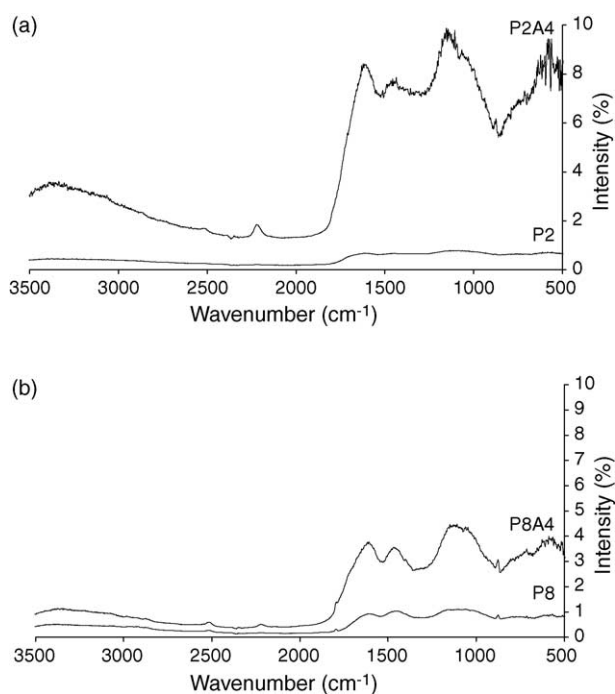


Fig. 4. DRIFTS spectroscopy of P2, P2A4 (a) and P8, P8A4 (b).



The air activation process increases the micropore volume of carbon-based adsorbents.

Carbon-based adsorbents obtained in this work lead to elevated  $\text{Fe}^{3+}$  removal (65.0 and 99.7% for P2A4 and P8A4, respectively) from water.

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