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Preparation of carbon-based adsorbents from the pyrolysis of sewage sludge with CO_2. Investigation of the acid washing procedure

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ABSTRACT

Carbon-based adsorbents were prepared through the physical activation of sewage sludge with CO_2. The effect of the acid treatment was investigated, either before or after the physical activation. The post-washing increases the porosity due to the removal of the inorganic fraction and the improvement in the accessibility of the carbon fraction. The post-washing is essential for high activation temperatures since the high reactivity of CO_2 leads to a high pore blockage. In fact, the material activated at 900˚C has a very low surface area (43 m^2/g), while after washing it reaches 654 m^2/g. The effect of the acid treatment prior to the physical activation depends on temperature: at 600˚C, it results in a huge pore development (mainly macropores), while at 900˚C, the microporosity increases. The adsorption capacity is not directly related to the BET surface area. For both adsorbates, the uptake ability depends on the textural properties (it is favoured by mesoporosity for methylene blue (MB) and microporosity for phenol) and surface chemistry (favourable effect of oxygen- and nitrogen-containing functional groups for MB and unfavourable effect for phenol).

Keywords: Sewage sludge; Acid washing; Adsorption; Phenol; Methylene blue

1. Introduction

Sewage sludge is an unavoidable by-product from wastewater treatment plants. In the last decades, its amount has rapidly increased with the urbanization and industrial development. Furthermore, sewage sludge is mainly composed of the substances responsible for the toxic and pathogenic characteristics of untreated wastewater. Consequently, its handling and disposal is an issue of great concern. The traditional methods to utilize or dispose sewage sludge include landfilling, energy recovery from incineration and composting for farmland application [1]. Nevertheless, these methods have serious limitations. Farmland application is limited by the potential pollution of the metals present in sewage sludge. Incineration is expensive, requires a strict control to prevent the emission of pollutants to the atmosphere [2] and gives way to significant amounts of potentially hazardous ash [1]. Landfilling will not be sustainable in the long

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term as a consequence of the increasing competition for land and more stringent environmental standards. Thus, the development of environmentally friendly solutions is of main interest. One promising alternative, from an environmental and economic point of view, is the conversion of sludge into carbon-based adsorbents [3,4].

Several attempts have been done to prepare effective adsorbents from sewage sludge. The preparation method includes the chemical activation with different reagents: H_2SO_4 [3,4], H_3PO_4 [5,6], KOH [5,7], NaOH [5], $ZnCl_2$ [6,8] and K_2CO_3 [9]. Physical activation has been performed using gasifying agents, such as steam [9], air [10] and CO_2 [5,9,11].

Physical activation can develop the porous structure of the material through various processes. During the heating stage, pores are formed through: (i) the loss of water and decomposition of organic matter [12,13] and (ii) the thermal decomposition of inorganic components, such as salts, which are released as gaseous products [14]. Furthermore, the gasifying agent leads to a progressive burn-off of the carbon fraction, which is useful to enhance the micropore structure [15]. The data in the literature suggest that steam is a better physical activation agent than CO_2 [12]. Nevertheless, it should be taken into account that CO_2 has lower reactivity than H_2O due to: (i) its larger molecular size, which hinders its diffusion through the porous network, and (ii) the more endothermic nature of its reaction with carbon (159 vs. 117 kJ/mol) [16].

The high inorganic content of sewage sludge, which is essentially non-porous, limits the development of a highly textured material. The specific surface area of sludge-based carbons can be greatly improved by acid washing, which leads to the partial removal of the inorganic fraction [5,13]. It has been reported that HCl treatment prior to physical activation is more effective than post-activation washing [5]. A possible explanation is the increase in the stability of the inorganic fraction. Indeed, high temperatures can convert the inorganic fraction into mineral-like compounds and induce the encapsulation of some metals by the carbon phase [17]. The partial removal of the inorganic fraction prior to physical activation would limit this phenomenon, thus resulting in a material with higher porosity.

This paper approaches the preparation of adsorbents through the physical activation of sewage sludge with CO_2. The activation process has been carried out at two temperature levels: 600 and 900℃. The highest temperature studied is higher than those commonly used in the literature (maximum of 800℃) [10,11,18], and has been selected to investigate whether an increased temperature favours the occurrence of the reaction of CO_2 with carbon, thus resulting in a better development of the porous structure. The lowest pyrolysis temperature (600℃) has been chosen to investigate the suitability of using a moderate value, which in conjunction with a suitable acid treatment could result in a cost-effective preparation protocol. On the other hand, the improvement of surface area by acid washing has been investigated. In this work, the effect of the acid treatment sequence (either before or after the physical activation of sludge) has been studied in order to improve the development of porosity. Moreover, a preliminary study of the activation mechanism has been made, using thermogravimetric analysis coupled to mass spectrometry. Finally, the performance of the materials in the removal of water pollutants (methylene blue (MB) and phenol) has been evaluated.

2. Experimental

2.1. Materials

Anaerobically digested and dewatered sewage sludge was collected from an urban wastewater plant. Raw sludge was dried in a convection oven at 105℃ for 48 h to achieve constant weight. Table 1 shows the proximate analysis of raw sludge. It is observed that sludge has high water content and a similar percentage of ash and volatile matter (42.2 and 49.2 wt%, respectively). The percentage of fixed carbon (8.6 wt%) is relatively low.

Dried sludge was analysed by thermogravimetry (TG) using a SDT 2960 thermobalance (T.A. Instruments), under a nitrogen atmosphere. The thermal analyzer exhaust gases were monitored online by means of an EM Thermostar mass spectrometer (Balzers Instruments). The operating procedure was as follows: the alumina crucible of the thermobalance was loaded with 15–20 mg of sample. Temperature was increased from room temperature to 1,000℃ at a heating rate of 10℃/min, under a nitrogen atmosphere.

2.2. Preparation of sludge carbon

The preparation protocol of sludge carbon was as follows. Dried sludge was grinded and sieved, and particles within the 0.5–1.0-mm range were selected. Physical activation was conducted in a CO_2 atmosphere (120 cm^3/min of flowing gas, corresponding to 8 min of residence time in furnace), using a quartz tube furnace. Sludge was heated from room temperature to 600 or 900℃ at a rate of 15℃/min. Samples were soaked at the final temperature for 30 min, and then cooled down in a N_2 atmosphere. Samples of

Table 1
Proximate analysis of raw dewatered sewage sludge (wt%). Results are expressed on a dry basis, except for water content

Constituents	Moisture	Volatile matter	Fixed carbon	Ash
Value	73.3	49.2	8.6	42.2

sludge carbon were coded according to the pyrolysis temperature: SC-600 and SC-900.

A set of physically activated samples was thoroughly washed with 3-M HCl, at a ratio of 30 $\mathrm{mmol_{HCl}/g_{carbon}}$ for 48 h. Another set of samples was washed with acid (HCl 3 M) prior to carbonization with CO_2, using operating conditions similar to those used in the post-activation washing. Those samples were not washed with water before the activation with CO_2 in order to take advantage of the effect of the acid during the heating process. Consequently, those samples undergo a combined physical and chemical activation process. Prior to their use in adsorption experiments, all samples were extensively washed in a fixed bed with 600 bed volumes of distilled water, until a constant pH was obtained.

Samples of acid-washed sludge carbon were coded indicating the temperature used for the physical activation, and if acid washing was performed prior (P) or after (A) physical activation: SCP-600, SCP-900, SCA-600 and SCA-900.

2.3. Characterization of sludge carbon

The textural properties of the prepared adsorbents were measured by nitrogen adsorption/desorption at 77 K (ASAP 2010, Micromeritics). Prior to the measurements, samples were outgassed at 200℃ under nitrogen flow for 15 h. The specific surface area of the materials was determined by the Brunauer–Emmett–Teller (BET) method. The micropore area and volume were obtained using the *t*-plot method. Mesopore and macropore values were measured based on the Barrett, Joyner and Halenda (BJH) method.

The acidity/basicity of the prepared samples of sludge carbon was determined based on the method proposed by Tessmer et al. [19]. One gram of carbon and 35 cm^3 of distilled water were equilibrated for 3 d in a 100-cm^3 Erlenmeyer flask, in a horizontal shaker. After this period, the pH of the slurry was determined. Fourier transform infrared (FTIR) measurements were performed using a Thermo Nicolet 6700 device in the absorbance mode, using the KBr self-supported pellet technique. Spectra were collected in the 400–4,000 cm^{-1} range with a resolution of 2 cm^{-1}. The ash content (percentage of inorganic fraction) of the materials was measured by heating the samples at 815℃ under air atmosphere for 1 h (UNE 32004 standard).

2.4. Adsorption tests

MB and phenol were selected as target adsorbates because of their different molecular size and physicochemical properties (Table 2). For adsorption experiments, samples of sludge carbon (about 10–15 mg) were contacted in stoppered glass bottles with 10 cm^3 of aqueous solutions of MB, in the 25–100 mg/L range, or phenol, in the 25–250 mg/L range. The flasks containing the suspension were shaken for 72 h using a rotary mixer placed in a thermostatic chamber at 20 ± 0.5℃. Preliminary adsorption tests indicated that a holding time of 72 h is enough for the suspension to reach equilibrium. After 72 h, samples were centrifuged and the residual concentration of solute in the supernatant was analysed by UV–vis spectrophotometry (Jasco V-630). The concentration of MB and phenol was estimated by recording UV absorbance at a wavelength of 662 and 270 nm, respectively. The spectrophotometer was calibrated with standard MB and phenol solutions.

The adsorption capacity of sludge carbons (q_e, mg/g) was calculated by mass balance:

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of the adsorbate (mg/L), respectively. V is the solution volume (l) and m is the adsorbent mass (g).

The adsorption isotherms of both adsorbates were determined. Equilibrium data were fitted to the Langmuir (2), Freundlich (3) and Redlich–Peterson (4) equations, which are the most frequently used models:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

$$q_e = K_F C_e^{1/n} \tag{3}$$

$$q_e = \frac{K_R C_e}{1 + \alpha C_e^{\beta}} \tag{4}$$

Table 2
Characteristics of the adsorbates

Adsorbates	Molecular size width (nm) × length (nm) × thickness (nm)	Indicative of the presence of	Acidity/basicity
Methylene blue (MB)	0.740 × 1.690 × 0.380	Large micropores and mesopores	Basic
Phenol	0.638 × 0.792 × 0.822	Small micropores	Acid

where q_m is the monolayer adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), K_F is the Freundlich constant ((mg/g) (L/mg)$^{1/n}$), n is a constant representing the adsorption intensity (dimensionless), K_R is the Redlich–Peterson constant (L/g), α is a constant having units of (L/mg)$^{\beta}$ and β is an exponent that lies between 0 and 1.

The best fitting parameters of these equations were calculated by non-linear regression. The goodness of fit between the experimental and predicted values was determined by means of the average percentage error (APE):

$$\mathrm{APE} = \frac{\sum_{i=1}^{N} |(q_{e,\exp} - q_{e,\mathrm{pred}})/q_{e,\exp}|}{N} \times 100 \tag{5}$$

where $q_{e,\exp}$ is the experimentally measured uptake capacity, $q_{e,\mathrm{pred}}$ is the model-predicted uptake capacity and n is the number of experiments used for model development.

3. Results and discussion

3.1. Characterization of raw sludge

Fig. 1(a) shows the behaviour of raw sewage sludge under nitrogen atmosphere (TG and DTG curves). The process of weight loss (52.4 wt%) could be divided into several steps. The initial weight loss (below 175˚C) corresponds to the evaporation of adsorbed water and capillary water. The main weight loss (35.3%) occurs in the 175–550˚C temperature range. This step is attributed to the release of constitution water, as well as to the decomposition and volatilization of organic matter [20]. The decomposition of carbon-containing compounds results in the production of tar, CO_2 and CO [21]. The TG profile of CO_2 (Fig. 1(b)) supports this hypothesis. In the main stage of mass loss, two peaks are observed in the DTG curve. The first peak (with its maximum near 300˚C) is ascribed to the decomposition of aliphatic compounds, whereas the second one (maximum at 400˚C) is attributed to carbohydrate and protein decomposition [21]. A final weight loss of 13.3% takes place at a high temperature (600–1,000˚C). This stage of mass loss should be mainly attributed to the thermal decomposition of calcium carbonate and sulphate, leading to the release of gases such as CO_2 and SO_2 [13,20,22]. The profile of CO_2 release (Fig. 1(b)) is in good agreement with this hypothesis.

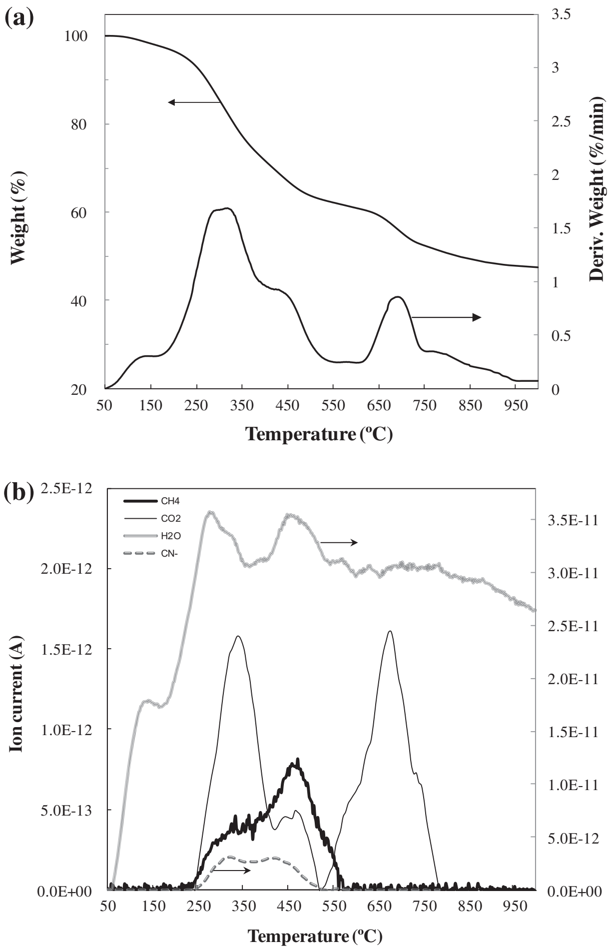

Fig. 1. Pyrolysis of raw sewage sludge under inert atmosphere. (a) TG and DTG curves. (b) MS curves of the main components: CH_4 ($m/z = 15$), H_2O ($m/z = 18$), CN^- ($m/z = 26$) and CO_2 ($m/z = 44$).

Fig. 1(b) displays the intensity of the mass spectrometric signals of the main compounds released during the pyrolysis of raw sludge (CH_4, CN^-, H_2O and CO_2). The figure shows the release of CN^- between 250 and 500°C. The formation of cyanides during the activation of carbonaceous materials has been reported in the literature. Robau-Sánchez et al. [23] detected CN^- during the chemical activation with KOH of a carbonaceous material (*Quercus agrifolia* char). These authors proposed alternative mechanisms which result in the formation of cyanides in either liquid or gas form (Eqs. (6) and (7)). Liquid cyanides might then be transformed into gaseous cyanides. According to the reaction mechanism, the essential condition for cyanide formation is the presence of OH^- functionalities and a source of carbon and nitrogen.

$$6KOH(l) + 5.5C + N_2(g) \leftrightarrow 2KCN(l) + 2K_2CO_3 + 1.5CH_4(g) \qquad (6)$$

$$6KOH(l) + 5.5C + N_2(g) \leftrightarrow K_2(CN)_2(g) + 2K_2CO_3 + 1.5CH_4(g) \qquad (7)$$

This mechanism of cyanide formation was confirmed in a previous paper [24], in which the chemical activation of bone char (a material containing about 10 wt% of carbon) was studied using different reagents (H_3PO_4, H_2SO_4, NaOH and K_2CO_3). In that study, the pyrolysis was performed under a helium atmosphere, and thus it was concluded that structural nitrogen (constituent of the precursor) effectively took part in the activation process. In this case, the pyrolysis has been performed under a nitrogen atmosphere. Consequently, it is expected that both gaseous nitrogen and structural nitrogen (constituent of sewage sludge) take part in the formation of cyanides.

The formation of HCN has also been reported in the pyrolysis of carbonaceous precursors such as sewage sludge [25] and meat and bone meal [26], under inert atmosphere. In our previous work [24], two possibilities were hypothesized for the formation of HCN during the chemical activation of bone char: (i) its direct synthesis, following a mechanism similar to that described by Eqs. (6) and (7), or (ii) its synthesis from cyanides, through the reaction of these components with H_2O, CO_2 or acids. In this work, HCN was not detected, evidencing that cyanides are preferentially formed. Under specific operating conditions, cyanides might evolve to HCN.

Hydrocarbons (in the C_1–C_4 range) were also detected in pyrolysis gases, CH_4 being the most important. These results are in good agreement with the product distribution reported in the literature for the pyrolysis of sewage sludge using either nitrogen [25] or helium [27]. The spectrometric signal of methane has its maximum near 500°C and a shoulder around 350°C. The release of CH_4 could be partially related to cyanide formation through Eqs. (6) and (7), which involves the simultaneous formation of methane. Nevertheless, the difference in the shape of the MS curve of both components (cyanides and CH_4) suggests the existence of another mechanism of methane (and hydrocarbon) formation.

The release of water takes place in the whole temperature range, as reported by Conesa et al. [25], in the pyrolysis of sewage sludge under nitrogen atmosphere. The first shoulder in the profile of water (around 175°C) should be related to the desorption of adsorbed and capillary water. The release of water at higher temperature could be explained by either the release of constitution water [20] or the occurrence of reaction mechanisms that involve the formation of this component.

Finally, CO_2 has been detected in pyrolysis gases, which is in good agreement with the product distribution reported by Conesa et al. [25]. The release of CO_2 takes place in two temperature ranges: 250–500°C and 500–800°C. The MS signal of CO_2 at 250–500°C is mainly attributed to the aforementioned decomposition and volatilization of organic matter [21]. The release of carbon dioxide at high temperature (coinciding with the last peak of mass loss of TG analysis) is ascribed to the thermal decomposition of salts, such as calcium carbonate, as reported in the literature for the thermal analysis of sewage sludge [20,22].

3.2. Sludge carbon yield

The physical activation yield (Y_{phys}) (on a dry weight basis) was calculated from sample weight before and after the pyrolysis with CO_2 at different activation temperatures. The yield of the acid washing step (Y_{acid}) was obtained dividing the mass of the sample after washing with HCl and before the acid washing. Finally, the overall yield of sludge carbon (Y_{SC}), based on raw sludge on a dry basis, was calculated as the product of the yield of both steps.

Table 3 summarizes the partial and overall carbon yields for the prepared samples of sludge carbon. It is observed that both the overall and physical yields decrease with temperature. The overall yield is reduced to half when physically activated samples are acid washed. When the treatment with HCl is performed before the activation with CO_2, the decrease in the overall yield is slightly lower.

3.3. Characterization of sludge carbon

Fig. 2 shows the FTIR spectra of samples of sludge carbon. All samples prepared at 600˚C (Fig. 2(a)) exhibit a similar and prominent peak at 1,060 cm^{-1}. This band, which is related to the silicon content of the materials, is indicative of the presence of structures such as Si–O–Si, Si–O–X (X = Al, Fe, Ca, Mg and Na) and Si–O–C [13,28]. The small peak near 800 cm^{-1} could also be assigned to Si–O–Si structure. In Fig. 2(a), the small bands located between 600 and 750 cm^{-1} (corresponding mainly to SC-600) could be ascribed to the vibration of complex components of sludge carbon [13]. Regarding the band located near 1,400 cm^{-1}, SC-600 exhibits a strong and well-defined peak, whereas for both acid-treated samples, it appears as a shoulder. This band could be related to: (i) $CaCO_3$ or (ii) long-chain aliphatic structures (C–H bending band) [5]. Every sample shows a band at 1,600 cm^{-1} (Fig. 2(a)), mainly attributed to carbonyl (C=O) groups [28]. The highest peak corresponds to the sample prepared by physical activation followed by acid washing, revealing the effect of the acid treatment on surface chemistry. Finally, the broad band with the maximum near 3,400 cm^{-1} is the characteristic of –OH and –NH surface functional groups [5,11]. The effect of the acid treatment on –OH and –NH surface functional groups is the same as that observed on C=O groups. The amount of functionalities decrease in the order: SCA-600 > SC-600 > SCP-600.

The FTIR spectra, corresponding to the physical activation at 900˚C, are much simpler (Fig. 2(b)). Indeed, the volatilization of a higher amount of organic matter results in an increase in the inorganic content of the materials. Thus, the sharp peak near 1,060 cm^{-1}, related to the silicon content, is the predominant peak. The small bands appearing between 600 and 750 cm^{-1}, attributed to complex components of sludge carbon, become slightly higher. The peak near 1,400 cm^{-1}, associated to either $CaCO_3$ or aliphatic compounds, is almost completely absent. This result could be explained by both the volatilization of the organic compounds and the thermal decomposition of calcite, which takes place at temperatures higher than 700˚C. The peak at 1,600 cm^{-1}, ascribed to C=O groups, is drastically diminished. Finally, the broad band corresponding to –OH and –NH functional groups is also reduced, compared to samples activated at 600˚C. The sample subjected to acid washing after the physical activation shows again the highest amount of surface functionalities. Consequently, both the activation temperature and the sequence of the acid treatment play an important role in surface chemistry.

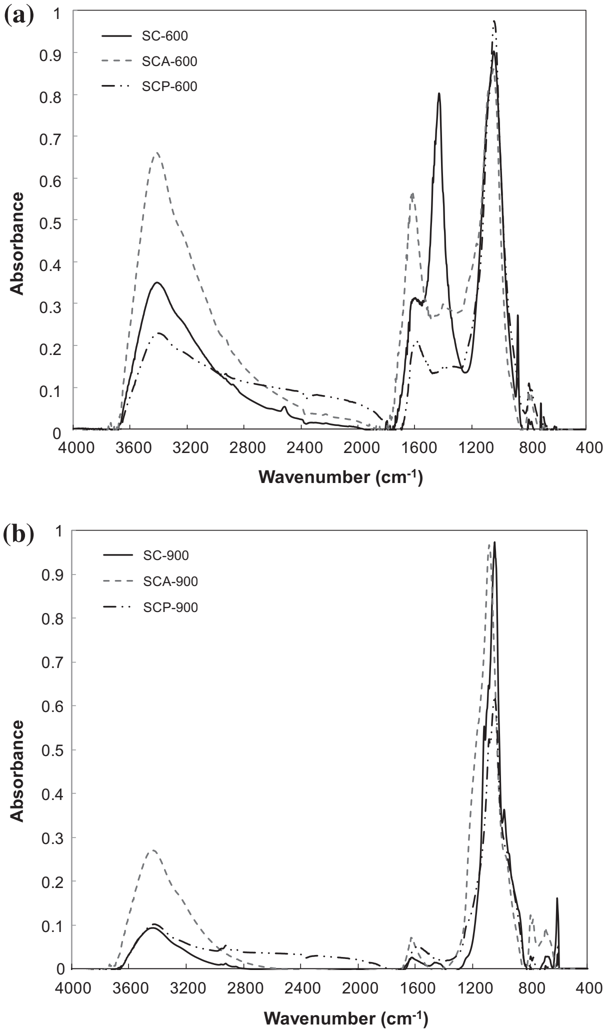

Fig. 2. FTIR spectra of sewage sludge-derived chars, prepared at different temperatures: (a) 600˚C and (b) 900˚C.

Table 3
Partial and total carbon yields at different preparation steps: physical activation, acid washing and overall yield

Sample	Y_{phys} (%)	Y_{acid} (%)	Y_{SC} (%)
SC-600	60.5	–	60.5
SC-900	42.2	–	42.2
SCA-600	60.5	50.4	30.5
SCA-900	42.2	47.8	20.2
SCP-600	53.1	66.3	35.2
SCP-900	36.4	66.3	24.2

Table 4 summarizes the textural properties of the prepared samples of sludge carbon. According to these results, when the materials are prepared by physical activation (SC), the highest activation temperature (900˚C) results in a lower specific surface area, compared to the sample activated at 600˚C.

This effect is mainly attributed to the great decrease in microporosity, both surface (3.5 vs. 15.0 m^2/g) and volume (0.0013 vs. 0.0063 cm^3/g). The total pore volume of both samples is very similar since the sample activated at 900°C shows a higher macropore volume (an increase of 45%).

The samples prepared by acid washing prior to physical activation (SC) show a different trend. The highest temperature (900°C) leads to a material with a higher S_{BET}, compared to the carbon prepared at 600°C (164 vs. 79.7 m^2/g). SCP-900 exhibits a much higher micro and mesoporosity, and a much lower macroporosity (a variation in pore volume of 216, 416 and −97%, respectively). In this case, the total pore volume is much lower for SCP-900.

Regarding the samples prepared by physical activation followed by acid washing (SCA), the highest activation temperature results in a carbon with a much higher S_{BET} (an increase of 152%) than the sample activated at 600°C (654 vs. 260 m^2/g). This increase in specific surface area is a consequence of the development of porosity in the micro, meso and macropore range (an increase in pore volume of 134, 178 and 358%, respectively).

Fig. 3 displays the effect of the acid treatment sequence (prior or after physical activation) on pore volume, in both temperature levels (600 and 900°C). It is evident that the effect of the treatment sequence is different at both temperature levels. At 600°C, the post-washing has the effect of increasing the pore volume in the micro, meso and macropore range (397, 115 and 106%, respectively, compared to the physically activated sample). The washing prior to the activation has the effect of increasing the microporosity (138%), and especially the macroporosity (a huge increase of 2,869% is obtained), while there is an important decrease in mesoporosity (83%).

Regarding the samples activated at 900°C, the acid washing after physical activation leads to a huge increase in pore volume (656%, compared to SC-900). The resulting sample has a high degree of meso and macroporosity (0.5311 and 0.4611 cm^3/g, respectively). The acid-washed sample also exhibits the highest volume of micropores of all samples (0.0734 cm^3/g). The sample washed before the activation (SCP-900) exhibits an increase in the porosity. This increase is mainly due to the development of microporosity (increase of 3,546%), while there is a decrease in macroporosity (37%).

Consequently, the post-washing step has the effect of increasing the porosity in both temperature levels (600 and 900°C). This effect could be attributed not only to the removal of the inorganic fraction, but to the improvement in the accessibility of the carbon fraction due to pore unblocking. This effect is more pronounced at high temperature. In this case, if samples are not acid washed, the material prepared by physical activation at 900°C has lower surface area (and similar pore volume) than that activated at 600°C. On the contrary, when the sample activated at 900°C is washed, its textural properties become visible. The effect on micropore volume is noteworthy, which is negligible for SC-900 sample, while SCA-900 exhibits a substantial amount (the highest value of all samples of sludge carbon). This microporosity, formed to a great extent as a consequence of the burn-off of carbon with CO_2 [15], stays hidden due to pore blockage. The washing step leads to pore unblocking (in the meso and macropore range), resulting in a better accessibility to micropores. Consequently, the post-washing stage is highly advisable (even necessary at high temperatures) to make visible the pore development that takes place during the physical activation with CO_2.

Table 4
Ash content (wt%), pH and textural properties of prepared chars. S m^2/g; V cm^3/g, D_p, Å

	Ash content	pH	S_{BET}	S_{micro}[a]	S_{ext}[a]	V_{micro}[a]	V_{meso}[b]	V_{macro}[b]	V_{total}[c]	D_p[d]
SC-600	64.4	11.1	58.4	15.0	43.4	0.0063	0.0885	0.0489	0.144	78.4
SC-900	92.2	11.3	43.1	3.5	39.6	0.0013	0.0693	0.0707	0.141	84.7
SCA-600	38.6	2.9	260	70.1	190	0.0313	0.1907	0.1006	0.323	47.6
SCA-900	72.7	3.1	654	168	486	0.0734	0.5311	0.4611	1.066	53.6
SCP-600	53.4	3.5	79.7	36.5	43.2	0.0150	0.0147	1.4517	1.4814	51.1
SCP-900	77.7	6.8	164	109	54.8	0.0474	0.0758	0.0442	0.1674	37.0

[a] *t*-plot method.

[b] BJH method (adsorption branch).

[c] Sum of *t*-plot method and BJH method.

[d] BET method.

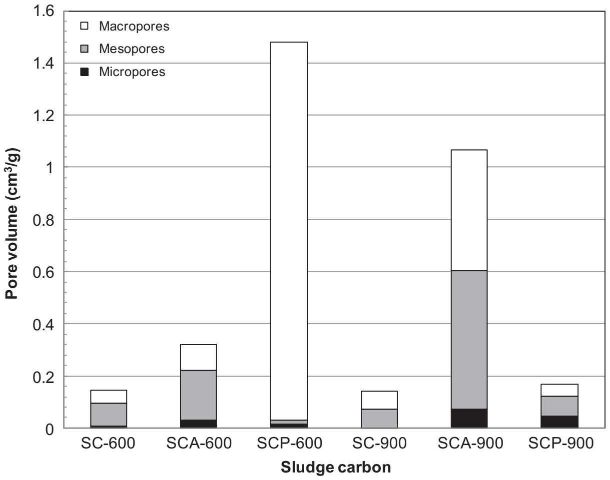

Fig. 3. Influence of activation temperature and acid washing on pore volume in the micro, meso and macropore range.

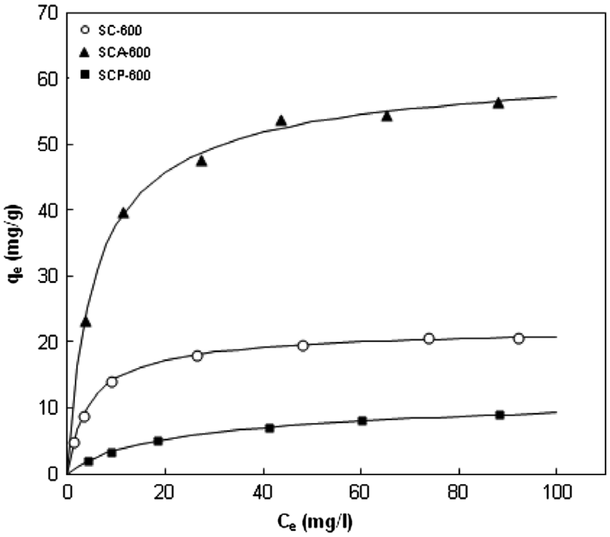

Fig. 4. Isotherm data for MB adsorption at 20℃ by sludge carbons prepared by physical activation at 600℃. Lines represent Redlich–Peterson model prediction.

The acid washing prior to physical activation has a different effect. At 600℃, a huge volume of macropores is obtained, which results in a high increase in total pore volume. This effect, which should not be attributed to ash removal, could be a consequence of the increase in the stability of the inorganic fraction. In fact, high temperatures can convert the inorganic fraction into mineral-like compounds and induce the encapsulation of some metals by the carbon phase, as reported by Bagreev et al. [17] during the carbonization of sewage sludge with nitrogen at 950℃. The partial removal of the inorganic fraction before the heating process could limit this phenomenon, leading to a higher pore development. At higher temperatures (900℃), these macropores could be destroyed to a great extent, as a consequence of the greater gasification reactivity of CO_2, which would result in a higher release of gaseous compounds. Another possibility for the increase in pore volume could be the interaction between the precursor (raw sludge) and impregnated HCl during the thermal treatment.

3.4. Adsorption performance of sludge carbon

3.4.1. Equilibrium adsorption of MB

Figs. 4 and 5 display the adsorption isotherms of MB at 20℃ for sludge carbons prepared by physical activation with CO_2 at 600 and 900℃, respectively. The fitting parameters for the Langmuir, Freundlich and Redlich–Peterson models are summarized in Table 5. The APEs indicate that Redlich–Peterson model best describes the adsorption equilibrium.

The Langmuir monolayer sorption capacities (q_m) have been used to reflect the MB uptake capacity of the prepared sludge carbons. According to the data in Table 5, when the adsorbents are prepared only by physical activation (SC), it is better to use the lowest temperature (600℃). The same behaviour is observed when these materials undergo a subsequent acid washing step (SCA-600 is more effective than SCA-900). On the contrary, when the acid treatment is performed prior to the activation with CO_2 (SCP samples), it is better to use an activation temperature of 900℃ since the uptake capacity is three times higher than that obtained at 600℃.

Regarding the election of the treatment sequence (that is, if the washing step is performed before or after the physical activation), it is essential to distinguish between both temperatures. When the activation process is carried out at 600℃, it is better to use the post-washing step. A q_m of 59.5 mg/g is obtained, well above the q_m of 10.9 mg/g measured, when the washing step is performed prior to the physical activation. Indeed, the adsorption performance of the sample prepared with acid treatment prior to physical activation is even worse than the sample obtained by physical activation only (10.9 vs. 21.6 mg/g). On the contrary, if the physical activation is carried out at 900℃, it makes no difference whether the acid washing is performed before or after the physical activation step. In both cases, the uptake capacity duplicates that of the only physically activated sample.

The highest adsorption capacity is obtained with the sludge carbon prepared by physical activation at

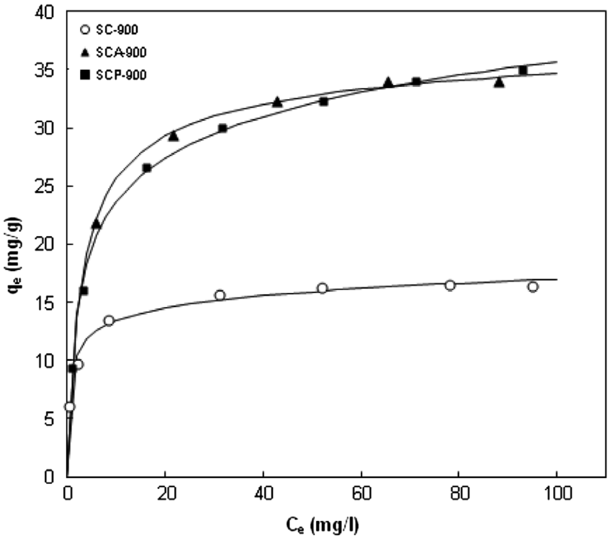

Fig. 5. Isotherm data for MB adsorption at 20 °C by sludge carbons prepared by physical activation at 900 °C. Lines represent Redlich–Peterson model prediction.

600 °C followed by acid washing with HCl. Comparing the data of Tables 4 and 5, the values of BET surface area do not directly influence the actual uptake capacity of the prepared adsorbents. As an example, although SCA-900 has the highest value of BET (654 m^2/g), its maximum Langmuir capacity (35.3 mg/g) is similar to that of SCP-900 (34.6 mg/g), its S_{BET} being 164 m^2/g. This result is in good agreement with others reported in the literature [12,28], suggesting that surface area is not the exclusive factor to determine the adsorption capacity of a material. Due to its relatively large size, the adsorption of MB molecule is favoured by materials with a high degree of mesoporosity [12,29]. Nevertheless, the correlation between the mesopore volume and MB uptake capacity is not high.

This result indicates the great significance of other factors, such as surface chemistry and surface charge. According to the data of FTIR analysis, a suitable surface chemistry can compensate for a limitation in the development of the porous structure. For example, SCA-600 has the highest uptake capacity (59.5 mg/g), although it does not exhibit the highest surface area or mesoporosity (it has the second highest value). Data on Fig. 2 show that this material has the highest amount of surface functionalities. Oxygen- and nitrogen-containing functional groups, which represent electron-rich surface sites, favour the adsorption of MB, a cationic dye. The material with the second highest uptake capacity is SCA-900, which has the most favourable textural properties (S_{BET} and mesopore volume).

A comparison of the uptake capacities of MB onto adsorbents prepared from sewage sludge is summarized in Table 6. Although the materials were prepared under different experimental conditions, the results are useful for comparison purposes.

3.4.2. *Equilibrium adsorption of phenol*

Figs. 6 and 7 show the adsorption isotherms of phenol at 20 °C for adsorbents prepared by physical activation with CO_2 at 600 and 900 °C, respectively. Table 7 summarizes the parameters of best fit for the Langmuir, Freundlich and Redlich–Peterson models. As occurred with MB, Redlich–Peterson model fits best the experimental data of adsorption equilibrium.

According to data in Table 7, it is advisable to use the lowest activation temperature (600 °C) to prepare sludge carbons by physical activation only. The same behaviour is obtained when physically activated materials undergo a subsequent washing stage, SCA-600 being more effective than SCA-900. The opposite trend is observed when the treatment with

Table 5
Best fit Freundlich, Langmuir and Redlich–Peterson isotherm parameters for MB adsorption

	Langmuir model			Freundlich model			Redlich–Peterson model			
	q_m (mg/g)	K_L (L/mg)	APE	K_F (mg/g) $(L/mg)^{1/n}$	n	APE	K_R (L/g)	α $(L/mg)^{\beta}$	β	APE
SC-600	21.6	0.215	1.33	6.97	3.91	13.6	5.04	0.262	0.973	0.54
SC-900	16.2	1.035	8.95	8.77	6.62	7.31	40.6	3.609	0.909	3.72
SCA-600	59.5	0.177	1.53	21.0	4.29	7.60	11.8	0.230	0.966	1.17
SCA-900	35.3	0.276	1.31	17.5	6.40	2.48	12.6	0.435	0.956	0.69
SCP-600	10.9	0.047	2.67	1.31	2.29	7.95	0.63	0.104	0.875	1.56
SCP-900	34.6	0.292	7.39	12.4	4.18	7.20	19.9	0.998	0.869	2.10
Mean value			3.86			7.69				1.63

Table 6
MB uptake of several sewage sludge-based adsorbents

Refs.	Sludge type	Preparation conditions	Uptake (mg/g)
[30]	Sludge from an urban WWTP	Chem. act.: H_2SO_4, 625℃, 30 min. Post-treatment: acid washing (HCl)	68
[31]	Sludge from an urban WWTP	Chem. act.: H_2SO_4, 700℃, 30 min. Post-treatment: acid washing (HCl)	14
[32]	Sludge from an urban WWTP	Carbonization: 625℃, 30 min	32
[32]	Sludge from an urban WWTP	Chem. act.: H_2SO_4, 625℃, 30 min. Post-treatment: acid washing (HCl)	25
[33]	Sludge from an urban WWTP	Carbonization: 650℃, 30 min	17
[33]	Sludge from an urban WWTP	Chem. act.: H_2SO_4, 650℃, 30 min. Post-treatment: acid washing (HCl)	25
[33]	Sludge from an urban WWTP	Chem. act.: $ZnCl_2$, 650℃, 5 min. Post-treatment: acid washing (HCl)	137
[20]	Paper mill sewage sludge	Carbonization: 300℃, 60 min	25
[20]	Paper mill sewage sludge	Carbonization: 300℃, 60 min. Phys. act.: H_2O, 850℃, 40 min	130
[34]	Sludge from an urban WWTP	Chem. act.: $ZnCl_2$, 650℃, 120 min. Post-treatment: acid washing (HCl)	91
This study	Sludge from an urban WWTP	Phys. act.: CO_2, 600℃, 30 min. Post-treatment: acid washing (HCl)	60

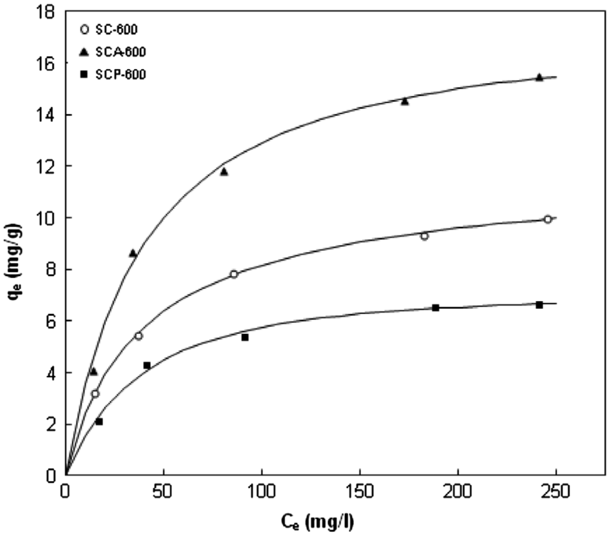

Fig. 6. Isotherm data for phenol adsorption at 20℃ by sludge carbons prepared by physical activation at 600℃. Lines represent Redlich–Peterson model prediction.

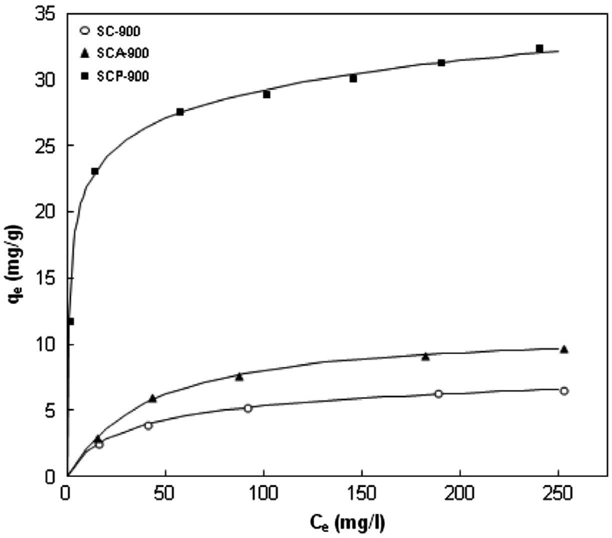

Fig. 7. Isotherm data for phenol adsorption at 20℃ by sludge carbons prepared by physical activation with CO_2 at 900℃. Lines represent Redlich–Peterson model prediction.

HCl is carried out prior to the activation with CO_2. In this case, it is more advisable to use a temperature of 900℃ since the uptake capacity is almost four times higher than that of the material prepared at 600℃.

The most suitable sequence for the preparation treatment (that is, if acid washing should be carried out before or after the activation with CO_2) depends on the temperature level employed, as occurred with the adsorption of MB. When physical activation is performed at 600℃, it is more adequate to use the washing step after the activation since a q_m of 18.0 mg/g is obtained vs. 7.8 mg/g, if the acid washing is carried out before. At this temperature, the adsorption capacity of the sample washed before the activation is lower

Table 7
Best fit Freundlich, Langmuir and Redlich–Peterson isotherm parameters for phenol absorption

	Langmuir model			Freundlich model			Redlich–Peterson model			
	q_m (mg/g)	K_L (L/mg)	APE	K_F (mg/g) (L/mg)$^{1/n}$	n	APE	K_R (L/g)	α (L/mg)$^{\beta}$	β	APE
SC-600	11.5	0.0254	1.36	1.50	2.85	7.00	0.318	0.036	0.956	0.92
SC-900	7.4	0.0290	2.76	1.17	3.15	4.67	0.283	0.069	0.897	1.18
SCA-600	18.0	0.0250	3.49	2.19	2.74	12.2	0.437	0.022	1.018	3.44
SCA-900	11.3	0.0243	1.81	1.46	2.86	10.6	0.258	0.019	1.034	1.64
SCP-600	7.8	0.0265	4.32	1.10	2.96	11.5	0.182	0.015	1.078	3.62
SCP-900	30.1	0.5169	7.16	14.0	6.38	5.21	33.2	1.784	0.900	0.68
Mean value			*3.48*			*8.53*				*1.91*

than that of the sample obtained by physical activation only (11.5 mg/g).

On the contrary, using an activation temperature of 900°C, the most suitable sequence is acid washing followed by physical activation (q_m is 30.1 vs. 11.3 mg/g for the post-washing). The highest adsorption capacity of all samples of sludge carbon is obtained with the carbon prepared by physical activation at 900°C, with previous acid washing (SCP-900).

As observed for the adsorption of MB, there is not a direct relationship between the values of S_{BET} and the phenol uptake capacity of sludge carbons. For example, although SCA-900 has the highest value of BET (654 m^2/g), its maximum Langmuir capacity (11.3 mg/g) is similar to that of SC-600 (11.5 mg/g), its S_{BET} being 58.4 m^2/g (11 times lower).

The adsorption of phenol is associated with materials with a high degree of microporosity due to the small molecular size of phenol. In this case, however, the material with the highest microporosity (SCA-900) does not exhibit the highest uptake capacity. SCP-900 is the material with the highest adsorption capacity (30.1 mg/g). This sludge carbon possesses the second highest S_{micro} and the lowest pore diameter (thus favouring Knudsen diffusion). Apart from the textural properties, numerous studies have shown the influence of surface chemistry. Although the mechanism of phenol adsorption is still not well understood, the presence of acidic surface functional groups has been reported to hinder the adsorption capacity of the material [19,35]. According to FTIR analyses (Fig. 2), SCP-900 has a very low amount of oxygen- and nitrogen-containing surface functionalities. This suitable surface chemistry, along with the aforementioned appropriate textural properties, makes this material the most adequate to remove phenol. It is clear that the influence of surface chemistry, since SCA-900, exhibits quite a low phenol

Table 8
Phenol uptake of several sewage sludge-based adsorbents

Refs.	Sludge type	Preparation conditions	Uptake (mg/g)
[31]	Sludge from an urban WWTP	Chem. act.: H_2SO_4, 700°C, 30 min. Post-treatment: acid washing (HCl)	27
[37]	Sludge from an urban WWTP	Chem. act.: $ZnCl_2$, 500°C, 120 min. Post-treatment: acid washing (HCl)	47
[4]	Sludge from an urban WWTP	Chem. act.: H_2SO_4, 625°C, 30 min. Post-treatment: acid washing (HCl)	30
[33]	Sludge from an urban WWTP	Carbonization: 650°C, 30 min	25
[33]	Sludge from an urban WWTP	Chem. act.: H_2SO_4, 650°C, 30 min. Post-treatment: acid washing (HCl)	25
[33]	Sludge from an urban WWTP	Chem. act.: $ZnCl_2$, 650°C, 5 min. Post-treatment: acid washing (HCl)	82
[38]	Sludge from an urban WWTP	Carbonization: 600°C, 60 min. Phys. act.: H_2O, 760°C, 30 min	44
[39]	Sludge from an urban WWTP	Chem. act.: H_2SO_4, 650°C, 60 min	26
This study	Sludge from an urban WWTP	Pre-treatment: acid washing (HCl). Phys. act CO_2, 900°C, 30 min	30

removal ability (11.3 mg/g), although it possesses the highest micropore area (168 m^2/g). It has also been proposed in the literature that phenol could be adsorbed not only by physisorption, but also by surface polymerization [36]. The presence of metals on the surface could then enhance this mechanism. Consequently, a high removal of inorganic fraction during the washing stage could negatively affect the uptake capacity of the material. In this case, SCP-900 is the acid-treated carbon with the highest ash content (77.7 wt%), which could favour its phenol uptake capacity.

Table 8 summarizes, for comparison purposes, the adsorption capacities of phenol onto different sewage sludge-based materials.

4. Conclusions

The post-washing stage with HCl has the effect of increasing the porosity of the material in the whole pore range. This effect could not only be ascribed to the removal of the inorganic fraction, but to the improvement in the accessibility of the carbon fraction due to pore unblocking. The washing step is essential when the activation is performed at 900˚C since the high reactivity of CO_2 at this temperature leads to a higher pore blockage. As a consequence, the material activated at 900˚C has lower surface area than that activated at 600˚C, while after acid washing, it exhibits a S_{BET} of 654 m^2/g.

The acid treatment prior to physical activation has a different effect at each temperature level. At 600˚C, it results in a huge pore volume development, mainly macropores, which could be a consequence of the increase in the stability of the inorganic fraction. At 900˚C, these macropores are likely to be destroyed to a great extent, as a consequence of the high amount of gases formed due to the higher reactivity of CO_2. At the high temperature level, this treatment leads to an increase in microporosity.

Both the activation temperature and the sequence of the acid treatment play an important role in surface chemistry. The amount of functionalities (C=O, −OH and –NH) decrease in the order: SCA > SC > SCP. When the physical activation is performed at 900˚C, the amount of functionalities is drastically diminished.

The most suitable materials for the adsorption of MB and phenol are SCA-600 and SCP-900, respectively. The maximum uptake capacity is not directly related to BET surface area. For both adsorbates, the uptake capacity depends mainly on the textural properties (favoured by mesoporosity for MB and microporosity for phenol) and surface chemistry (favourable effect of oxygen- and nitrogen-containing functional groups for MB and unfavourable effect for phenol).

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