Spent coffee-based activated carbon: Specific surface features and their importance for H$_2$S separation process

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ABSTRACT

Activated carbons were prepared from spent ground coffee. Zinc chloride was used as an activation agent. The obtained materials were used as a media for separation of hydrogen sulfide from air at ambient conditions. The materials were characterized using adsorption of nitrogen, elemental analysis, SEM, FTIR, and thermal analysis. Surface features of the carbons depend on the amount of an activation agent used. Even though the residual inorganic matter takes part in the H$_2$S retention via salt formation, the porous surface of carbons governs the separation process. The chemical activation method chosen resulted in formation of large volume of pores with sizes between 10 and 30 Å, optimal for water and hydrogen sulfide adsorption. Even though the activation process can be optimized/changed, the presence of nitrogen in the precursor (caffeine) is a significant asset of that specific organic waste. Nitrogen functional groups play a catalytic role in hydrogen sulfide oxidation.

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1. Introduction

Increasing amount of wastes produced by modern society direct the attention of policy makers and scientists towards their recycling, remediation, and reuse. Many of these waste have organic or biomass origin. Such materials can be converted into energy sources via pyrolysis or fermentation [1]. Another way of organic/biomass wastes reuse is converting them into activated carbons. These materials are obtained either by pyrolysis at high temperature followed by physical activation or by chemical activation combined with carbonization [2,3]. Coal, wood, pitch, peat, fruit stones, coconut shells or other biomass can be used as precursors for activated carbons. The final properties of carbons are governed by the properties of these precursors and activation technology.

A large specific surface area and high volume of micropores cause that activated carbons are widely used in separation processes where strong dispersive forces are responsible for the retention of species on their surface. Besides dispersive forces, which govern a nonspecific physical adsorption, surface chemistry of carbon is also of paramount importance. A significance of surface chemistry increases when the selective/specific separation is

required and when the catalytic process or reactions on the surface are encouraged to take place [4,5]. "Natural" chemistry of an activated carbon surface originates either from its content of ash/an inorganic phase or from heteroatoms such as oxygen, sulfur, or nitrogen having their source in the precursors. Oxygen functional groups are the most abundant ones owing to the susceptibility of a carbon surface for reaction with oxygen from air. All species present on a carbon surface determine its overall reactivity.

It is well known that surface groups and their location in the pore network determine an application of certain carbons for specific separations [6,7]. In majority of cases an activated carbon surface is modified using various techniques, such as impregnation, grafting, oxidation, or ammoxidation in order to make their surface more reactive [6]. All of these significantly increase the cost of adsorbents.

One of the heteroatoms, which is often introduced to a carbon surface is nitrogen. Its presence was found to increase the basicity [8,9], ability of carbon to activate oxygen [10,11] and to enhance pseudocapacitive properties of carbon-based supercapacitors [12–16]. The most common method to introduce nitrogen functionalities to activated carbons is their treatment with nitrogen containing precursors such as ammonia, melamine, urea or aliphatic amines [6,17,18]. In the field of gas phase adsorption activated carbons containing nitrogen are very important media for desulfurization of air or digester gas [19].

Even though the chemistry can be employed to derive very active nitrogen containing carbons [20], one should not neglect the natural biomass that is rich in this element. An example is spent

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coffee. This waste produced in a significant quantity by the contemporary society can be the source of carbon of interesting properties. Here caffeine, $C_8H_{10}N_4O_2$, is the natural source of nitrogen. Taking these into account, the objective of this paper is to synthesize carbons from spent coffee waste, to describe their properties and to suggest their application in separation technology related to environmental pollution. In such a case an inexpensive hydrogen sulfide sorbent can be derived, which might be competitive to costly catalytic commercial adsorbents such as Centaur® [20]. Even though an accelerated test was run to assess the adsorbents' breakthrough capacity, such a test is commonly accepted to evaluate carbon adsorbents since it reflects the real contact time conditions used in sewage treatment plants [19].

2. Experimental

2.1. Materials

The carbon precursor was a residual/waste ground coffee (Goya). The received ground coffee was dried in oven at 120 °C for 48 h. $ZnCl_2$ powder reagent grade >98% from Aldrich was used as an activating agent.

In a first step 25 g of dried ground coffee were added to a specific amount of $ZnCl_2$ dissolved in 100 mL of distilled water. The ratios of dry coffee to $ZnCl_2$ were 1:0.5, 1:1, and 1:2. The obtained slurry was homogenized and heated at 80 °C. The samples were put in oven at 120 °C until the mixture was completely dried (for 2–3 days). Then the dried materials were carbonized in a horizontal furnace (Lindberg/Blue Mini-Mite™ Tube Furnace) under a flow of nitrogen (80 mL/min) with a heating rate of 10 °C/min and up to 800 °C with a holding time of 60 min. The samples were washed with distilled water in a Soxhlet apparatus to remove all residual soluble impurities until a constant pH was reached and no chloride ions were detected in the filtrate. The carbons obtained are referred to as COFAC-0.5, COFAC-1 and COFAC-2, according to the ratio of the activating agent to the precursor. 10 g of carbonized samples were mixed with 100 mL of 18% concentrated HCl in order to remove inorganic mater. After extensive washing the samples were dried. Suffix A is added to their names. For comparison 10 g of ground coffee were carbonized at the same experimental conditions without prior activation or washing step and that sample is named COFC.

2.2. Methods

2.2.1. Evaluation of H_2S breakthrough capacity

In order to determine the breakthrough capacities of the materials studied, dynamic breakthrough tests were performed at room temperature. In a typical test, a flow of H_2S diluted with moist air (1000 ppm H_2S, 80% humidity) was passed through a fixed bed of adsorbent with a total inlet flow rate of 250 mL/min. The adsorbent's bed (10 mm in diameter, 30 mm height) contained about 3 cm^3 of carbon with particle sizes between 1 and 2 mm. The concentration of H_2S in the outlet was measured using an electrochemical sensor (Multi-Gas Monitor RAE system). The adsorption capacity of each adsorbent was calculated in mg/g of the material by integration of the area above the breakthrough curve. The adsorbent bed was prehumidified for 1 h prior to running the breakthrough tests. The suffix EPM is added to the name of the samples after the exposure to H_2S.

2.2.2. Sorption of nitrogen

Nitrogen isotherms were measured at −196 °C using an ASAP 2010 instrument (Micromeritics). Prior to each measurement, initial and exhausted samples were outgassed at 120 °C to vacuum 10 Torr. The surface area, S_{BET} (Brunauer–Emmet–Teller method),

the micropore volume, V_{mic} (calculated from the t-plot), the mesopore volume, V_{mes}, and the total pore volume, V_t, were calculated from the isotherms. The pore size distributions were calculated using density functional theory [21].

2.2.3. FT-IR spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was carried out using a Thermo Nicolet Nexus 470 spectrometer using the attenuated total reflectance (ATR) method. The spectra were obtained from 650 to 4000 cm^{-1} with 6 cm^{-1} resolution, collected 16 times and corrected for the background noise.

2.2.4. Thermal analysis

Thermogravimetric (TG) curves were obtained using a TA instrument thermal analyzer. The initial and exhausted samples (0.010–0.020 mg) were exposed to an increase in temperature (10 °C/min) while the nitrogen flow rate was held constant (100 mL/min). From the TG curves, differential TG (DTG) curves were derived. The ash content was estimated as residual at 650 °C after heating in air.

2.2.5. Environmental scanning electron microscopy

A detailed characterization of the activation process was conducted by coupling a heating plate inside an environmental scanning electron microscope (ESEM FEI QUANTA 200). About 20 mg of $ZnCl_2$ impregnated coffee (1:1, w/w) were placed in a heating plate located in the microscope's analysis chamber operated at 190 Pa and 15 kV. The sample was heated from room temperature to 750 °C at 10 °C/min, and scanning electron micrographs were taken throughout the process. These micrographs were compiled in a video that is included as Supporting Information. After the thermal treatment, a selected sample (COFAC-1) was analyzed by energy dispersive X-ray spectroscopy to determine its elemental composition.

2.2.6. Elemental analysis

The chemical composition (C, N, and H) of carbonized ground coffee and $ZnCl_2$ activated samples was determined by elemental analysis using a Costech - ECS 4010 CHNSO Analyzer. Every sample was analyzed twice and the content of oxygen was calculated as difference to 100%.

3. Results and discussion

3.1. Performance of carbons as H_2S adsorbents

The H_2S breakthrough curves measured on our adsorbents are collected in Fig. 1. An increase in the $ZnCl_2$/precursor ratio significantly increases the breakthrough time. Interestingly, COFAC-1 performs better than COFAC-2. This trend is preserved after treatment with HCl although the breakthrough times are shorter and the curve for COFAC-2 changes its shape. A gradual (almost linear) increase in H_2S concentrations indicates the chemical reactivity of the carbon surface. A steep increase in H_2S concentration for COFAC-0.5 suggests the rapid breakthrough after all adsorption centers, likely pores, are filled with the adsorbate. In the case of COFC the immediate breakthrough of H_2S was measured.

The calculated breakthrough capacities are listed in Table 1. The amount adsorbed is expressed in mg/g of adsorbent and per unit volume of the adsorbent bed. The latter is related to the practical applications where the volume of the adsorbent is the limiting factor. For the purpose of understanding the performance of our carbons, the capacities per unit mass will be analyzed in this paper. The capacity measured on COFAC-2 is the smallest one, owing to the low packing density of this material. On the other hand, COFAC-1

Table 1
H$_2$S breakthrough capacities, surface pH values and ash contents.

Sample	Ash content (%)	H$_2$S breakthrough (mg/g)	H$_2$S breakthrough (mg/cm^3)	pH$_{in}$	pH$_{exh}$
COFAC-0.5	3.78	81.3	15.3	6.81	3.55
COFAC-1	2.29	127.0	22	6.27	2.65
COFAC-2	4.98	18.3	0.53	6.54	6.50
COFAC-0.5A	1.02	26	5.97	5.20	2.81
COFAC-1A	0.87	58	11.38	4.92	2.48
COFAC-2A	0.93	20.7	0.64	4.81	3.31

has a relatively high capacity comparable to those of other carbons from wood, coconut or coal on which maximum 240, 122, and 95 mg/g, respectively, was measured [4,19]. Catalytic carbon, Centaur®, is able to adsorbed 104 mg/g H$_2$S at hour experimental conditions [22]. Treatment with acid significantly decreases the capacity of carbons suggesting that some HCl-soluble inorganic species participate in H$_2$S retention. Some of these species are likely basic in their chemical character since after acid washing the surface pH decreased almost 2 pH units. Comparison of the ash contents before and after acid washing clearly indicates the removal of a significant quantity of an inorganic matter. Even though the removal of ash results in a decrease in the capacity, the carbons

after acid treatment differ in their performance as H$_2$S adsorbents, in spite of the similar ash contents. This suggests that H$_2$S breakthrough capacity is not directly governed by the inorganic matter present in our carbons.

3.2. Effects of surface chemistry on H$_2$S adsorption

The results of elemental analyses for the samples without acid washing are collected in Table 2. The char obtained from coffee without any activation agent was also analyzed. It is referred to as COFC. The COFAC carbons have much less alkali and alkaline earth metals than the char. This can be explained by water solubility of these species and their removal during washing following carbonization. On the other hand, zinc species are not totally removed from the carbon surface and their content reaches 2% for COFAC-2 where the ratio of ZnCl$_2$ to coffee was the highest. The order in zinc content follows that in the ash content. The results suggest that apparently it is not zinc species or alkali and alkaline metals, which are responsible for the enhanced capacity on COFAC-1 carbon, or they are not the only factors governing the capacity. As proposed in the literature, the basic species on the surface of carbons shift the dissociation of H$_2$S to the right and thus enhance oxidation of sulfide ions either to elemental sulfur or sulfur oxides [4,19]. The latter are formed when the pores are small and sulfur radicals are isolated for each other and the formation of bulky sulfur polymers is inhibited.

To further analyze important surface features that might affect H$_2$S reactive adsorption on our carbons, the content of nitrogen was analyzed (Table 2). Nitrogen is expected to be incorporated to the carbon matrix as a result of the presence of caffeine in an organic precursor. The coffee-derived carbons analyzed by Rufford et al. contained 1.5% of nitrogen detected using XPS analysis [23]. Our materials contain between 2 and 3% of nitrogen. Besides nitrogen, a significant amount of oxygen is also detected. That oxygen likely affects the average pH; it is close to 7 but still in the acidic range. From the point of view of heteroatoms, COFAC-1 and COAC-0.5 appear to be the similar materials. The capacity of these two carbons for H$_2$S removal is much higher than that of COFAC-2.

Analysis of the pH values of the carbon surface after H$_2$S adsorption clearly suggests formation of sulfuric acid, especially on the surface of COFAC-1 and COFAC-0.5 A and COFAC-1A (Table 1). This is an indication that the porosity of the materials differs, as expected, and it affects the mechanism of reactive adsorption. That effect of pore sizes on the products of surface reactions has been addressed in details previously [4,19]. As mentioned above, sulfuric acid is expected as the product of surface when sulfur radicals are first deposited in small pores where their oxidation to sulfuric acid is favorable.

3.3. Porosity development and its effects on H$_2$S removal

The parameters of the porous structure calculated from nitrogen adsorption isotherms are collected in Table 3. As seen, an increase in the amount of the activation agent causes an increase in the specific surface area from 645 to 1121 m^2/g. Even though the volume of
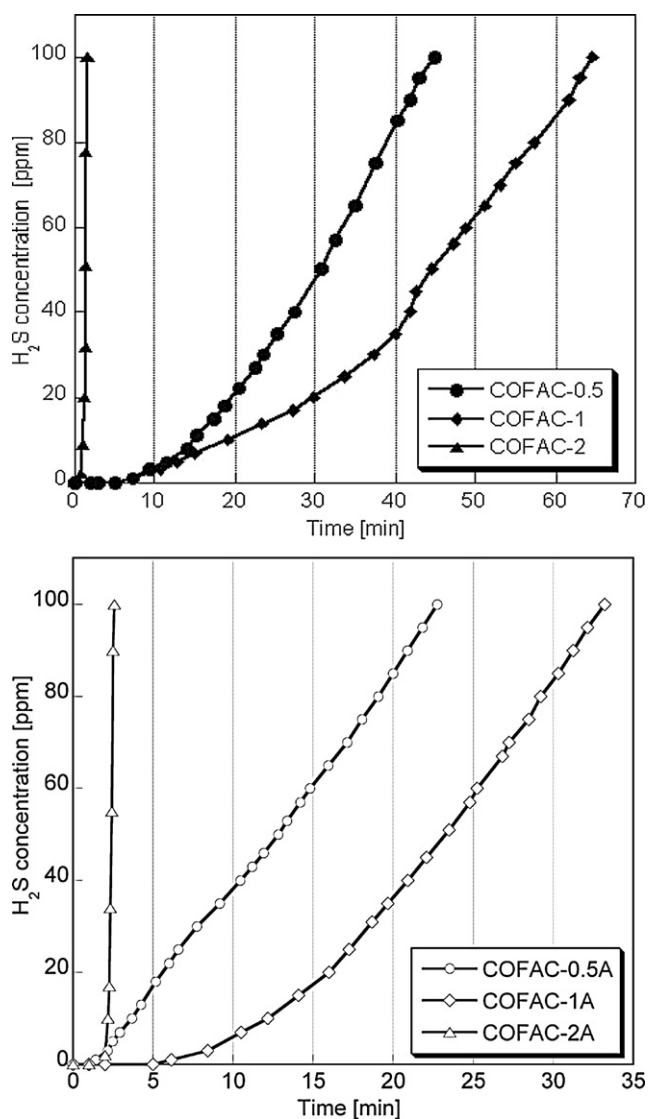

Fig. 1. H$_2$S breakthrough curves.

Table 2
Chemical composition and elemental analyses of ground coffee and $ZnCl_2$ activated samples.

Sample	ppm						%[a]			
	Ca	Fe	K	Mg	Na	Zn	C	O	H	N
COFC	5798	1166	438	5750	1009	67	80.1	15.0	1.4	3.5
COFAC-0.5	2618	623	56	813	30	12,374	78.1	17.2	1.7	3.0
COFAC-1	1792	352	23	552	21	8326	77.3	17.7	2.1	2.9
COFAC-2	888	393	56	438	234	18,560	71.5	23.9	2.5	2.1

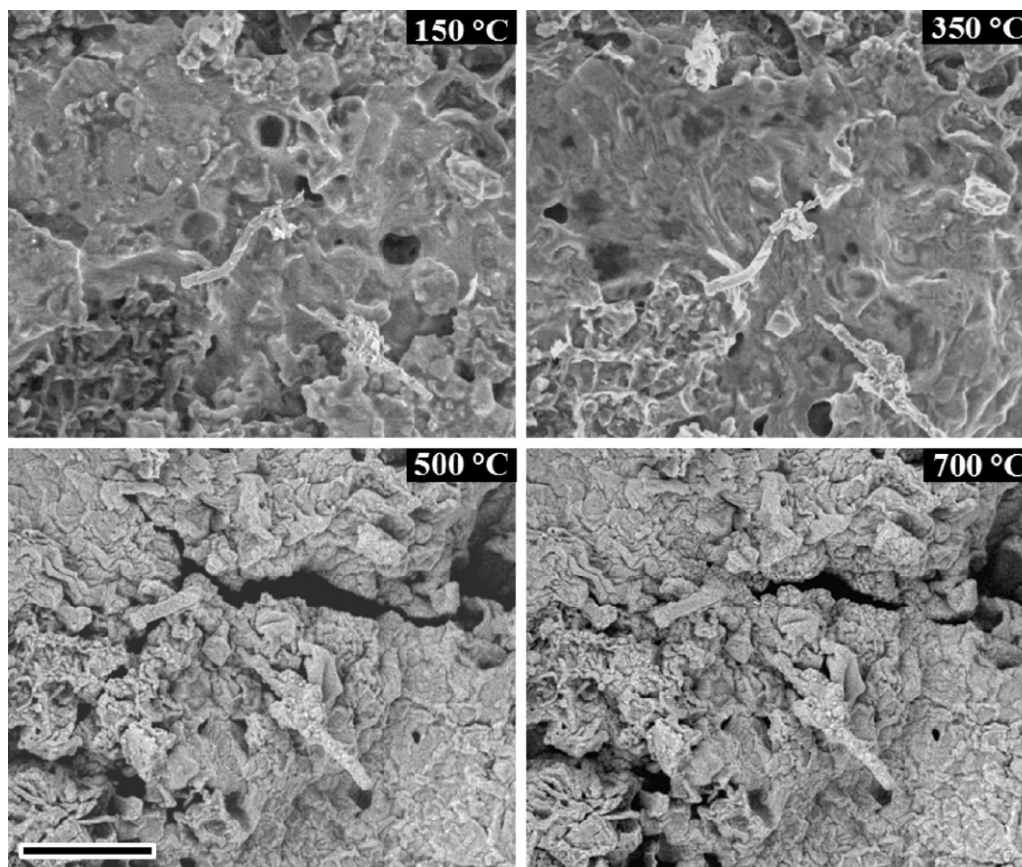[a] These values do not consider ash content.

Fig. 2. Snapshots of ground coffee/$ZnCl_2$ 1:1 during thermal treatment (for more detail, please see the video in Supporting Information). The scale bar on this figure represents a length of 100 μm.

micropores increases about 30% when the ratio of $ZnCl_2$ to the precursor increased from 0.5 to 2, the most pronounced effect is seen in the volume of mesopores. This must be related to the chemistry of the carbonization process. These pores are likely formed when a large quantity of zinc is removed from the hot carbon matrix (boiling point of zinc chloride is 732 °C [24]). Interestingly, treatment with HCl decreases the surface of COFAC-2 whereas a slight increase is found for COFAC-0.5 and COFAC-1. This must be related
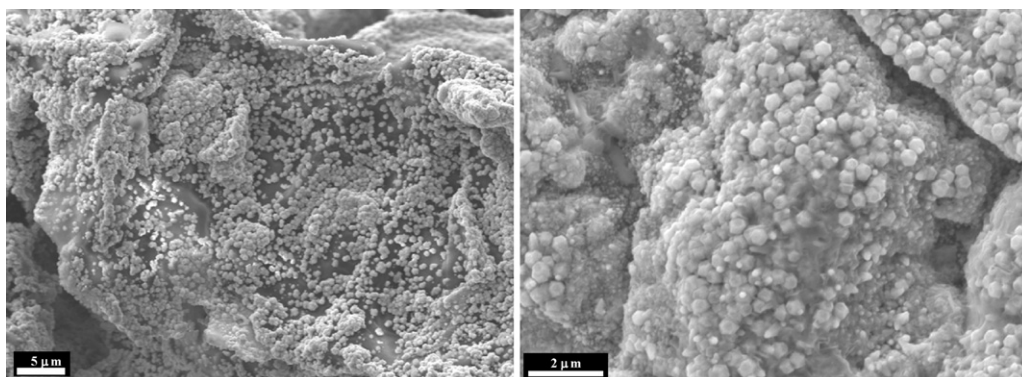

Fig. 3. Micrographs of a $ZnCl_2$ activated carbon sample (COAFC-1) after thermal treatment.

Table 3
The parameters of porous structure calculated from nitrogen adsorption isotherms.

Sample	S_{BET} (m²/g)	V_T (cm³/g)	V_{meso} (cm³/g)	V_{mic} (cm³/g)	V_{mic}/V_T	$V_{<10Å}$ (cm³/g)
COFAC-0.5	645	0.328	0.002	0.326	99	0.200
COFAC-1	905	0.492	0.093	0.399	81	0.157
COFAC-2	1121	0.954	0.509	0.445	53	0.117
COFAC-0.5-EPM	528	0.274	0.014	0.260	95	0.132
COFAC-1-EPM	741	0.387	0.059	0.328	85	0.116
COFAC-2-EPM	936	0.629	0.263	0.366	58	0.103
COFAC-0.5A	710	0.359	0.005	0.354	99	0.212
COFAC-1A	850	0.486	0.115	0.371	76	0.156
COFAC-2A	933	0.681	0.308	0.373	55	0.104
COFAC-0.5A-EPM	755	0.393	0.043	0.350	89	0.152
COFAC-1A-EPM	794	0.460	0.132	0.328	71	0.116
COFAC-2A-EPM	848	0.560	0.219	0.341	61	0.105

to the removal of different quantities of ash and a residual inorganic matter soluble in hydrochloric acid. The volume of very small pores is not affected by acid treatment. The decrease in porosity observed for COFAC-2A suggest that residual zinc in COFAC-2 is located in large pores and some secondary porosity exists either in this inorganic deposit and/or on the interface between the surface of a carbon pore and an inorganic deposit.

Important information about the development of porosity in our samples is observed at the ESEM images taken at various temperatures (Fig. 2). Between 150 and 340 °C, melting of ZnCl₂ and also the removal of volatile matter from the decomposition of ground coffee take place. This is followed by shrinking of the organic matter and cross-linking reactions in the carbon matrix that create porosity within carbon particles and between them (cracks). No apparent changes are observed in texture between 500 and 700 °C, but this may be due to the low magnification used. Moreover, small pores should develop around 650 °C owing to the proximity of the zinc chloride boiling point and to its evaporation from the matrix: more details are observed at the video included in Supporting Information. Moreover, Fig. 3 presents SEM images in which crystals are seen on the surface of sample COFAC-1, before the washing step. These crystals according to EDX analysis (spectrum not included in this manuscript) correspond to ZnCl₂ and/or Zn oxide.

The pore size distributions presented in Fig. 4 clearly show the differences in the porosity of our samples. Even though COFAC-0.5 has a very high volume of small pores, which should enhance the physical adsorption of hydrogen sulfide, the limited volume of larger transport pores has a negative effect on the capacity. Moreover, the pores smaller than 10 Å can be too small to work as nanoreactors where H_2S can be dissolved and dissociated in the film of water. Only in this form its efficient oxidation takes place [4,19]. On the other hand, in COFAC-2 pores larger than 30 Å occupy a significant volume of the material. These pores are too large to strongly physically attract hydrogen sulfide [25]. Moreover, they are also not active in the retention of water. Molecular simulations suggested that at 80% humidity mainly pores smaller than 50 Å are filled with water [26]. The lack of water in the majority of pores causes that they do not participate in H_2S adsorption. An intermediate ratio of ZnCl₂ to the precursor (1:1) results in the materials with pores of predominate size between 10 and 30 Å. These sizes are considered as optimal ones to host the H_2S dissociation and oxidation reaction in the water phase. Moreover, the small pores, less then 10 Å, are also present in their vicinity and sulfur radicals can migrate there and be oxidized to sulfur oxides [27]. In this scenario sulfuric acid is formed, which causes the low pH of the exhausted samples. That acid is likely removed from the surface during outgassing before the nitrogen adsorption measurement. Nevertheless, it is able to

activate the surface, which results in the appearance of larger pores in the range of micropores and small mesopores [2,3]. A decrease in the volume of all pores after H_2S adsorption also suggests that some elemental sulfur is deposited on the surface. Moreover, zinc sulfide and/or zinc sulfate are also expected the products of surface reactions taking onto account the chemical reactivity of the species existing in our systems. Those bulky species are likely deposited in larger pores. A significant decrease in their volume is found in the case of COFAC-2 after H_2S adsorption even though the small amount of H_2S was adsorbed on this carbon.
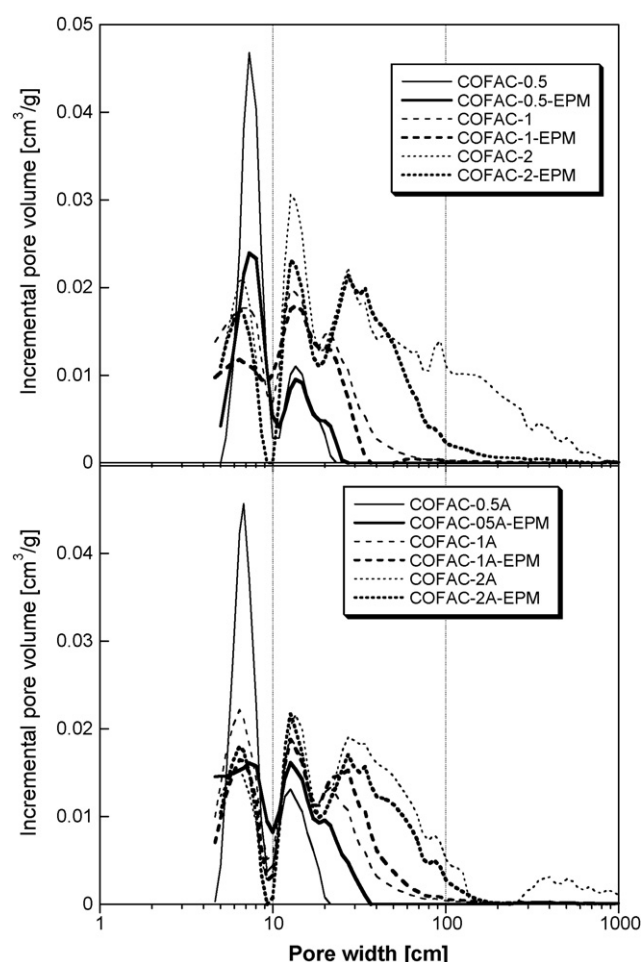

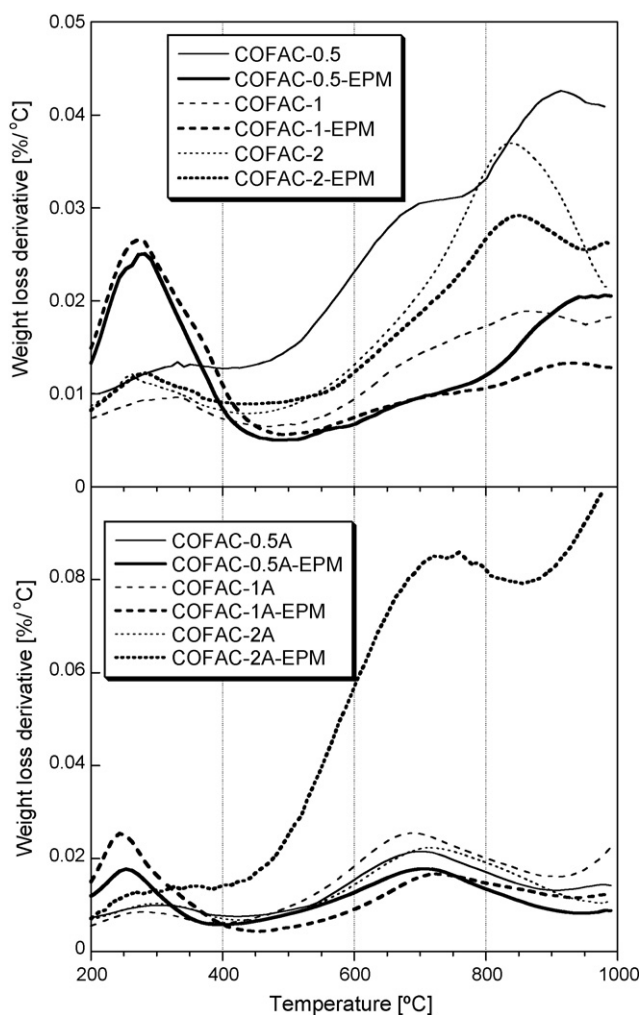**Fig. 4.** Pore size distribution for carbons before and after (EPM) exposure to H_2S.

Fig. 5. DTG curves in nitrogen for the initial and exhausted samples.

Fig. 6. FTIR of carbonized ground coffee (a) and ground coffee/ZnCl$_2$ 1:1 activated carbons (b).

In the case of acid treated samples exposed to H$_2$S opposite changes are found (Fig. 4). For COFAC-0.5A and COFAC-1A an increase in the sizes of pore is found which can be explained by the oxidative effect of sulfuric acid formed in surface reactions. Since the content of inorganic matter is very small, the acid cannot be neutralized to the same extent as that on the surface of COFAC-0.5 and COFAC-1. Thus the species likely responsible for a relatively high capacity on COFAC-1A are nitrogen functional groups located in the pores where water can be adsorbed. These groups are expected to be incorporated the carbon matrix and therefore are not affect by HCl treatment. It was demonstrated previously that carbons containing the high volume of small pores with incorporated nitrogen species, such as Centaur®, are known to have high selectivity for sulfuric acid formation [20]. This is owing to their basicity [7] and the capability to activate oxygen [10,11].

3.4. Surface reaction products

Analysis of the weight loss between 200 and 400 °C for the exhausted samples can bring some information on the importance of specific adsorption centers. In the case of no-acid-treated samples one broad peak centered at about 250 °C, with an indication of a shoulder at about 280 °C, is visible on the DTG curves (Fig. 5). It represents removal of strongly adsorbed sulfuric acid [19]. The shoulder is likely related to the removal of zinc sulfate, which is expected to boil at 280 °C [24]. Since the carbons were obtained at 850 °C, the weight loss over 800 °C is not analyzed. Taking into
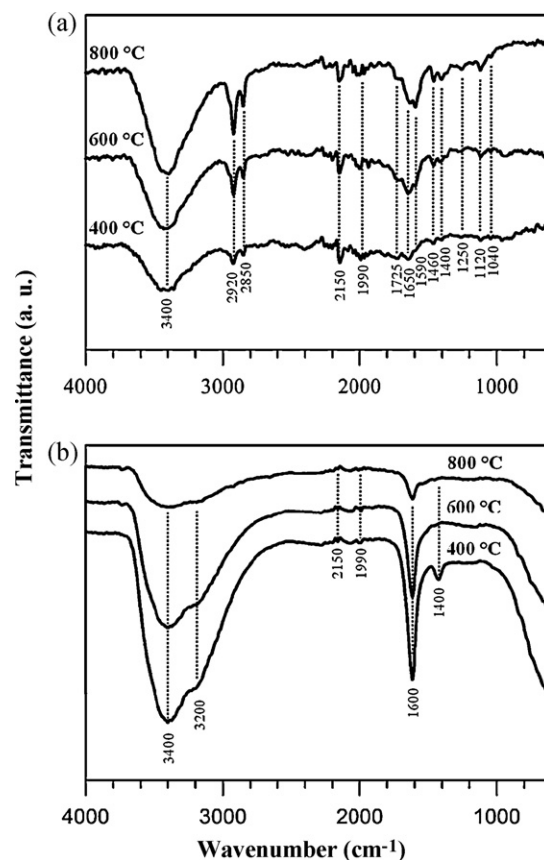
account that the weight loss represented by this peak is between 2 and 6 wt% for all samples and the amount of zinc in the samples, zinc sulfide should consist of a significant percentage of the surface reaction products. It is expected to be removed/decompose at temperatures much higher than 1000 °C. The results suggest that H$_2$S or sulfide ions first react with zinc before the sulfuric acid is formed. Another scenario, more plausible one, is that the difference in physical locations of sulfuric acid (in small pores) and zinc (in larger pores) limits the formation of sulfates. In the case of acid-washed samples only small peaks linked to the removal of sulfuric acid [19] are found on DTG curves.

3.5. Analysis of surface functional groups

Fig. 6 shows the FTIR spectra of carbonized ground coffee samples (Fig. 6a) and ZnCl$_2$ activated carbons (Fig. 6b) at three different temperatures. The carbonized samples display many bands that could be related to both oxygenated and nitrogenated functional groups, and no significant difference in the bands between the samples is observed: the broad band between 3000 and 3700 cm^{-1} includes many vibration modes of O–H and N–H functional groups [28], and so it is hard to figure out what functional groups contribute to this broad band. The presence of methyl and methylene groups is confirmed by the bands at 2850 and 2950 cm^{-1} that are attributed to the C–H and –CH$_2$– stretching modes of aliphatic said chains [28,29]. The bands at 2150 and 1990 cm^{-1} can be related to diverse vibration modes of C–N groups [28] plus the bands at 1590 and 1650 cm^{-1} can be associated with both C=N stretching modes or to C=C aromatic ring stretching [28,30]. However, the band at 1650 cm^{-1} can be also related to quinine and quinone groups [29]. The presence of this last nitrogenated group in carbonized ground

coffee could be confirmed by the bands at 1250–1000 cm^{-1}, however, due to their low intensity it is hard to be conclusive. Finally, the bands at about 1725 and 1400 cm^{-1} are often related to carboxyl groups [28,30]. On the other hand, the ZnCl$_2$ activated carbons (Fig. 6b) shows a broad band from 2700 to 3700 cm^{-1} that includes many vibration modes of diverse O–H and N–H functional groups. This broad band shows a maximum intensity at 3400 cm^{-1} and a shoulder at 3200 cm^{-1}. Such a peak bifurcation is often observed in compounds that have primary amines on their chemical structure [28,31]. The presence of amino groups could be confirmed by the intense band at 1600 cm^{-1}, however, this is also a characteristic band of aromatic rings [28,31]. Something to remark is, on one hand, the presence of a band at 1400 cm^{-1} for the activated sample at 400 °C, which is related to carboxyl groups, and on the other the absence of this band at higher activation temperatures, which could be related to the elimination of oxygenated surface groups promoted by the activating agent. Finally, the broad band below 800 cm^{-1} can be related to C–Cl groups that can form during the ZnCl$_2$ activation.

4. Conclusions

The results discussed in this paper show that spent coffee waste can be used as a precursor for efficient desulfurization adsorbents. Even though the residual inorganic matters takes part in the H$_2$S retention via salt formation, the specific features of the carbons' surface govern the separation process. The chemical activation method chosen resulted in formation of large volume of pores with sizes between 10 and 30 Å, optimal for water and hydrogen sulfide adsorption. Thus the efficient nanoreactors were formed. Even though activation process can be optimized/changed, the presence of nitrogen in the precursor is a significant asset of that organic waste. That nitrogen is expected to play a catalytic role in hydrogen sulfide oxidation.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.11.053.

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