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Preparation of activated carbons from coffee husks utilizing FeCl_3 and ZnCl_2 as activating agents

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ABSTRACT

Ferric chloride was used as a new activating agent, to obtain activated carbons (AC) from agro industrial waste (coffee husks). This material was compared with two samples from the same raw material: one of them activated by using the classical activating agent, zinc chloride, and the other, activated with a mixture of the two mentioned activating agents in the same mass proportion. The carbonaceous materials obtained after the activation process showed high specific surface areas (BET), with values higher than $900 \text{ m}^2 \text{ g}^{-1}$. It is interesting to observe that the activation with FeCl_3 produces smaller pores compared to the activation with ZnCl_2 . An important fact to emphasize in the use of FeCl_3 as activating agent is the activation temperature at 280°C , which is clearly below to the temperature commonly employed for chemical or physical activation, as described in the bibliography. All the studied materials showed different behaviors in the adsorption of methylene blue dye and phenol from aqueous solutions.

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1. Introduction

The contamination of natural water is an environmental problem that has been frequently discussed by several sectors of the society. One alternative to attack this problem is by using adsorbents to remove pollutants from aqueous effluents. This, has generated an increasing interest in the search for efficient and low cost materials to be used as adsorbents for the elimination of water-borne pollutants. Among those materials, activated carbons (AC) are the most efficient. Activated carbons have themselves demonstrated to be highly efficient [1] for the removal of many compounds such as dyes, metals, and low molar mass organic compounds. As a result, activated carbons have been used in treatments such as purification, deodorization, filtration, discoloration, dechlorination, flavor removal and the concentration of a great number of materials from liquid or gaseous substances, with several applications in wastewater treatment [2–4].

To obtain AC, different precursors of vegetable origin (wood, oils, husks, pits and seeds of plants and fruits) and polymeric materials can be used. The use of agricultural residues presents significant advantages, because of their low cost and also because they come

from renewable sources. Consequently, in recent years many works have been reported involving the manufacture of AC using agricultural residues, such as apricot and/or cherry pits, wheat straw, bean and rice husks, nut husks, corn husks [5–10] and many others [11,12].

In Brazil, coffee is one of the primary agricultural products, and it generates a large volume of residues, not only due to the sizeable annual production, but also because of the small fraction of fruit that is used as a final product. Every year about 30 million tons of solid residues (husk and pulp) are produced, and most is inadequately disposed. Only a portion of those residues is used for limited practical applications, such as raw material for the production of fuel; feedstock for obtaining chemical compounds; or as an additive to animal food, as a nutritional supplement. There are some antecedents in the use of coffee residues from Thailand and Colombia as the precursor of activated carbons [13,14], and then this is a possible use for Brazilian coffee residues.

To prepare activated carbon, chemical activation is widely employed, mainly using the reagents ZnCl_2 , KOH or H_3PO_4 as activating agents [15–17]. Although the iron chloride salt has similar characteristics to zinc chloride, in aqueous solution the iron cation is smaller than the zinc cation, and this opens up the possibility of producing AC with smaller pore sizes upon their activation. On the other hand, the zinc cation present in aqueous solution is a well-known pollutant. Moreover, the Fe salt has a low cost in com-

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parison with the Zn salt. The use of iron chloride is not completely new. Sing and co-workers [18] used it as an additive to prepare activated carbon cloths by physical activation, later on; it was widely used to obtain porous carbons from coals/coal tar pitches [19–24]. It has also been used in the chemical activation of precursors such as rayon [25] and studied over pyrolysis effect in lignocellulosic matter [26]. However, there are no descriptions of the use of iron chloride salt as an activating agent, for example instead of zinc chloride, to prepare activated carbon from agricultural wastes.

In this work the iron (III) salt, FeCl_3 , was tested as an alternative-activating agent to produce AC starting from coffee husks. The commonly employed activating agent, zinc chloride, was also used, in order to compare their characteristics and evaluate the efficiency of the resulting activated carbons as adsorbents of pollutants from aqueous medium.

To evaluate the adsorptive properties of the prepared materials two well known probe molecules are chosen: *methylene blue dye* (MB) and *phenol* representative pollutants from aqueous effluents of textile and tannery industries, respectively.

2. Experimental

2.1. Activated carbon preparation

The solid residue of the coffee fruit (husk) was collected from the experimental farm of EPAMIG (Empresa de Pesquisa Agropecuária de Minas Gerais-Brazil), located in the municipal district of Machado-MG. This raw material was dried at 110°C for 24 h and then treated with ZnCl_2 solution in a 1:1 mass proportion (salt: raw material) and pyrolyzed in a tubular oven (Lindberg Blue), under a N_2 flow of 100 mL min^{-1} , at 550°C , for 3 h. After the activation, the excess of ZnCl_2 was removed with a 0.1 M solution of hydrochloric acid, and then the product was washed with hot distilled water until a neutral pH was reached, obtaining the sample labeled “AC husk-Zn.” The same procedure was followed for the preparation of the carbon activated with ferric chloride (AC husk-Fe), and with a zinc chloride plus iron chloride mixture (AC husk-Zn/Fe), differing only in the pyrolysis temperature, which was 280°C when the iron salt or the mixed salts were used.

It is important to remark that other relations salt: raw material were studied, but the relation 1:1 was chosen because the resultant material presents the best textural characteristics, in particular specific surface area and porosity development.

2.2. Characterization of the materials

The carbon was characterized by physical N_2 adsorption/desorption at 77 K (using an AUTOSORB-1 instrument from Quantachrome). The specific surfaces (S_{BET}) were derived from N_2 adsorption isotherms by means of the BET equation. The pore size distributions and medium pore diameter were determined using the Density Functional Theory (DFT). The micropore volume ($V_{\mu\text{p}}$) were obtained by Dubinin–Raduskevich equation and the total volume of porous (V_{T}) by Gurvitsch rule at $P/P_0 \approx 0.985$. The surface groups were analyzed by infrared spectroscopy with a FTIR (Digilab Excalibur - FT3000) and by the potentiometric titration. Analyses of elemental carbon and hydrogen, carried out in a CHN 500A Shimadzu equipment, were accomplished to verify their level in the composition of the final materials. Thermogravimetric and Differential Thermal analysis (simultaneous TGA-DTA Shimadzu MOD 8065 D1) was made in the following conditions: N_2 or air atmosphere with heating rate of $10^\circ\text{C min}^{-1}$. Mössbauer spectra were obtained in a spectrometer CMTE model MA250 with a $^{57}\text{Co/Rh}$

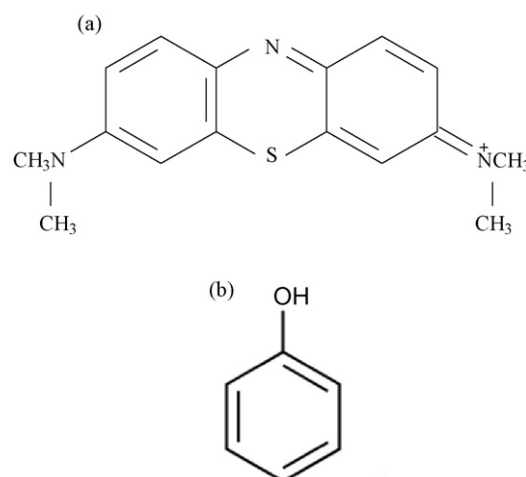


Fig. 1. Chemical structures of methylene blue (a) and phenol (b).

source at room temperature, to evaluate the presence of different type of iron the samples.

2.3. Adsorption tests

The adsorbents were used in adsorption tests from aqueous solutions of two well known organic pollutants: methylene blue organic dye and phenol. Fig. 1 shows the molecular structures of the organic dye and phenol. The adsorption tests were made in a batch-type system, beginning with solutions of the adsorbents at concentrations of 25, 50, 100, 250, 500 and 1000 mg L^{-1} . The adsorption experiments were made at room temperature ($25^\circ\text{C} \pm 1$) and at the proper pH of the solutions (5.7 ± 0.3). To obtain the adsorption isotherms, the solutions (10 mL) were left in contact with the adsorbent materials (10 mg) for a period of 24 h, and then they were centrifuged at 1000 rpm for 15 min. The collected supernatants were analyzed by UV–visible spectroscopy (Shimadzu-UV-1601 PC) in the following wavelength (λ_{max}): 645 nm for the methylene blue and 275 nm for the phenol.

3. Results and discussion

In the first item are introduced the results of the synthesis condition and characterization of the resultant materials, with the inherent discussion. In the second one, a special application in the adsorption of aqueous pollutants is discussed.

3.1. Synthesis and characterization analysis

3.1.1. Thermal, elemental and morphological studies

To evaluate the behavior of the samples as a function of the temperature, thermal analysis were realized in nitrogen and air atmospheres. Fig. 2(a) and (b) shows the thermogravimetric analysis profiles for the AC samples prepared from ZnCl_2 and FeCl_3 , before the calcination process, in a nitrogen atmosphere. To highlight the temperature at which a process involving a change of mass occurs, the differential curves (DTG) are also displayed in the figures. The curves corresponding to the two samples show distinctly different thermal responses. Whereas the sample activated with Zn salt presents several and complex transition regions as the temperature increases, the sample activated with the Fe salt does not show such transition regions. When assessing these patterns it becomes clear that the highest thermal process occurs at a temperature close to

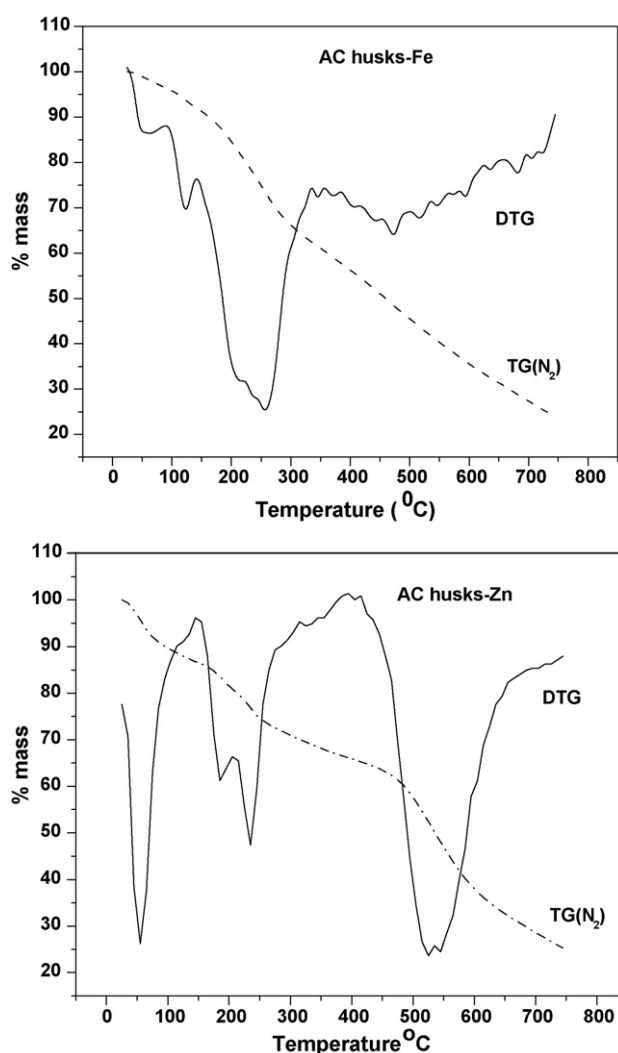


Fig. 2. Thermogravimetric analyses (TGA) in a nitrogen atmosphere of the precursor of activated carbon prepared with FeCl₃ (a); and ZnCl₂ (b).

550 °C for AC husk-Zn, and to 280 °C for AC husk-Fe. Accordingly, these temperatures were selected to activate the samples.

Fig. 3 displays the profiles of the thermogravimetric analyses in air, for the different activated carbons. The TG analyses of the samples in a flux of air show a different behavior at low temperature (until 300 °C) for the different types of activating agents employed. The samples prepared with Fe showed a major loss of mass in this temperature region; maybe the iron compounds produced a weak carbon structure in the samples. At temperature over 300 °C the behavior of the samples in TGA is similar. The very low percentage of residual sample at temperature near 800 °C reveals a low ash content.

To evaluate the content of carbon and hydrogen in the materials, an elemental analysis was realized and the obtained data are shown in Table 1. The samples prepared from iron salts present the higher levels of carbon, which could be associated to the temperature of activation. The presence of different contents of hydrogen (minor in samples prepared with iron) could be a consequence of the apparition of different surface centers during the synthesis process.

To observe the morphology of the prepared samples, the scanning electron microscopy-SEM shown in Fig. 4. Fig. 4(a) presents the micrograph for coffee husk, employed as the raw material for

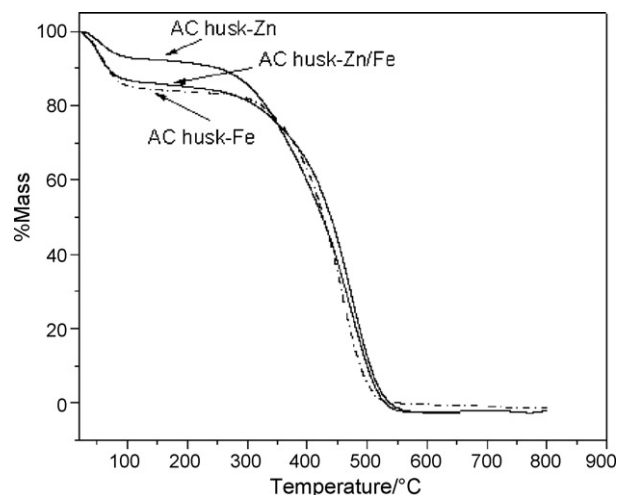
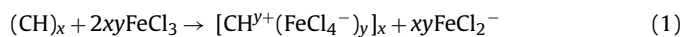


Fig. 3. Thermogravimetric analyses (TGA) under air atmosphere of all the activated carbons prepared in this study.

the preparation of the activated carbons. The material presents a surface morphology in the form of plates, possibly with a low specific surface area. On the other hand, the micrographs shown in Fig. 4(b)–(d) correspond to the materials collected after the activation process with FeCl₃, with the salt mixture (FeCl₃ + ZnCl₂), and with ZnCl₂, respectively. The morphology of the samples after the activation process has changed; surface craters were produced, which contributes to the increase of the surface area after the activation. For this analysis, it is clear that the presence of iron species in the preparation of the samples produces “craters” with thinner walls on its surfaces then, a weaker structure was created, which is in accordance with TG analysis.

The presence of iron in the samples during the activation process was studied by Mössbauer spectroscopy, and the results are shown in Fig. 5 and summarized in Table 2. It is interesting to note that all iron species formed during the activation process were completely removed after the pyrolysis and the treatment with HCl solution (Fig. 5(a)), since no resonance lines were observed on the Mössbauer spectrum. The removal of iron species is important to avoid the blockage of the pores and, consequently, a decrease in the adsorption capacity of the adsorbents produced after activating with Fe salts. The Mössbauer spectrum of the coffee husks impregnated with FeCl₃ before pyrolysis (Fig. 5(b)) showed one high-spin Fe²⁺ doublet, related to FeCl₂·2H₂O, and a broader singlet with isomer shift slightly smaller than in ferric chloride ($\delta = 0.44 \text{ mm s}^{-1}$), probably corresponding to $[\text{CH}^{\nu+}(\text{FeCl}_4^-)_y]_x$ species formed due to guest-host charge transfer reaction, in agreement with Eq. (1) [27]:



After the pyrolysis of this sample at 280 °C, the Mössbauer spectrum (Fig. 5(c)) presented magnetic ordering due to the presence of metallic iron (4.3%) and magnetite (26.8%). Quadrupole splitting distribution showed two Fe³⁺ doublets corresponding to akaganeite ($\beta\text{-FeO}(\text{OH},\text{Cl})$) and three high-spin Fe²⁺ doublets. One

Table 1
Elemental analysis (CH) for the obtained carbon from coffee husk (results in % in mass).

Sample	C	H
Husk raw	38.70	5.40
AC husk-Fe	61.27	3.58
AC husk-Zn	51.73	4.62
AC husk-Zn/Fe	62.94	3.23

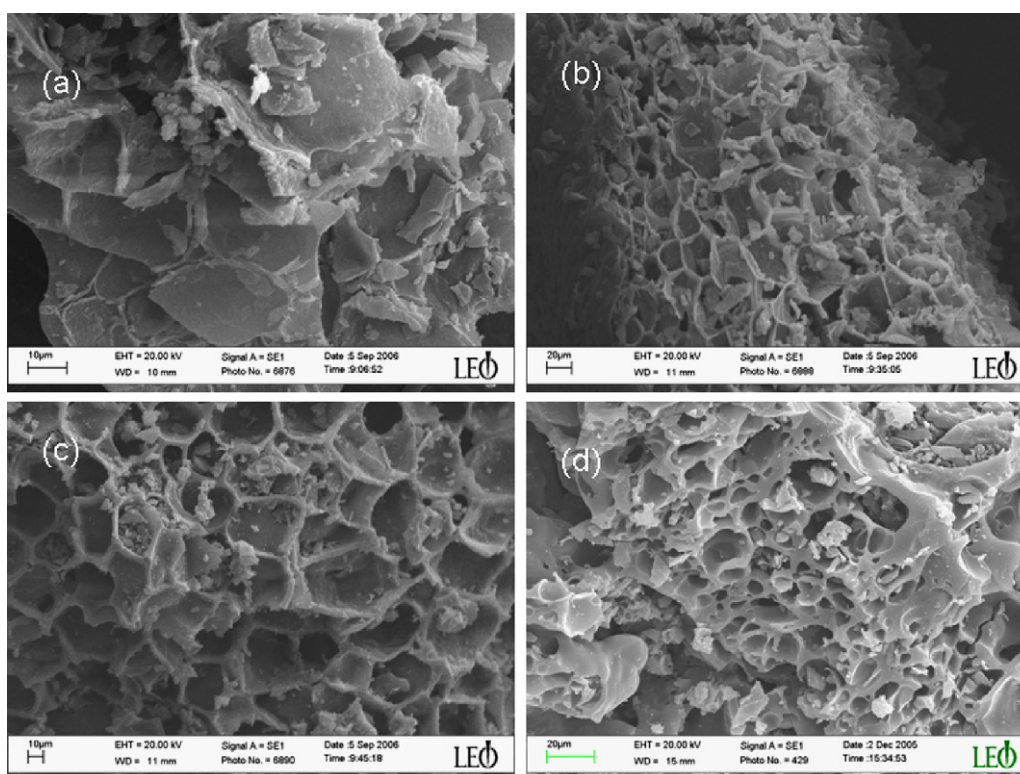


Fig. 4. SEM micrographs of (a) coffee husk; (b) carbon activated with FeCl₃; (c) carbon activated with the salt mixture (FeCl₃ + ZnCl₂) and (d) carbon activated with ZnCl₂.

doublet with larger quadrupole splitting ($\Delta = 3.05 \text{ mm s}^{-1}$) was identified as FeCl₂·4H₂O, one with $\Delta = 2.29 \text{ mm s}^{-1}$ as FeCl₂·2H₂O, and one was ill-determined and had an isomer shift very similar to FeCl₂·H₂O ($\delta = 1.13 \text{ mm s}^{-1}$), but with different quadrupole splitting. This component would be associated with iron forms in slightly compressed octahedral arrays of chlorine atoms. Although the variability of the Fe²⁺ quadrupole splitting is difficult to ascertain, we cannot fully exclude that the latter doublet is also associated with the existence of various structural forms of FeCl₂ [27].

3.1.2. Textural properties and surface groups analysis

To study the specific surface and the porosity of the samples the standard N₂ sorption method was realized. Fig. 6 displays the isotherms of N₂ adsorption/desorption (Fig. 6(a)) and pore size distribution (Fig. 6(b)) for the activated carbons obtained from coffee husk. All the isotherms present a high adsorption at low relative pressure, characteristic of microporous materials, where the

adsorption branch resembles that of a type I isotherm in the IUPAC classification. After reaching a monolayer, a slight increase appears in mesoporous region, where the desorption presents a hysteresis loop of type H4, which is characteristic of slit shaped pores, such as those present in typical activated carbons. The results show that the different activating agents were efficient in terms of generating an activated carbon with a high specific surface area by using coffee husks as the precursor. The AC obtained by the activation of the coffee husk show specific surface areas of 1522, 1374 and 965 m² g⁻¹, respectively, by using only ZnCl₂; a mixture of ZnCl₂ and FeCl₃; and only FeCl₃. AC obtained with ZnCl₂ as activating agent showed a greater surface area compared to the alternative material, FeCl₃, proposed in this work. However, it is important to emphasize that the activation with ferric chloride, and the activation with the mixture of ferric and zinc salts, were accomplished at 280 °C, while the activation with just the zinc salt was only efficient at 550 °C. This represents substantial savings in terms of energy costs involved to produce adequate AC adsorbents from coffee husks. It is important

Table 2
Mössbauer parameters corresponding to spectra recorded at 298 K. δ = isomer shift with respect to αFe ; ϵ = quadrupole shift; B_{hf} = hyperfine field; Γ = full line-width at half height; AR = relative sub-spectral area.

Sample	⁵⁷ Fe site	δ (mm s ⁻¹)	ϵ , Δ (mm s ⁻¹)	B_{hf} (T)	Γ (mm s ⁻¹)	AR (%)
(b)	FeCl ₂ ·2H ₂ O	1.14(1)	2.34(1)		0.51	77.2(9)
	Fe ³⁺	0.41(1)			0.63	22.8(8)
(c)	Fe ²⁺	1.14(2)	1.66(1)		0.44	15.8(4)
	FeCl ₂ ·2H ₂ O	1.20(1)	2.29(1)		0.35	13.0(4)
	FeCl ₂ ·4H ₂ O	1.19(1)	3.05		0.31	12.9(3)
	FeO(OH, Cl)	0.35(1)	0.99(2)		0.36	13.2(9)
	FeO(OH, Cl)	0.34(1)	0.53(2)		0.42	14.0(9)
	αFe	0	0	33.2(1)	0.31	4.3(4)
	{Mt}	0.69(1)	-0.03(2)	45.9(1)	0.45	17.3(5)
	[Mt]	0.27(1)	-0.02(1)	49.1(1)	0.32	9.5(5)

(b) Before pyrolysis and without treatment with HCl and (c) after pyrolysis and without treatment with HCl.

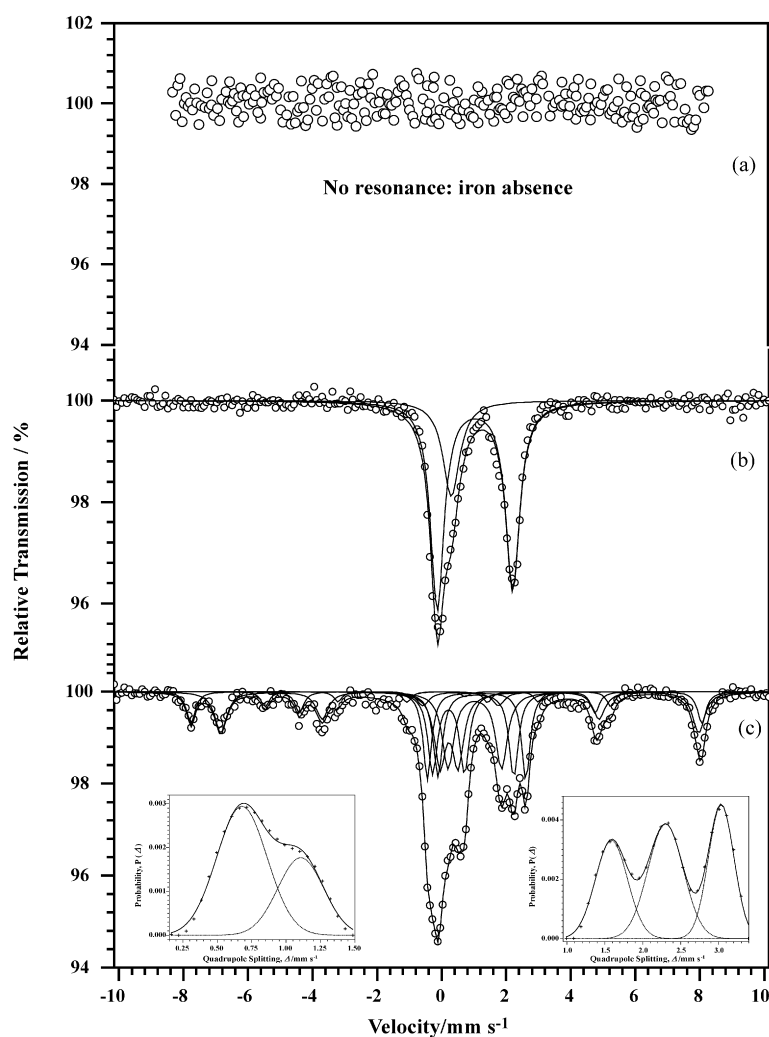


Fig. 5. Room temperature Mössbauer spectra for the coffee husks with FeCl_3 treated at $110^\circ\text{C}/24\text{h}$ (a) after pyrolysis and after treatment with HCl solution; (b) before pyrolysis and without treatment with HCl; and (c) after pyrolysis and without treatment with HCl.

to remark that the activation with FeCl_3 at 550°C did not produce a porous material (result not presented) because of the FeCl_3 boiling point (285°C).

Fig. 6(b) presents the pore size distributions for the activated carbons made in this study. This figure shows that the pore structure of these materials consists basically of micropores, which are defined by IUPAC as pores smaller than 20Å in diameter. The materials that were activated using the zinc salt, whether pure or mixed with ferric chloride, presented a small portion of pores above 20Å in diameter (mesopores) as well. It is interesting to observe that the AC obtained with ferric chloride showed the formation of better-defined pores centered at approximately 8Å . This result could be due to the smaller ionic radius of the Fe^{3+} ions (55pm) when compared to Zn^{2+} (74pm). This in turn suggests that it may be possible to obtain an AC with very small pores and/or a more uniform pore size distribution through the proper choice of activation agent. It could be expected such treatments to allow the use of suitably activated materials in different industrial adsorption processes, even beyond liquid-based applications—for example, those involving the separation or storage of gases such as H_2 or CH_4 .

Table 3 summarizes the textural data of the samples, where the characteristics observed in Fig. 6 are quantified. The sample AC husk-Fe presented the minor medium pore diameter, but the minor microporous volume, therefore the minor specific surface.

All the data are in accordance with the predictions in base to the salts used.

To characterize surface groups on activated carbon, FTIR (Fourier transform infrared) transmission spectra were obtained. FTIR of coffee residue (husk), and of activated carbons prepared with either ZnCl_2 or FeCl_3 , are shown in Fig. 7.

The infrared spectra for AC husk-Zn, as well as that for AC husk-Fe, suggest the complete carbonization of the material, which can be monitored by the complete disappearance of the bands associated with C–H stretching, at 2928 and 2855cm^{-1} , after the preparation of the activated carbon. The bands around 1613cm^{-1} , corresponding to quinonic and carboxylate groups, and the bands at 1241cm^{-1} have been assigned to the C–O stretching vibration of lactonic and phenolic groups, present in different activated carbons surfaces [28]. A broad band located around at 3400cm^{-1} is typically attributed to hydroxyl groups or adsorbed water. Fig. 7

Table 3

Textural data obtained by nitrogen isotherms, using BET and DFT methods.

Samples	S_{BET} (m^2g^{-1})	$V_{\mu\text{p}}$ (cc g^{-1})	V_{T} (cc g^{-1})	d_{p} (nm)
AC husk-Zn	1522	0.60	0.75	0.90
AC husk-Zn/Fe	1374	0.53	0.65	0.77
AC husk-Fe	965	0.40	0.51	0.63

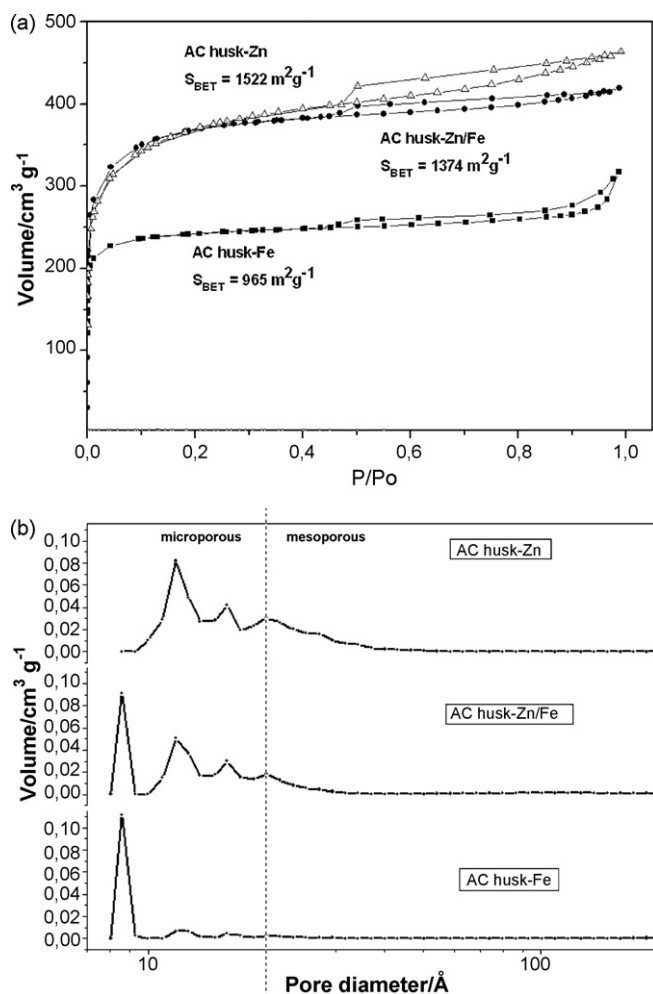


Fig. 6. Isotherms of N₂ adsorption/desorption (a) and pore size distribution (b) for the activated carbons obtained from coffee husk using different activating agents.

shows that both activated carbons present similar characteristics in their study by the FTIR technique, behave the band corresponding to quinonic and carboxilate groups is little more intense for AC husk-Fe.

3.2. Adsorption tests and potentiometric titration experiments

Adsorption tests in water decontamination processes were carried out to evaluate the performance of the synthesized samples in specific applications. The adsorption capacity of the activated carbon samples was tested using a dye as model molecule, and phenol as a representative pollutant.

The dye employed possesses either cationic property (methylene blue dye). The adsorption isotherm for the methylene blue dye is shown in Fig. 8(a). The carbon activated with zinc salt (AC husk-Zn) presented an elevated adsorption capacity for the cationic dye—approximately 263 mg g⁻¹ which is inside the highest values reported with different activated carbons [29], which proves the excellent adsorption capacity presented for the coffee husk carbon introduced in this work.

The adsorption capacity of the activated carbon was also tested with phenol as the model adsorbate. The adsorption isotherms for each tested adsorbent are shown in Fig. 8(b). The adsorption capacities were of approximately 167, 117 and 65 mg g⁻¹ for the samples AC husk-Zn/Fe, AC husk-Zn and AC husk-Fe, respectively. These values are similar to other reported results [30], which show that

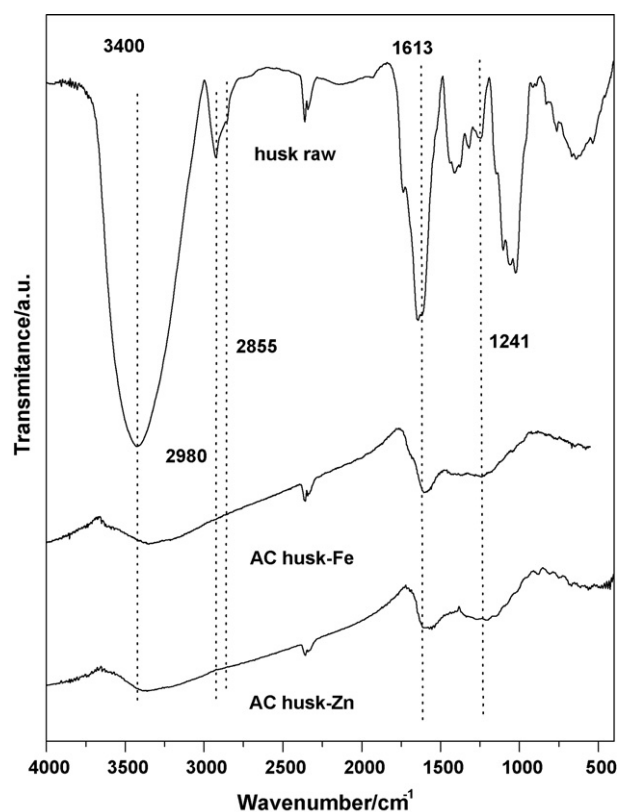


Fig. 7. FTIR of the coffee husk-based carbon activated with FeCl₃ and ZnCl₂.

the activated carbons prepared in this study are potentially good adsorbents for pollutants like phenol.

It is clear that the adsorption capacities of the probe molecules on each activated carbon is different suggesting that the adsorption processes are associated with different chemical affinities towards the sample surfaces.

In fact, information from potentiometric titration experiments shows that the surface acidity or pK_a distributions are very different on all the tested samples. The pK_a values, as well as the concentrations of groups calculated using NaOH as titrate and the SAIEUS method for titration curve deconvolution, are summarized in Table 4. Species with pK_a values smaller than 8 can be considered as carboxylic acids and those with pK_a values greater than 8 can be ascribed to OH functional groups present in the surface [31]. All the samples prepared with a part of iron, show an increasing lineal dependence in the mmol of NaOH versus pK_a, but the sample synthesized with just iron salt (AC Husk-Fe) has the biggest values in mmol of NaOH. On the other hand, the sample prepared with zinc salt (AC Husk-Zn) has a decreasing lineal behavior. Then, the strong presence of acidic centres in the samples prepared with iron salt could be the responsible for this adsorption behavior, and perhaps it is influencing in the textural obtained data.

Table 4

Peak positions (pK_a values) and the amount of surface groups (in mmol/g; in parentheses) calculated from potentiometric titration using the SAIEUS approach.

Sample	pK _a 4–6	pK _a 7–9	pK _a > 10	All groups
AC husk-Fe	5.73 (0.183)	8.10 (0.218)	11.0 (0.305)	0.706
AC husk-Zn	5.58 (0.160)	8.36 (0.127)	11.9 (0.109)	0.396
AC husk-Fe/Zn	5.34 (0.139)	7.67 (0.160)	10.8 (0.202)	0.501

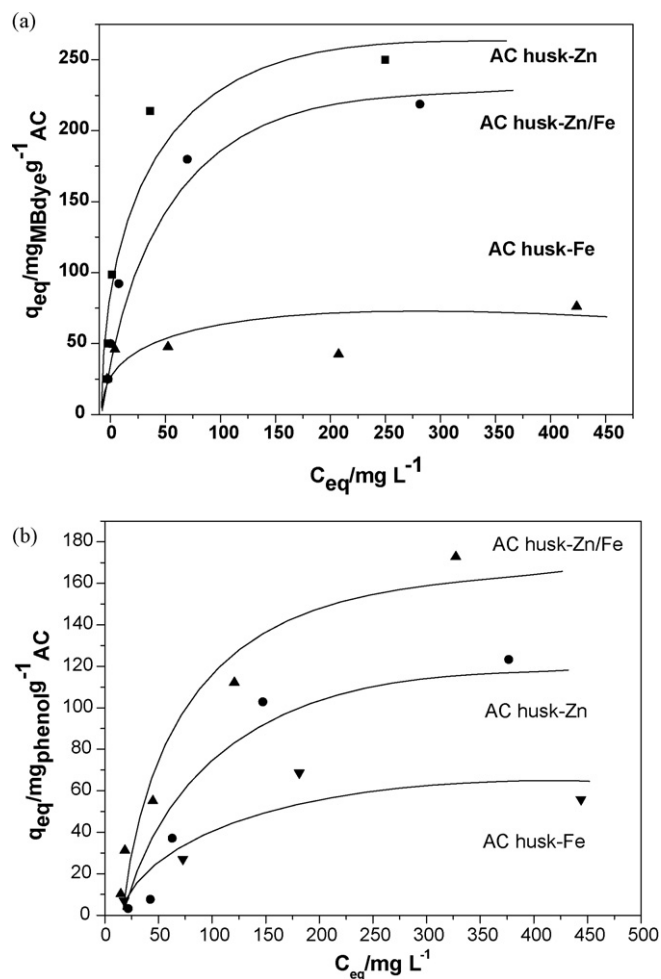


Fig. 8. Isotherms of adsorption of the methylene blue dye (MB dye) (a) and phenol (b) using the different activated carbons.

4. Conclusions

This work describes the use of ferric chloride as the activating agent in the preparation of activated carbons from coffee husks. The iron salt allowed the preparation of a material with high specific surface area ($965 \text{ m}^2 \text{ g}^{-1}$) and very small pores, through an activation at temperatures far below to those employed with the activating agents commonly described in the bibliography. The characterization studies showed that there was a complete pyrolysis of the components present in the iron-impregnated material at a temperature of 280°C . Mössbauer analysis indicates that the activation process took place by the action of the ferrous chloride formed after the previous thermal treatment at 110°C , but before the final pyrolysis process.

The use of iron salt in the synthesis process produces different surface centres than the use of zinc salt, then, it is an important aspect to take into account for different applications.

The activated carbons obtained in this work presented high adsorption capacities for cationic dyes and phenol; in fact, the carbon obtained by activating coffee husks with ZnCl_2 and a mixture of iron and zinc salts, presented adsorption capacities in a superior range than those described in the bibliography for methylene blue and phenol, respectively.

For a better understanding of the properties of these activated carbons, it is necessary to expand this work to include the adsorption of other potentially polluting molecules.

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