

Porosity and adsorption properties of an activated charcoal

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Abstract

Activated Carbons were prepared from esparto grass (*Stipa tenacissima*) by activation with different amounts of KOH and different temperatures of pyrolysis. The study of carbonization was carried out by thermal analysis (DSC, Tg, DTg and simultaneous Mass spectroscopy). Moreover, the characterization of surface carbons was performed by means of measurement of surface area, by BET method (S_{BET}), the micro and mesopore area, by Dubinin–Radushkevich (S_{mic} and S_{ext}), the pore size distribution, by DFT and the surface charge distribution, by potential Zeta and Mass Titration. Probes of adsorption with anionic surfactant were carried out. These results suggest that the fundamental factor over adsorption was the development of mesoporosity in carbons activated at great ratios of KOH impregnation. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the main fields of Activated Carbons (AC) employment is pollution control. The high adsorption capacity of ACs over a wide range of substances, joined to their low production cost, justifies their use in the removal of different pollutant agents of medium both gas and liquid [1–6]. An example is the surfactants [7–10], one of the most commune water pollutants due to their wide employment on very large industrial processes [11]. These pollutants imply a risk for fauna, due to some types of surfactant employed and give rise to intermediate compounds with estrogenic activity [12].

Since the adsorption is a surface process, the principal goal has been the obtaining of carbons with the best possible surface characteristics for adsorption. These optimum characteristics depend on the type of molecule to adsorb, but generally the aim is to obtain carbons with a very large surface area and the maximum micropore volume. Moreover, according to the adsorbate, it is possible to modify the surface of carbon creating or destroying acid or basic surface groups [13,14], which could change the non-polar character of the carbon surface.

The ACs are constituted principally by carbon atoms, which form aromatic sheets cross-linked in a random manner, and other heteroatoms as oxygen, principally, nitrogen, sulphur or hydrogen, depending on the raw material employed and of the physical or chemicals treatments. The arrange-

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ment of the aromatic sheets is irregular and gives rise to a solid with free interstices between the sheets [1] (porosity). Moreover, are other heteroatoms present.

It is possible to obtain ACs from a wide range of raw materials (lignocellulosic materials, cokes, tars or coals) [15,16], by means of the carbonization in an inert atmosphere (usually N_2). Moreover, different procedures (activation methods) are employed for enhance the surface area values and pore volume of carbon, creating new pores during the carbonization process. Thus, the impregnation with large amounts of KOH, or other compounds (Chemical activation), is a widely used method to obtain ACs with a very large surface area and great micropore volume. Although the mechanism of the activation process is not completely understood yet, some studies [17–19] indicate that the formation of K_2CO_3 or K_2O from KOH causes the separation of carbons layers. This enhances the porosity and, therefore, the surface area of carbon.

The final pore structure and surface area development depend on the raw material employed and the carbonization history (heating rate, final temperature, atmosphere, activated agent employed, ratio of activation, etc.) [1].

However, besides these structural facts, the adsorption could be strongly affected by the presence of acid or basic surface groups (carbonyls, phenols, lactones, quinones, etc.) in carbon. Thus, the surface could change their non-polar character, making it more or less hydrophilic, change the point of zero charge and the negative surface charge density.

The aim of this work is the study of properties of an AC obtained from a lignocellulosic material activated with different KOH ratios, some of their textural and chemicals properties and their possible use as surfactant adsorbent.

2. Experimental

Carbon was obtained from esparto-grass (*Stipa tenacissima*), which was impregnated with aqueous solutions of KOH (analysis grade) at different ratios (0, 20, 50, 100 and 400% by

weight) in a rotary evaporator. After impregnation, the pyrolysis was carried out under N_2 atmosphere (100 ml min^{-1}) in a tubular furnace up to 673, 873 and 1073 K, keeping the maximum temperature for 30 min. The heating rate employed was 10 K min^{-1} . The carbon was left cooled under N_2 atmosphere up to room temperature. With the purpose of eliminate the K-compounds from the carbon surface; the samples were washed in a soxhlet extractor with HCl dissolution and bidistilled water. The samples were denoted by the E letter followed by ratio (in%) of impregnation and pyrolysis temperature, in Kelvin. The non-impregnated samples were denoted as E-0 (temperature).

The surfactant employed was an anionic type with a polyoxietilenic chain (C_9H_{19} -ph-(OCH_2-CH_2) $_{10}$ $SO_4^-Na^+$), which was supplied by CFPI (France).

The thermal analyses Tg (Thermogravimetry), DTg (Derivative of Tg) and DSC (Differential Scanning Calorimetry) of the carbonization process were carried out under the same conditions of pyrolysis. The measurements were performed in a Seiko SSC/5210 System, equipped with Tg/DTA 320 and DSC/320 cells.

Simultaneously to Tg/DTg, mass spectrometry (MS) measurements were also produced to follow the evolution of gases in the carbonization process with a Thermostar Balzers Mass Quadrupole Spectrometer.

Specific surface areas were determined by N_2 adsorption isotherms at 77 K applying the BET method in a Micromeritics ASAP 2010 Volumetric System. The time employed in measurements was considered long enough for achieving the equilibrium [20]. Pore size distributions were calculated by the Density Functional Theory (DFT) method by means of the DFTplus program. Moreover, the area of micropores (S_{mic}) was obtained by mean of Dubinin–Radushkevich equation and macro and mesopores (S_{ext}) was calculated by difference.

Zeta potentials were measured by a Zetameter 3.0+ with the aim to obtain the Isoelectric Point (IEP). With this purpose, ten solutions of 50 ppm of each sample were prepared in plastic

bottles with CO₂-free bidistilled water. The pH values were fixed between 3 and 12 by adding small amounts of KOH and NaOH. The bottles were sealed and left to stabilize for 24 h before the measurements.

Mass Titration (MT) of activated carbons aqueous slurries were carried out following the method proposed by León y León et al. [21] which is a modified version of the model proposed by Schwarz et al. [22]. Around 1 g of each carbon was placed in a plastic bottle with 10 ml of CO₂-free bidistilled water and left to stabilize for 48 h. After this time, the pH was measured and small volumes of water were added periodically prior to the next pH measurement. The samples were left stabilize for 24 h shaking between measurements.

The surfactant adsorption isotherms from water solutions were obtained by the immersion method [23] at 25°C and with shaking for 24 h. The adsorbed amount was calculated on the basis of the concentration change, determined by UV spectroscopy with a Varian Cary 1 Spectrophotometer at 275.08 nm, before and after surfactant adsorption on activated carbons.

3. Results and discussion

3.1. Carbonization process and characterization of non-activated carbons

The different carbonization steps, the temperature at which it occurs and extension of process were followed by Tg and DTg data (Fig. 1). These, coupled with the data of DSC, that indicates the kind of process (exo or endo), and the kind of gases evolved measured by MS (Fig. 2), allow better understanding of the carbonization process.

Thus, it was possible to see that the principal carbonization process of esparto takes place between 470 and 670 K, with a mass loss of about 75% accompanied by a large evolution of CO₂ and, in smaller amounts, the rest of organic molecules as CH₄ ($m/z^+ = 15$ and 16), O₂ ($m/z^+ = 16$ and 32), H₂O and OH⁻ ($m/z^+ = 17$ and 18) (Fig. 2).

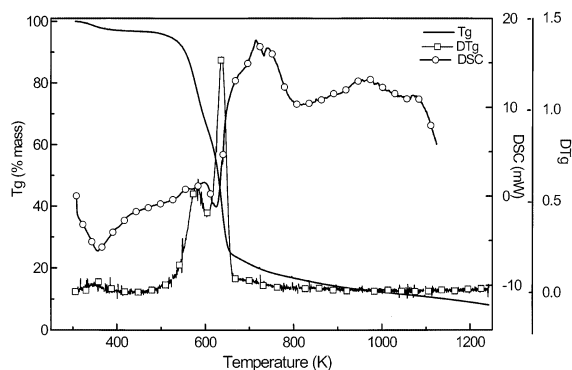


Fig. 1. Thermal analysis data (Tg, DTg and DSC) of non-impregnated samples carbonization.

This first mass loss takes place by means of two consecutive steps, clearly indicated by two peaks in DTg-curve (Fig. 1). The DSC curve shows weak exotherm and endotherm peaks in this range of temperatures. These processes were due to the different temperature at which two of the principal constituents of lignocellulosic materials decompose: the hemicellulose and cellulose, while the lignin decomposes in a wider range and higher temperatures [24,25].

The carbonization at this temperature leads to a non-porous char (E-0 673 K) with very low surface area (only 2 m² g⁻¹). This low area value was due to the fact that the carbonization process was not finished, and the rest of tar is still present and many surface groups were not removed from the surface yet.

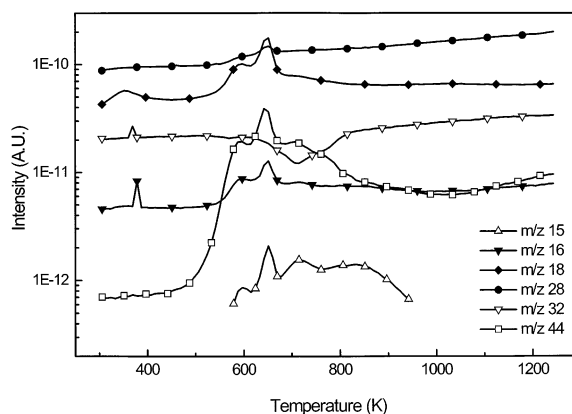


Fig. 2. Gas evolution of non-impregnated sample carbonization registered by mass spectroscopy.

Table 1
Surface characterization of carbons^a

Sample	S_{BET} (m ² g ⁻¹)	V_{mic} (cm ³ g ⁻¹)	V_{tot} (cm ³ g ⁻¹)	S_{mic} (m ² g ⁻¹)	S_{ext} (m ² g ⁻¹)	W_0 (cm ³ g ⁻¹)
E-0 (673 K)	2	—	—	—	—	—
E-0 (873 K)	456	0.176	0.186	—	—	—
E-0 (1073 K)	254	0.082	0.090	—	—	—
E-KOH 20% (673 K)	4	—	—	—	—	—
E-KOH 400% (673 K)	7	—	—	—	—	—
E-KOH 20% (873 K)	260	0.093	0.101	227	17	0.082
E-KOH 100% (873 K)	620	0.214	0.233	590	23	0.231
E-KOH 400% (873 K)	815	0.264	0.287	677	31	0.297
E-KOH 20% (1073 K)	820	0.270	0.278	800	30	0.291
E-KOH 100% (1073 K)	1625	0.477	0.642	1495	217	0.567
E-KOH 400% (1073 K)	1960	0.496	1.01	900	860	0.653

^a The surface area was calculated by BET method, in N₂ at 77 K. The volume of nitrogen adsorbed by microporous (V_{mic}) and the total volume adsorbed (V_{tot}) were calculated by DFT. The surface area due to micropores (S_{mic}), the surface area due to mesopores (S_{ext}) and the total volume of micropore system (W_0) were calculated by Dubinin–Radushkevich.

In a second process, between 673 and 873 K, an important microporosity development took place, which consequently involved a great increment of surface area values (from 2 m² g⁻¹ at 673 K to 456 m² g⁻¹ at 873 K Table 1). Practically all nitrogen adsorbed volume of E-0 (873 K) sample was due to micropores (95%), whereas the volume of mesopores was negligible. In this carbon, it was possible to distinguish three different kinds of micropores by DFT analysis, with a pore width size of 8, 12 and 15 Å (Fig. 3). This development was due principally to two facts. In first place, the complete (or quasi-complete) carbonization of sample, that required the removal of the tar, was registered in Tg-analysis as a mass loss of about 10%. On the other hand, the decomposition of lignin took place in this range of temperature too. This decomposition has not a great effect over the mass loss but caused strong energetic effects. The DSC analysis reveals great exothermic processes between these temperatures (Fig. 1).

When the temperature of pyrolysis was increased up to 1073 K, the surface area and pore adsorption values decreased. Moreover, in Tg-curve, the mass loss trend was to stabilize and only in DSC curve could a very weak exotherm at 900 K be observed. This fact seems to indicate to us that a structural crumbling takes place and, as a consequence, the narrower pores were destroyed whence the surface area decreased (from 456 to

254 m² g⁻¹). The differences between carbons obtained at 873 and 1073 K are mainly reflected on the pore size distribution. Thus, the lower temperature carbon has three different size pores, meanwhile the higher temperature carbon has only one of 16 Å (Fig. 3).

3.2. Carbonization process and characterization of activated carbons

The characteristics and surface properties of ACs obtained were strongly affected by the two parameters studied: the temperature of pyrolysis and the amount of KOH employed.

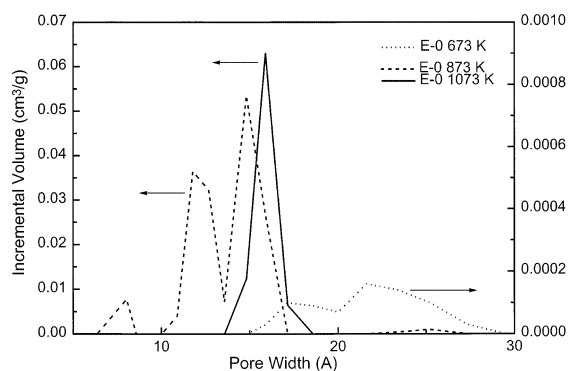


Fig. 3. Pore size distribution (Å) of no-activated samples obtained by DFT analysis.

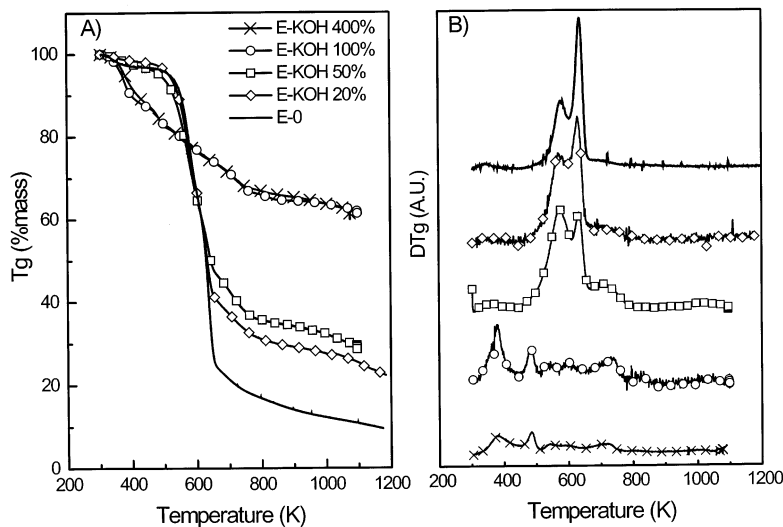


Fig. 4. Comparison of Tg (A) and DTg (B) analysis of samples carbonization.

The activation process not only changed the textural properties of samples, but also modified their evolution. Thus, whereas in non-activated samples (E-0) the maximum development of surface area was obtained at 873 K, in impregnated samples the surface area increased continuously with pyrolysis temperature (Table 1).

When the samples were activated, the carbons presented a great enhancement of surface area and porosity, especially when they were treated with high amounts of KOH (100 or 400%) and pyrolysis was carried out at the maximum temperature (1073 K). This last factor was fundamental for the development of surface area and porosity. Only at high temperatures (873 and 1073 K) did the amount of KOH employed have any influence on carbon porosity (Table 1).

Fig. 4 shows the Tg and DTg curves of impregnated samples carbonization. The profile of impregnated samples with a low amount of KOH (20 and 50%) presents a similar behaviour to E-0; only a progressive shifting of temperature at which point the carbonization and different mass loss (75 and 70%, respectively) were observed.

The greater differences were observed in samples E-KOH 100% and E-KOH 400%. The Tg curves of these samples were practically equal and the mass loss was about 40%. The effect of KOH

at these concentrations is clearly seen in DTg curves. Thus, the peaks of hemicellulose and cellulose decomposition observed at 575 and 630 K in the lower impregnated samples practically disappear, and two new peaks were registered at 380 and 480 K.

For KOH ratios higher than 20%, the DSC curves (Fig. 5) show an increasing exothermic peak with the amount of KOH employed at 490 K, which correspond to the formation of K_2CO_3 from KOH, which reacts with the CO_2 evolved from the cellulose and hemicellulose decomposi-

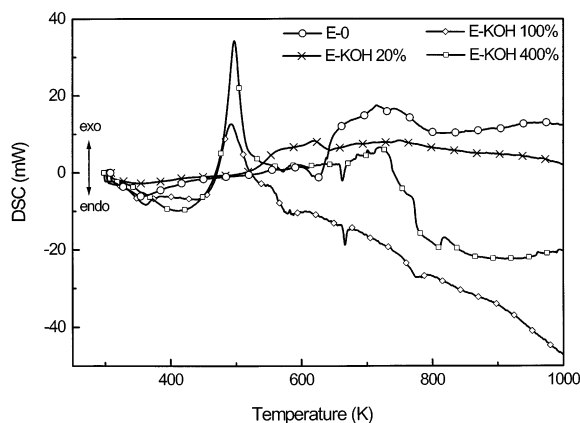


Fig. 5. Comparison of DSC profile of samples carbonization.

tion. Moreover, in samples with 100 and 400% of KOH, a sharp endothermic peak at 660 K was detected. These peaks correspond to the melting of KOH that rests in the samples.

The development of porosity and surface area has been explained by the transformation of KOH to K_2CO_3 [17–19], which caused the lamellae separation in the carbon bulk.

Nevertheless, carbon obtained at 673 K show a very similar surface area values to E-0 carbon. This seems to indicate that, at this temperature, the K_2CO_3 formed remains in the carbon surface and, therefore, did not give rise to porosity development. This is due to the fact that E-0 673 was a non-porous carbon and the KOH could not penetrate deeper into the carbon bulk.

When the temperature of pyrolysis increases between 673 and 873 K the surface areas and porosity increase like in the E-0 samples. The difference with these samples occurred when temperature was increased up to 1073 K; then a great development in porosity and surface area took place (Table 1).

The reason for this different behaviour could be that when the KOH impregnated melted (near 670 K) it filled the carbon pores, producing two effects. On one hand, it was transformed, totally or partially, to K_2CO_3 , and this last is responsible of pore development due to the lamellae separation on carbon bulk. On the other hand, it could avoid the micropore destruction at higher temperatures.

As we said above, the amount and pore size formed by activation and therefore, the surface area development, depend on the temperature of pyrolysis as well as of amounts of KOH employed (Fig. 6). At higher temperatures we obtained larger amounts of micropores with smaller pore size, which were reflected in micropore adsorption values (samples treated at 1073 K adsorbed twice amount of N_2 than samples treated at 873 K, as it seen in Table 1). However, at the same time, it enhanced the formation of mesopores as well. The surface areas of micropores (S_{mic}) and mesopores (S_{ext}), calculated by means of the Dubinin–Radushkevich equation [26] in (Table 1), show the dramatic increase of surface area due to mesopores in sample E-KOH 400%, where the S_{ext} grew up from $31 \text{ m}^2 \text{ g}^{-1}$, in carbon obtained at

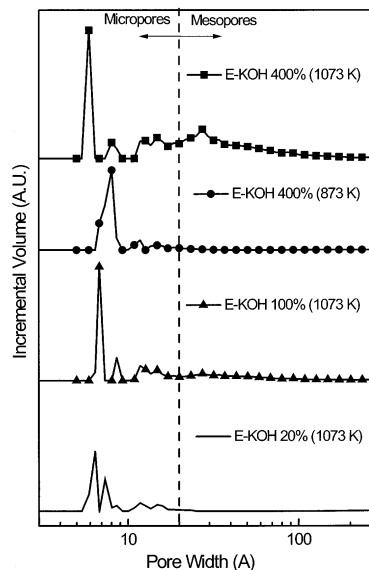


Fig. 6. Pore size distribution (Å) of activated carbons obtained by DFT analysis.

873 K, to $860 \text{ m}^2 \text{ g}^{-1}$ at 1073 K. Thus, whereas the mesopore percentage was less than 10% of the total in the rest of the samples (including the non-impregnating samples), in E-KOH 100% (1073 K) and E-KOH 400% (1073 K) samples, these percentages were 25% and nearly 50%, respectively (Fig. 7).

The differences observed in the mesoporosity between carbons obtained at 873 and 1073 K was

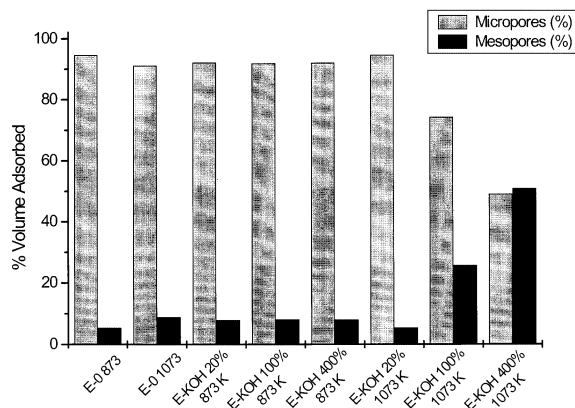


Fig. 7. Percentage of volume adsorbed by micropores and mesopores of carbons.

Table 2

Values of Isoelectric Point (IEP) calculated by electrophoretic measurements, Point of Zero Charge (PZC) calculated by means of mass titration and pH of carbons

Sample	IEP	PZC	PZC-IEP	pH
E-0 673 K	5.6	7.30	1.7	7.24
E-0 873	5.0	8.4	3.4	8.65
E-0 1073 K	3.70	9.1	5.4	11.78
E-KOH 400% (873 K)	3.65	7.52	3.87	7.26
E-KOH 20% (1073 K)	3.80	7.57	3.77	7.35
E-KOH 50% (1073 K)	3.53	7.36	3.83	6.20
E-KOH 100% (1073 K)	3.51	7.57	4.06	6.80
E-KOH 400% (1073 K)	3.36	7.3	3.9	7.65

probably due to the major extension of K_2CO_3 formed at higher temperatures and the possibility of formation of other potassium compounds (different oxides) that could be influential in mesopores formation.

In the case of sample E-KOH 400% (1073 K), different results were obtained when applying the DFT or Dubinin–Radushkevich equations. By DFT the volume adsorbed by micropores, and therefore, the area of micropores, was larger than in sample E-KOH 100% (1073 K). However, by Dubinin–Radushkevich the surface area due to micropores decreased from 1495 to 900 $m^2 g^{-1}$. This is due to the increased mean pore size from 7.6 to 14.5 Å, respectively.

3.3. Surface charge

Activation process not only had influence on porosity and surface area, it also produced chemical changes on carbon surfaces. Thus non-impregnated carbons present a basic character (Table 2), which was increased by effect of temperature, as a consequence of destruction of acidic groups located on the surface [14]. The basic character of carbons is not totally explained yet, but probably is associated to the presence of delocalised electrons in the basal planes of the graphitic microcrystals [27]. This factor is predominant in the

absence of oxygenated surface groups, which usually have acid character.

In ACs, this basic character was lost, and quasi-neutral carbons were obtained. This could be due to a break of aromatic rings of carbon bulk as a consequence of activation treatment.

The surface charge and its distribution on the carbon surface are two important factors which can determinate the behaviour of carbons in processes such as adsorption. The net surface charge can be obtained by both electrophoresis (determination of potential Zeta) and MT measurements [25].

The Zeta potential, the potential at the shear plane which is adjacent to external surface, yield information about the external surface charges of carbon particles in water solution, through the IEP. IEP is defined as the pH value below which the average charge of external surface of the AC will be positive [26].

Meanwhile, MT information involves the transfer of ions (OH^- and H^+) between the bulk of ACs and their surface. The point of zero charge (PZC), which is obtained from MT measurements, is defined as the pH value below which the average charge of all AC surfaces accessible to solution will be positive [26].

The difference between IEP and PZC can be considered as a measurement of surface charge distribution [26,27]. As shown in Table 2, The PZC values were higher than IEP. This fact indicates that the internal surface of the AC particles was more positively charged than the external surface.

In non-activated carbons, the increment of temperature involved a greatly enhanced difference between PZC and IEP. However, in ACs, this difference was more stable due to the changes of PZC values as well IEP were smaller than in E-0 samples.

3.4. Surfactant adsorption

Fig. 8 shows the adsorption isotherm of surfactant on different carbons. The highest adsorption capacity observed corresponds to E-KOH 400% (1073 K) with a value of nearly 825 $mol g^{-1}$, and the lowest adsorption was obtained with non-acti-

vated carbons (8 mol g^{-1}). The adsorption capacity followed the surface area (S_{BET}) trend. Nevertheless, the great difference observed between E-KOH 100% (1073 K) and E-KOH 400% (1073 K) was not justified by the relatively small difference in S_{BET} . The net surface charge or surface charge distribution neither too explained these differences in surfactant adsorption, since as we saw before, the surface charge distribution in ACs was very similar. Thus, the great adsorption difference between E-KOH 400% and E-KOH 100% should be attribute to the major amount of mesopores presents in the first one. This carbon adsorbed more than three times surfactant amount than E-KOH 100%, that is in good agreement with the difference between the mesopore area of these samples.

In fact, due to the great size of the surfactant molecules, these will penetrate easily in greater pores than in micropores.

When carbons had similar mesoporosity, other factors such as S_{mic} , explain the differences in adsorption, like in the case of E-KOH 400% (873 K) and E-KOH 20% (1073 K) samples.

4. Conclusions

The development of surface area and porosity in the studied carbons is strongly influenced by both thermal treatments and impregnation processes. Thus, for the non-impregnated samples,

the maximum surface area and total pore volume is obtained by pyrolysis at 873 K. The porosity is due, essentially, to micropores.

The development of porosity of AC was due to the action of K_2CO_3 formed from the melting KOH, which was introduced in the pores created at temperatures higher than 673 K.

In impregnated samples the maximum texture development is observed by impregnation with 400% KOH and pyrolysis at 1073 K. In these conditions, the obtained carbons exhibit high BET surface values and also a well developed porous structure, constituted by both micro and mesopores, with a relatively well-defined radii distribution.

The activation process, moreover, causes the loss of non-impregnated carbons basic character, probably due to the breakage of carbons aromatic rings.

The behaviour of these materials against liquid adsorption seems to be determined by external surface and mesoporous texture (micropores are not accessible to the large molecules of adsorbate), rather than the electric or chemical properties of the surface. So, we can conclude that, when we are working with these kinds of adsorbates, the activation processes should be directed to enhance the external surface and mesoporous texture rather than the chemical or electric properties.

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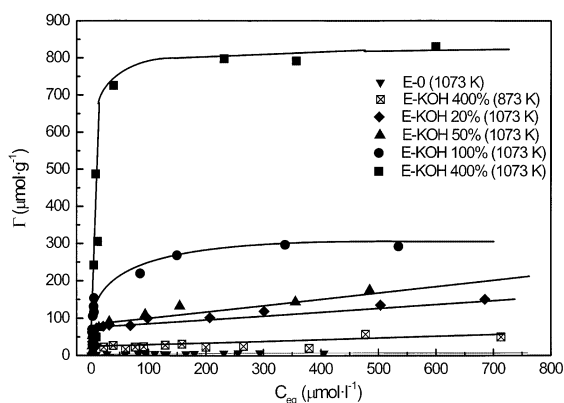


Fig. 8. Surfactant adsorption isotherms of carbons.

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