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Preparation and calorimetry characterization of nitrogen-enriched activated carbons and their application in the removal of carbon dioxide

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ABSTRACT

This paper reports the preparation and characterization of granular carbon materials those were prepared using chemical activation of African palm stone with $ZnCl_2$ and then chemically modified in order to increase the nitrogen content. Functionalization processes with activated carbons, modify their textural and chemical characteristics, this fact was observed using N_2 adsorption at 77 K, Boehm titration, infrared Spectroscopy using immersion calorimeter in liquids with different chemical nature (H_2O, C_6H_6, NaOH and HCl). The results show that the solids obtained have BET surface area and pore volume up to 1200 m^2/g and 0.44 cm^3/g, respectively. Immersion enthalpies of samples are between -9.87 and 141.9 J/g. The results show that with the process of functionalization employed in this work, increasing in the nitrogen content and the modification of the adsorbents surface is achieved. Finally, we found that with this activation and modification procedure, the activated carbons produced have a CO_2 adsorption capacity until 174 mg CO_2 /g.

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1. Introduction

Climate change is one of the greatest environmental threats of the century, with economic, social and environmental consequences of great magnitude. Today we face an increase in the concentration of greenhouse gases such as NO_x, SO_x and CO_x, these substances have a direct effect on the average global temperature because they form a layer which absorbs the thermal energy released from the Earth and prevents its release into atmosphere [1]. One of the most environmentally detrimental species is the CO_2 which is generated from a large number of natural and anthropogenic activities: volcanic activity, forest fires and use of fossil fuels are primarily responsible for carbon dioxide emissions indiscriminate into the atmosphere, being this latter aspect of concern in the international community. Currently, there are no sufficiently developed technologies that allow to replace the use of fossil fuels (carbon, petroleum, and its derivatives) as polluting energy source by other less harmful to the environment; therefore, it is necessary to strike a balance between necessary reduction or stabilization of CO_2 emissions and the negative effects that such reduction has on economic activity. While this goal is achieved, it is important to search for technological alternatives to remove CO_2 and mitigate its impact on the environment. There are three CO_2 removal processes that are employed commercially; the name of technology depends on the time when the gas is captured within a conventional combustion process [2]. Thus if the CO_2 is removed from the chimney after combustion has ended this technology is called Post-Combustion, on the other hand when the CO_2 production in the combustion is prevented, is named a removal Pre-Combustion and finally when CO_2 removal is during combustion is then called Oxy-combustion. Post-combustion CO_2 Capture technology has been the most widely used because of the ease to adjust methods of CO_2 removal as: chemical absorption with amines, cryogenic separation, storage geological reservoirs, membrane separation and adsorption at the end of the chimney [3]. Adsorption has been considered as one of the most interesting alternatives for CO_2 removal. For that purpose, materials adsorbents such as: zeolites [4], mesoporous silica [5], activated clays [6] molecular sieves [7], aluminum oxides [8], Metal Organic Framework (MOF) [9] and activated carbons [10-13] have been used. These last materials have textural and chemical characteristics that give great versatility and that can be controlled during the process of preparation of solid or after obtaining it, which it is ideal for specific applications.

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Table 1. Characterization techniques used.

Characterization techniques	**Conditions**	**Parameter**
N_2 adsorption at 77 K	Quantachrome, Autosorb 3-B, Outgassing at 523 K for 24h	S_{BET} V_0 (N_2), V_{meso}
CO_2 adsorption at 273 K	Quantachrome, Autosorb 3-B, Outgassing at 523 K for 24h	V_0 (CO_2)
Infrared spectroscopy (FT-IR)	0.1 g Activated carbon, Thermo-Nicolet 6700 FT-IR	Groups
Boehm titrations	100 mg adsorbent, 25 mL solutions NaOH and HCl 0.1 M, T= 298 K, t= 40 hours, Constant stirred	Content of groups: Carboxylic acids, Lactone, Phenol, Total acidity and Basicity
Immersion calorimetric	0.1 g adsorbent, C_6H_6, H_20, HCl and NaOH 0.1 N solution (8 mL)	Immersion Enthalpy

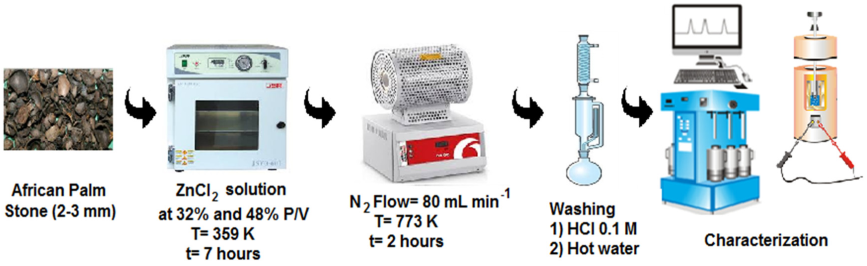

Figure 1. Scheme of process activated carbons preparation.

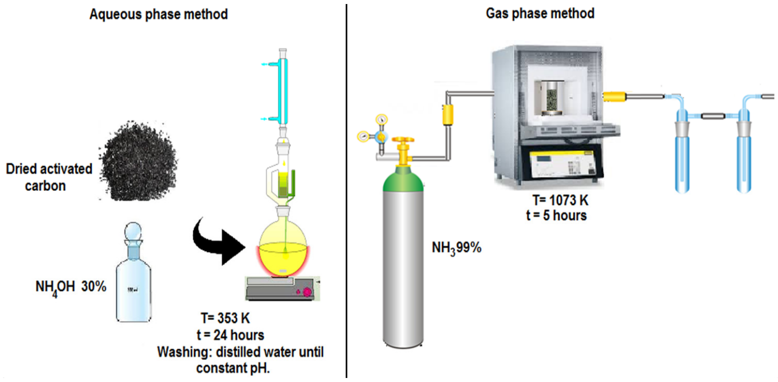

Figure 2. Scheme of process activated carbons functionalization.

In the last years the incorporation of nitrogen functional groups on carbon surface with the objective to increase the CO_2 adsorption capacity has been an important investigation topic. Functionalization of surface has been made by the reactions of carbon with ammonia, urea or amines, other alternatives are the use of rich in nitrogen plastics as carbon precursors and impregnation of carbons with solutions of amines or covering the surface with a layer of nitrogen-containing polymer [10,14,15]. Through the methodologies mentioned above, it is possible to obtain carbonaceous materials with different chemical and textural properties, moreover of nitrogen content suitable for increase of CO_2 adsorption.

The aim of this work was the preparation and characterization of nitrogen-enriched activated carbons for CO_2 adsorption. Granular activated carbons were prepared by chemical activation of African Palm Stone (*Elaeis Guineensis*) with $ZnCl_2$ at 32%, then, were chemically modified using NH_4OH solution and NH_3 separately. The characteristics of the solids were determined by N_2 adsorption at 77 K, infrared spectroscopy, Boehm titration and using immersion calorimeter in liquids with different chemical nature (H_2O, C_6H_6, NaOH and HCl). Finally the granular carbons were used for CO_2 adsorption at 273 K and 1×10^5 Pa. The capacities of CO_2 capture of the solids were related with textural and chemical parameters determined by characterization techniques.

2. Experimental

2.1. Materials preparation

Activated carbons were prepared from African palm stone materials, the precursor was initially crushed and then was subjected to chemical activation with $ZnCl_2$ solutions at 32 and 48 % P/V [16-18], after this, the carbonization process was carried out and finally the activated carbons were washed. The samples were named using the initials AC (Activated carbon), Zn (activating agent) following of a number that represents the concentration of the activating specie. Figure 1 shows the preparation conditions of carbonaceous materials.

Activated carbons obtained were chemically modified with the aim of increase the nitrogen content, for this, two methods of functionalization are used, the first liquid phase with NH_4OH and other gas phase with NH_3 [19,20]. Figure 2 shows the procedure used and experimental conditions of materials functionalization.

2.2. Characterization

In order to determine the textural and chemical characteristics of activated carbons, were used the techniques mentioned in Table 1 [21-24].

Table 2. Textural parameters for carbonaceous materials obtained from the N_2 adsorption isotherm at 77 K and CO_2 adsorption isotherm at 273 K. Total single point volume calculated at relative pressure 0.99.

Sample	**N_2 Adsorption at 77 K**				**CO_2 Adsorption at 273 K**
	S_{BET} (m^2/g)	**V_0 (cm^3/g)**	**V_{meso} (cm^3/g)**	**$V_{0.99}$ (cm^3/g)**	**V_n (cm^3/g)**
ACZn32	1200	0.44	0.12	0.58	0.28
ACZn32Am	1037	0.38	0.15	0.53	0.30
ACZn32H	903	0.35	0.14	0.49	0.32
ACZn48	516	0.24	0.02	0.26	0.23
ACZn48Am	420	0.17	0.03	0.21	0.25
ACZn48H	352	0.13	0.03	0.16	0.27

2.2.1. Nitrogen adsorption-desorption measurements

The BET surface area and porous properties of each activated carbon prepared in this research (AC's) were determined from N_2 adsorption experiments. The ACs were characterized by N_2 adsorption at 77 K using a Quantachrome, Autosorb 3-B analyzer. The carbon samples were outgassed for 24 h at 573 K to remove any moisture or adsorbed contaminants that may have been present on their surface. The manufacturer's software can provide BET surface area (S_{BET}) of the carbons by applying the BET equation to the adsorption data.

The Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) were determined by a multipoint BET method using the adsorption data in the relative pressure P/P^o range of 0.05-0.25. The total pore volume was estimated at a relative pressure of 0.99, assuming that full surface saturation had been achieved with nitrogen [21,22].

2.2.2. Fourier transform infrared spectroscopy

The FT-IR spectrum of the synthesized adsorbent was recorded using Nicolet 6700 spectrometer (Thermo electron, USA) with a resolution of 2.0 cm^{-1} well equipped with an OMNIC program. The experiments were conducted on the powdered samples ground in an agate mortar to produce KBr pellets and spectra were obtained by adding 64 scans and corrected for the background noise. Diameter and thickness of KBr pellets were 12.7 mm and 1 mm which were prepared in a manual hydraulic press at approximately 8 tones. The spectra of the samples were recorded in transmission mode and the wavenumber range of 4000-400 cm^{-1} [25]

2.2.3. Boehm's method

Boehm's method [25,26] was used for surface functional groups. Briefly, 0.1 g of the carbons samples were added to a beaker containing 25mL of the following 0.10 M solution: NaOH, Na_2CO_3, $NaHCO_3$ and HCl. The beaker was sealed and shaken for 24 h and then 10ml of the filtrate was pipetted in an excess of 20 mL 0.05 M HCl for the determination of acidic functional groups or 0.05 M NaOH for the basic functional groups. The filtrate was titrated with 0.10 M NaOH or HCl using phenolphthalein indicator and the volume required to reach the endpoint was noted. For Na_2CO_3 reaction base, an excess of 30 mL 0.05 M HCl was added rather than 20 mL due to the diprotic property of the base to ensure complete reaction with acid. The number of acidic sites was calculated under the assumption that NaOH neutralizes carboxyl, phenolic, and lactonic groups; Na_2CO_3 neutralizes carboxyl and lactonic, and $NaHCO_3$ neutralizes only carboxyl groups. The number of surface basic sites was calculated from the amount of hydrochloric acid required.

2.2.4. Determination of pH_{pzc}

The pH_{PZC} values were determined according to the methodology described by Prahas *et al.* [27,28]. NaCl solutions (0.1 mol/L) were prepared at pH values ranging from 2.0 to 10.0, using HCl (0.10 mol/L) and NaOH (0.10 mol/L) aqueous solutions. Aliquots of 25.0 mL of each solution were placed in contact with 0.100 g of AC sample in polypropylene flasks, which were shaken for 24 h. The pH of solutions after mixing was measured and graphics of ΔpH (pH_{final} - $pH_{initial}$) versus $pH_{initial}$ were plotted. The pH_{PZC} is assigned to the point at which ΔpH = 0.

2.2.5. Immersion calorimeter

Additionally, the samples were characterized by immersion calorimetric into H_2O, C_6H_6, NaOH and HCl 0.1 N solutions. Calorimetry experiments were performed with a Calvet-type heat conduction calorimeter. To determine immersion enthalpies, an activated carbon sample (0.100 g) was placed in a glass bulb attached to the calorimetric cell. Next, 8 mL of solvent was added to the cell. The cell and glass bulb were placed in the main heat reservoir and left until thermal stability was reached (approximately 1 h). Once thermal equilibrium was achieved, the carbon sample was immersed in solvent and the resulting temperature changes were recorded until a stable baseline was obtained. Recordings were then continued for an additional 20 min after immersion, followed by electrical calibration of the calorimeter [23,29-31]. For each test five replicates were made.

2.3. CO_2 Adsorption

CO_2 adsorption capacity of the activated carbons was determined at 273 K and until 1×10^5 Pa using a volumetric system (Quantachrome, Autosorb 3-B). Before the adsorption experiments, the different samples were outgassed at 423 K for 24 h.

3. Results and discussion

Figure 3 shows the N_2 adsorption isotherms at 77 K for the activated carbons prepared. Is possible to observe in Figure 3 that the samples obtained for the all-porous solids are of type I according to the IUPAC classification [32,33], this isotherm type is characteristic of microporous solids. Is observed a closed elbow in the isotherms of the materials with narrow porosity. Materials prepared in this study are mainly microporous, the isotherms are type Ib with closed elbows, indicating the existence of narrow micropores, it was not observed a slope above $P/P^0 \sim 0.2$ that can be relate to a significant development of mesopores. With the functionalization process done on ACZn32 and ACZn48 samples, it is observed a decrease in the nitrogen adsorption capacity of activated carbons, associated with a decrease in the textural parameters.

Table 2 shows the textural characteristics of the carbonaceous materials, the BET area of samples are between 785-1320 m^2/g and micropore volume between 0.22 and 0.47 cm^3/g. As $ZnCl_2$ increases, the surface area and volume pore of activated carbon decreases, this trend is contrary to the expected and reported in similar studies [34,35], in which the surface area and porosity increase with the concentration of the activating agent, the behavior obtained in this work can be attributed to the fact that activation process was not uniform and complete, so that the activating agent remained on the

Table 3. Content of surface functional groups and point of zero charge.

Sample	Carboxylic acids (μmol/g)	Lactone (μmol/g)	Phenol (μmol/g)	Total acidity (μmol/g)	Total basicity (μmol/g)	pH_{PZC}
ACZn32	159.1	0	163.6	322.7	66.73	5.91
ACZn32Am	115.4	0	63.21	178.6	152.7	6.82
ACZn32H	70.90	0	85.80	156.7	185.7	6.95
ACZn48	198.6	12.91	172.1	383.6	95.61	5.31
ACZn48Am	140.7	8.45	85.4	292.9	178.4	5.72
ACZn48H	98.4	5.68	73.2	200.3	194.2	6.54

surface of precursor particles and hence the amount of $ZnCl_2$ obstructs the porosity and hence decreasing the textural parameters is attributed to the partial retraction/ destruction of the porous structure by the excess activating agent.

It is noted that in the activated carbons prepared, the reaction with ammonia and ammonium hydroxide, results in a decrease in nitrogen adsorption capacity and therefore in the BET area and pore volume. This decrease can be attributed to a blockade in the carbonaceous structure produced by the surface groups nitrogen generated during reaction with these substances. Additionally in the case of solid functionalized in gas phase this effect has been attributed to partial obstruction of microporous system by ammonia decomposition products at high temperatures with the formation of radicals such as NH_2, NH and H [36,37].

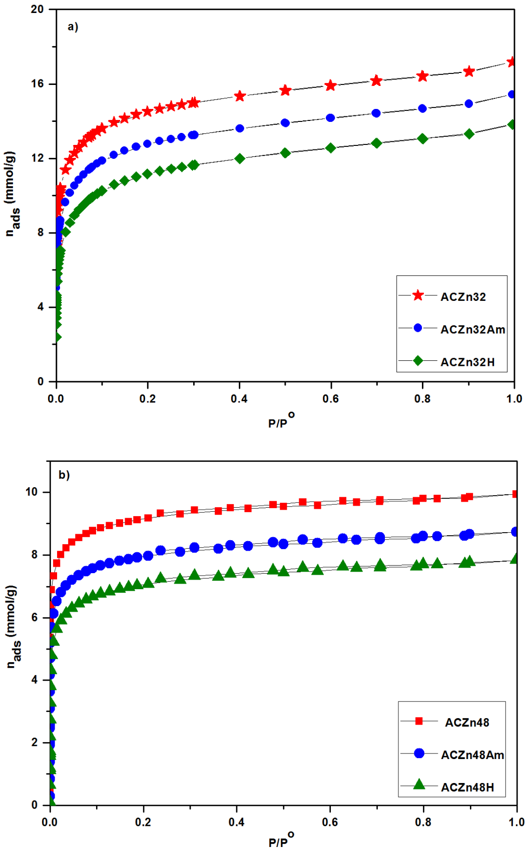

Figure 3. Nitrogen adsorption isotherms at 77 K for activated carbons obtained.

3.1. Boehm titrations and point of zero charge

Table 3 shows the activated carbon surface functional groups content, as determined by Boehm titrations, and the point of zero charge. Experimental data allow to observe changes in the surface chemical properties of each sample with the functionalization treatment. The starting materials have a wide surface chemistry consisting of carboxylic, lactonic and phenolic groups, the carbons used for the functionalization process have greater total acidity with respect to the total basicity, and so the character of the surface is acid evidenced by a pH_{PZC} less than 7. In activated carbons it is evident that the process of functionalization generated a decrease of the carboxylic groups in the starting materials, in similar studies have been stablished that the reaction of ammonia and ammonium hydroxide with carboxylic groups present on the carbon surface can form ammonium salts that through a dehydration reaction leading to the formation of amides and nitrile groups [15,38,39]. Additionally, the consumption of surface acidic groups during functionalization, is evidenced by a decrease in the acidity of the coals, likewise the increase in the basicity indicates a change in surface chemistry manifested by an increase in pH_{PZC} of solids.

It is observed that the functionalization process of carbonaceous materials is favored with the content of carboxylic groups, this behavior is explained due to that the carboxylic groups having a higher acidic strength (pKa = 2-5) than the lactonic groups (pKa = 8.2) and phenolics groups (pKa = 10), react more easily with NH_3 and NH_4OH, giving rise to nitrogenous groups that modify the chemical nature surface of carbonaceous materials.

It has been established that the reaction of ammonia with the carboxylic groups present on the surface of the carbon, can form ammonium salts, which through a dehydration reaction leads to the formation of amides and nitrile groups, as shown by the following reaction [35]:

$$-COO^{-}\ NH_4^{+} \rightarrow H_2O + -CO\text{-}NH_2 \qquad (1)$$

$$-CO\text{-}NH_2 \rightarrow H_2O + C{\equiv}N \qquad (2)$$

Additionally it is known that the amines can also be easily formed by the substitution of OH groups present on the carbonaceous surface of materials according to the following reaction [9]

$$-OH + NH_3 \rightarrow H_2O + -NH_2 \qquad (3)$$

3.2. Infrared spectroscopy

Figure 4 shows the FTIR spectra of the samples. In the spectra of Figure 4a belonging to the activated carbons ACZn32, ACZn32Am, and ACZn32H, it is possible to distinguish several common bands of interest. For the first band located between 700 and 1400 cm^{-1}; in this region, it is difficult to assign the bands as there are overlap bands of some groups. However, this region is commonly associated with C-O stretching, there is a band in spectra at 1600 cm^{-1}, characteristic of C=O and C=N stretching of the aromatic ring, moreover is observed a band located between 3200 and 3600 cm^{-1}, associated to O–H stretching vibration of alcohols and carboxylic acids [37,38], the band intensities decrease with the functionalization process by reaction of carboxylic groups with ammonia and ammonium hydroxide.

Figure 4b shows the spectra of the ACZn48, ACZn48Am, and MZn48H samples. In all the samples, there are three bands: a band located between 700 and 1400 cm^{-1}, other band at 1600 cm^{-1} and a band between 3200 and 3600 cm^{-1}, groups

Table 4. Elemental analysis of carbonaceous materials.

Sample	Elemental analysis			
	Carbon, %	**Hydrogen, %**	**Oxygen, %**	**Nitrogen, %**
ACZn32	72.5	1.42	19.1	0.25
ACZn32Am	67.4	1.76	26.1	0.36
ACZn32H	71.3	1.95	23.5	0.75
ACZn48	75.9	0.81	22.2	0.56
ACZn48Am	69.2	0.97	29.3	0.75
ACZn48H	75.3	1.09	23.1	1.37

Table 5. Immersion enthalpies of activated carbons in C_6H_6, H_2O, HCl and NaOH 0.1 N solutions.

Sample	$-\Delta H_{imm}$ C_6H_6 * (J/g)	$-\Delta H_{imm}$ H_2O * (J/g)	Hydrofobic factor $-\Delta H_{imm}$ C_6H_6/$-\Delta H_{imm}H_2O$	$-\Delta H_{imm}$ HCl * (J/g)	$-\Delta H_{imm}$ NaOH * (J/g)
ACZn32	-141.9±0.7	-31.21±0.1	4.55	-9.870±0.7	-29.76±0.3
ACZn32Am	-115.1±1.1	-25.65±0.7	4.49	-26.13±0.1	-20.43±0.1
ACZn32H	-99.89±0.8	-23.13±1.4	4.31	-29.21±0.6	-16.74±0.1
ACZn48	-58.37±0.6	-49.21±1.3	1.19	-14.62±0.3	-35.31±0.4
ACZn48Am	-38.98±0.5	-36.78±0.6	1.06	-23.48±0.5	-29.15±0.3
ACZn48H	-31.24±0.2	-30.23±0.3	1.04	-27.36±0.4	-26.51±0.6

* The standard deviations of the immersion calorimetry are between ±0.1-1.4 J/g.

belonging to each of the bands were assigned previously, it is observed that the intensities of these signals decrease with functionalization processes indicating a change in the surface chemistry of activated carbon.

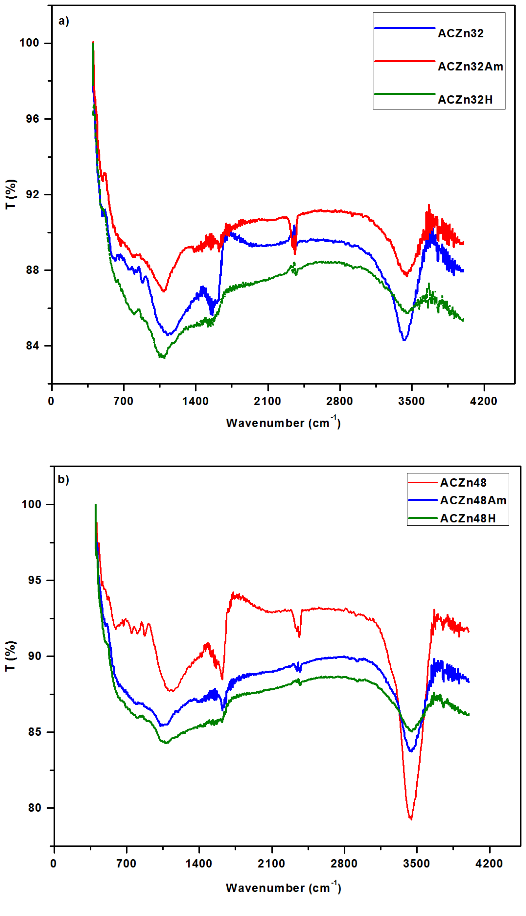

Figure 4. FT-IR spectra for the raw and functionalized samples a) ACZn32 series, b) ACZn48 series.

3.3. Elemental analysis

Table 4 shows the results of elemental analysis for functionalized samples and starting materials. Through this analysis is possible to measure the nitrogen content in the materials, is observed an increase of this element between 34-44% for functionalized samples with gaseous ammonia and between 145-200% for modified samples with ammonium hydroxide, also the content hydrogen increases with modifycations, this behavior can probably be attributed to the formation of NH groups [34-36]. The oxygen content has increased, mainly in samples functionalized with gaseous ammonia, this tendency has shown in similar studies [37-39], where surface of two commercial activated carbons (Norit R is studied and C) and activated carbon fibers was modified with ammonia in order to improve the CO_2 adsorption capacity of solids, this work stablishes that with the high temperature treatment a lot of oxygenated groups on surface materials are removed, however after functionalization remain unsaturated carbon atoms in the porous solid, able of being combined in varying proportion with other heteroatoms such as oxygen, generating a new surface chemistry on the activated carbons [37,38].

3.4. Immersion calorimetry

Figure 5 shows the thermograms obtained for the actived carbons immersion in HCl and NaOH solutions. The magnitude of the interaction between the activated carbon and the HCl or NaOH solution, is represented by the size of the peak shown in Figure 5, it is possible to observe differences in the size of the immersion peaks justifying the enthalpy values obtained in this study. There is a relationship between the area under the curve of peak and immersion enthalpy of each sample, is so a greater area of the peak, the higher immersion enthalpy.

Table 5 shows immersion enthalpies in C_6H_6, H_2O, HCl and NaOH solutions, with the hydrophobic factor calculated as the relation between the immersion enthalpy in C_6H_6 and immersion enthalpy in H_2O. It is observed that all the immersion enthalpies are exothermic, in accordance with surface process that takes place between solid and liquid. Immersion enthalpies, for sets of solid obtained are among -9.87 and -141.9 J/g, these data are comparable with results obtained in similar works [23,36-39].

Immersion enthalpies in C_6H_6 have a relationship with the surface area of activated carbons, Due to the fact that this liquid is non-polar therefore does not have specific interaction with the solids, such that immersion enthalpy is proportional to the surface area accessible of liquid molecule. It is possible to observe that in the activated carbons there are an increase of immersion enthalpy when the BET area is greater, this behavior is coherent because a greater surface area the porous structure is more developed in solids and therefore there is more space available for the entry of molecules C_6H_6 as immersion liquid.

The chemical surface properties of the activated carbon were related with immersion enthalpies; the immersion enthalpy in water is between -23.13 and -49.21 J/g. Is observe a decrease in hydrophobic factors with the functionalization process this behavior has been shown in other studies in which was established that oxygenated groups on the activeted carbon surface act as primary interaction centers with the water [37-39], and therefore play a significant role in the immersion enthalpy of these solids in this polar liquid [37-40]. Likewise it has been determined that the presence of other heteroatoms in the carbon surface, as nitrogen surface complexes can to improve the interaction of the carbon surface with water especially at low relative pressures. It was possible to use the immersion calorimetry to determine the chemical changes on the activated carbons surface. It is noted that the ammonia and ammonium hydroxide reaction with activated carbons, produced an increase in immersion enthalpy in HCl 0.1 N solution and a decrease in immersion enthalpy in NaOH 0.1 N solution, which is consistent with changes evidenced in the carbon surface chemistry (groups content, acidity, basicity) (Table 3). It is also important to note that by increasing the nitrogen content on the carbon surface (Table 4) the basicity increases and therefore the interaction between the solids and HCl solution consequently increases.

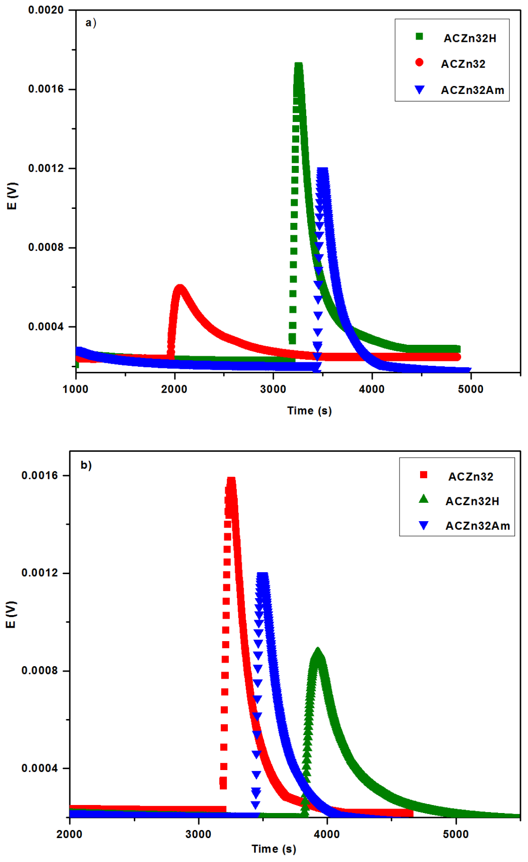

Figure 5. Comparison between the thermograms obtained for the immersion enthalpy in a) HCl 0.1 N solution, b) NaOH 0.1 N solution.

3.5. CO_2 adsorption

Figure 6 shows the CO_2 isotherm adsorption for activated carbons, it is observed an increase of adsorption capacity with the functionalization process. Is evident that the enriched activated carbons with Nitrogen have better interaction with CO_2 molecule, which is explained by the chemical nature of this gas, it is widely known that CO_2 is a Lewis acid and therefore the presence of electron donating groups such as nitrogen (Lewis base) in the carbonaceous matrix increases the affinity adsorbate-adsorbent [39-43].

According to previous works where the CO_2 adsorption mechanism on activated carbons prepared by physical activation of anthracite was studied, and the CO_2 capture with activated carbons enriched with nitrogen, is analyzed the form of CO_2 adsorption isotherms at 273 K and is related to the adsorption mechanism of this gas, the researchers said that if CO_2 molecule interacts with the walls of the pores size smaller at 2 nm, adsorption may occur by filling micropores and/or by a coverage surface mechanism, according to the results of the studies mentioned a tendency of the isotherms near the rectilinear can be related with a CO_2 adsorption mechanism on the surface coverage and is associated with pore sizes of twice the CO_2 molecular dimension (0.33 nm) [40], in this work all isotherms presented in Figure 6 show a rectilinear trend similar to that described in the above studies.

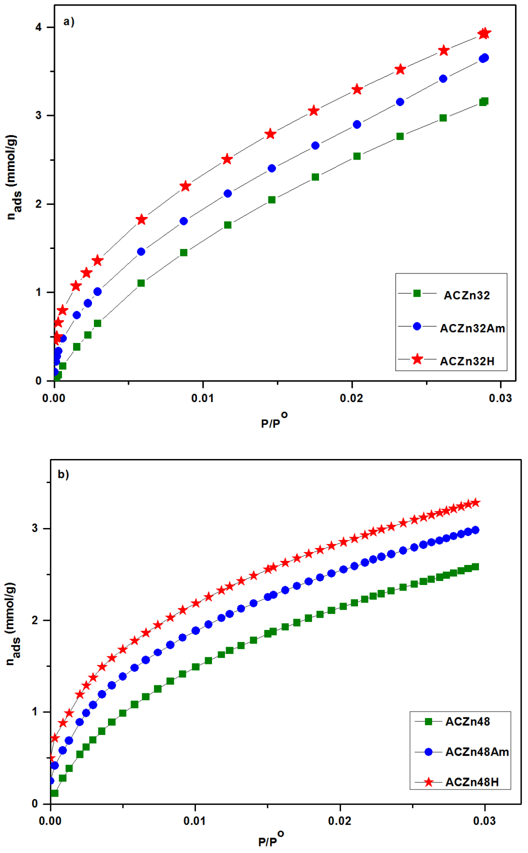

Figure 6. CO_2 Adsorption capacity of activated carbons at 273 K and 1×10^5 Pa.

Table 6 is reported the amounts of CO_2 adsorbed in carbonaceous materials at 273 K and 1×10^5 Pa. It is observed that the solids have an adsorption capacity between 114-174 mg CO_2/g. Samples of the ACZn32 series can adsorb between 140-174 mg CO_2/g., these samples adsorb between 10 to 18% more CO_2 than the ACZn48 samples, this behavior is attributed to solid of ACZn32 series have higher: BET surface areas, total volume of micropores (V_0), the total volume adsorbed ($V_{0.99}$), mesopore volume (V_{meso}) and narrow micropore volume (V_n), moreover the functionalization process increase the nitrogen content in materials, therefore is possible to establish that CO_2 adsorption capacity depends of the mix between textural and chemical parameters suitable in the activated carbons.

Table 6. CO_2 adsorption capacity of activated carbons at 273 K and 1×10^5 Pa.

Sample	**ACZn32**	**ACZn32Am**	**ACZn32H**
mgCO_2/g	140	161	174
Sample	**ACZn48**	**ACZn48Am**	**ACZn48H**
mgCO_2/g	114	132	157

4. Conclusions

Were prepared nitrogen-enriched activated carbons with surface areas between 352-1200 m^2/g and pore volumes between 0.13 and 0.44 cm^3/g. The results obtained using the three characterization techniques employed: FTIR, Boehm titration and immersion calorimetry, show that the functionalization processes used are able to modify the surface chemistry of the materials, increasing the content of nitrogen groups in the carbonaceous solids. Furthermore, it was established that the most effective method of functionalization, in this study is in liquid phase with ammonium hydroxide.

It is established that the CO_2 adsorption capacity of the solids is related to the presence of narrow micropores, with the surface area developed, also the surface chemistry of materials is important, because it affects the interaction of the surface with the gas molecule. The functionalization process of the materials generates a decrease in the textural characterristics but an increase in nitrogen content and therefore in the basicity of the carbonaceous surface, which favors the CO_2 molecule affinity by solid. These results in an increased between 10 to 18% in the CO_2 adsorption capacity of the solids. It reached a maximum adsorption capacity of 174 mg CO_2/g. in the ACZn32H sample.

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