

# Activated carbons developed in different activation conditions to improve nitrate adsorption performance

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## Abstract

The suitability of activated carbons (ACs) with dissimilar textural and surface chemistry characteristics was studied for nitrate removal, under different pH conditions. For this task, four ACs were used; two of them were manufactured by chemical and physical steam activation from orange peel and almond shell, while the other two were commercial adsorbents. It was found that both the precursor and activation methodology influence the adsorbents characteristics. Regarding nitrate uptake, their chemical surface was very relevant, while the textural properties did not exert a remarkable effect. Also, nitrate adsorption under acid pH was improved, especially for basic adsorbents, in contrast with neutral conditions, in which case no adsorbent stood out. The amelioration of nitrate removal for basic adsorbents and acidic pH conditions was associated to a greater prominence of electrostatic contributions as well as a lower extent of adsorption competition between hydroxyl and nitrate ions.

## Resumen

La idoneidad de carbones activados (CAs) con características texturales y de química superficial diferentes se estudió para la eliminación de nitratos bajo diferentes condiciones de pH. Para ello se utilizaron cuatro CAs; dos de ellos comerciales y otros dos manufacturados mediante activación química y física a partir de cáscara de naranja y de almendra, respectivamente. Los resultados obtenidos mostraron que el precursor y la metodología de activación influyen en las características adsorbentes. En cuanto a la capacidad de adsorción, su superficie química fue muy relevante, mientras que las propiedades texturales no ejercieron un efecto notable. Además, la adsorción de nitrato mejoró a pH ácido, especialmente en el caso de los adsorbentes básicos, lo cual se asoció a una mayor importancia de las contribuciones electrostáticas así como, una menor adsorción competitiva entre los iones hidroxilo y nitrato.

## 1. Introduction

The discharge of nitrogen compounds to the environment has become a major question of concern, due to their severe effects on living species and ecosystems. In the particular case of nitrate compounds (NO<sub>3</sub><sup>-</sup>), due to its high water solubility, they are considered one of the most widespread groundwater contaminants in the

world, imposing a serious threat to drinking water supplies and promoting eutrophication [1-2]. High nitrate concentrations in surface and ground water reservoirs are mostly related to agricultural activities; precipitation, irrigation, and sandy soils allow nitrates to move around and find its way into surface water and groundwater [3]. Consumption of water with nitrates can lead to the formation of carcinogenic compounds such as nitrosamine, and also causes an increase in the rate of formation of methemoglobin in the blood, decreasing its oxygen-carrying capacity and leading to tissue hypoxia [4].

Among the several ways for nitrate removal, adsorption onto Activated Carbons (ACs) is an attractive option due to its simplicity and low cost, also because it usually does not require additional post-treatments and does not involve the generation of additional by-products [1].

The presence of heteroatoms on ACs surfaces has a significant effect on the chemical character, acidity and degree of hydrophobicity of its surface and hence plays a significant role on the adsorption performance of these materials. Some previous works have already pointed out that the surface chemistry of the adsorbent have a significant influence onto its nitrate adsorption behaviour. For example, Ota et al. [5] found that nitrate adsorption was almost negligible onto acidic ACs, while it was enhanced after the adsorbents had been outgassed at high temperatures (800-1000 °C), due to the elimination of oxygen surface groups. Afkhami et al. [6] studied the adsorption of nitrates onto activated cloths chemically modified with H<sub>2</sub>SO<sub>4</sub> and found that acid adsorbents yielded greater adsorption nitrate capacities; they concluded that acidic treatments protonated surface groups, enhancing electrostatic adsorption of ions, at the working pH.

Although the convenience of optimizing the ACs surface chemistry rather than its porous structure for this particular application has been confirmed, all of the assays were made without any adjustment of the solution pH, despite its great influence on nitrate adsorption performance.

The very few works on nitrate adsorption systems under different pH conditions have given evidence about the important role of this parameter, which can modify the adsorption mechanism, due to the enhancement of electrostatic contributions, in such a way that the trend can be totally inverted. For example, Nunell et al. [10] investigated the

adsorption of nitrates on ACs under different pH conditions and found that decreasing pH gave rise to an improvement in its nitrate uptake, since it promoted the adsorbent surface protonation. The variety of results found in the bibliography, as well as the lack of unified experimental conditions makes the understanding of the mechanisms governing nitrate adsorption very difficult, and demonstrates the need of studying each particular system.

On the other hand, both physical and chemical characteristics of ACs depend on the precursor used and the activation process applied for its preparation. With the motivation of searching new precursors, this work studied the production of ACs from orange peel (OP) and almond shells (AS), by chemical and physical activation, respectively, and their use as nitrate adsorbents. Adsorption was also studied on two commercial ACs (COM1 and COM2), to provide a variety of porosity and surface chemistry features.

## 2. Experimental

### 2.1. Precursors

Both commercial (COM1, *Chemviron Carbon*, from coconut shell, COM2, *Sigma Aldrich*, from bituminous coal) and home-made ACs were used. In the case of prepared adsorbents, almond shells (Extremadura, Spain) and orange peel (Buenos Aires, Argentina) were used as precursors.

### 2.2. Preparation of Activated Carbons

The ACs were produced from OP and AS by chemical and physical activation, respectively. Chemical activation was carried out according to the procedure described elsewhere [8]. Physical activation was made according to the procedure described in ref. [9], using an AS char previously obtained by pyrolysis (873 K, 1 h). Activation of the char was made with steam ( $0.10 \text{ g min}^{-1}$ ) diluted in nitrogen ( $100 \text{ mL min}^{-1}$ ) during 60 min, at 1123 K.

### 2.3. Characterization of activated carbons

#### 2.3.1. Textural characterization

ACs were characterized by means of  $\text{N}_2$  and  $\text{CO}_2$  adsorption at 77 K and 273 K, respectively (Micromeritics ASAP 2020 HV). Nitrogen adsorption data were used to calculate typical textural parameters by means of suitable models [10].

The surface morphology of the adsorbents was

examined by Scanning Electron Microscopy (SEM, Quanta 3D FEG, FEI). The sample was prepared by depositing about 50 mg on an aluminum stud covered with conductive adhesive carbon tapes, and then coating with Rh-Pd for 1 min to prevent charging during observations. Imaging was done in the high vacuum mode at an accelerating voltage of 30 kV, using secondary electrons under high vacuum conditions.

### 2.3.2. Chemical characterization

The total amounts of acidic/polar oxygen functional groups on the surface of the adsorbents ( $m_{\text{eq}}$  per gram of AC) was determined following a modified procedure based on Boehm's method. Also, the content of basic surface groups ( $m_{\text{eq}}$  per gram of AC) was determined by contacting  $0.5 \text{ g}$  of each AC with  $50 \text{ mL}$  of  $0.05 \text{ mol L}^{-1}$  acid solutions. Subsequently, the slurries were stirred for 24 h and filtered. Afterwards, a  $10 \text{ mL}$  aliquot of the solutions was titrated with  $0.05 \text{ mol L}^{-1}$  NaOH. Finally, the point of zero charge (PZC) of the adsorbents was determined following the procedure described by Carrot et al. [11].

### 2.3. Determination of adsorption isotherms

Nitrate adsorption isotherms were determined on the basis of batch analysis; a fixed mass of adsorbent was allowed to equilibrate with solutions of ions of known initial concentrations. Isotherms were made with different pH conditions: a) neutral pH, b) pH=2 with no addition of buffer, and c) pH=2 with the addition of buffer (HCl and KCl). In all cases, a stock sodium nitrate solution ( $16.1 \text{ mmol L}^{-1}$ ) was firstly prepared, and from it, standard solutions of concentrations in the range  $0.05\text{--}8.00 \text{ mmol L}^{-1}$  were obtained. Nitrate concentration was determined by UV-Vis spectrophotometry (Shimadzu UV mini-1240 analyzer) at 201 nm, obtaining a calibration correlation coefficient higher than 0.999.

## 3. Results and discussion

### 3.1. Characterization of Activated Carbons

Figure 1.a displays  $\text{N}_2$  adsorption isotherms at 77 K. From the plots it is evident that the adsorbents differ in both their  $\text{N}_2$  adsorption capacity and the porosity type.

While COM1 and CAS exhibit a type-I isotherm, denoting their microporous nature, COM2 and COP adsorption data depict a gradual increase of

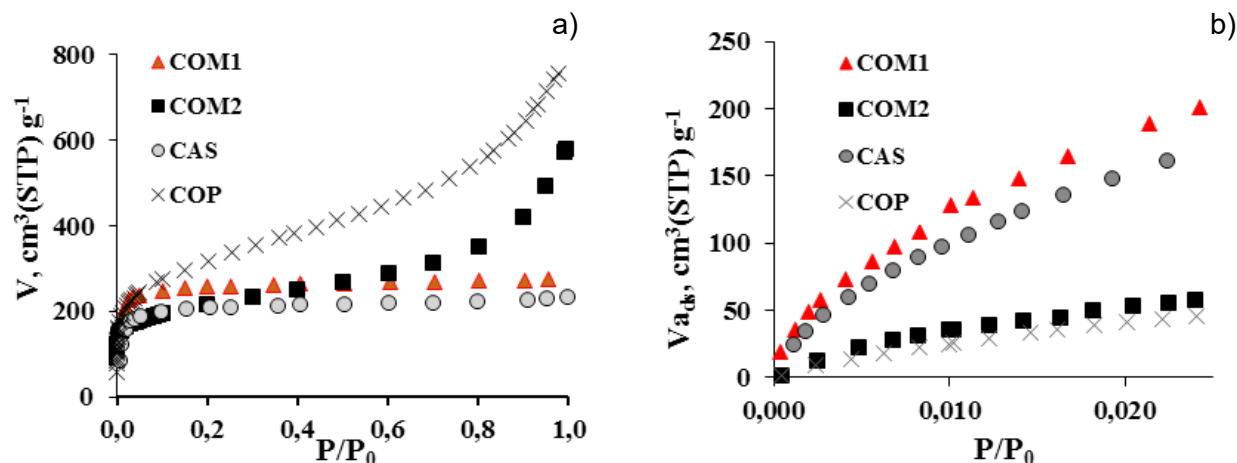


Figure 1.  $\text{N}_2$  (a) and  $\text{CO}_2$  (b) adsorption isotherms at  $-196$  and  $0$  °C, respectively.

Figura 1. Isotermas de adsorción de  $\text{N}_2$  (a) y  $\text{CO}_2$  (b) a  $-196$  y  $0$  °C, respectivamente.

**Table 1.** Textural parameters as derived from N<sub>2</sub> and CO<sub>2</sub> adsorption data.**Tabla 1.** Parámetros texturales derivados de los datos de adsorción de N<sub>2</sub> y CO<sub>2</sub>

	$S_{\text{BET}}$ [m <sup>2</sup> g <sup>-1</sup> ]	$V_{\text{miN}_2}$ [cm <sup>3</sup> g <sup>-1</sup> ]	$V_{\text{me}}$ [cm <sup>3</sup> g <sup>-1</sup> ]	$S_{\text{EXT}}$ [m <sup>2</sup> g <sup>-1</sup> ]	% $S_{\text{int}}$ [m <sup>2</sup> g <sup>-1</sup> ]	$V_{\text{miCO}_2}$ [cm <sup>3</sup> g <sup>-1</sup> ]
<b>COM1</b>	857	0.413	0.010	25	97	0.717
<b>COM2</b>	710	0.310	0.254	119	83	0.253
<b>CAS</b>	641	0.340	0.011	29	96	0.616
<b>COP</b>	1090	0.298	0.758	540	50	0.217

adsorbed volume up to high relative pressure values, which suggest their mesoporous character. Besides, from Fig. 1, as well as from the textural parameters obtained from N<sub>2</sub> adsorption data, collected in Table 1, it can be observed that COP had the highest value of BET surface while CAS had the lowest.

This information can also be deduced from CO<sub>2</sub> adsorption isotherms (see Fig. 1.b), which show a greater adsorption for these two ACs, indicating a higher volume of primary micropores.

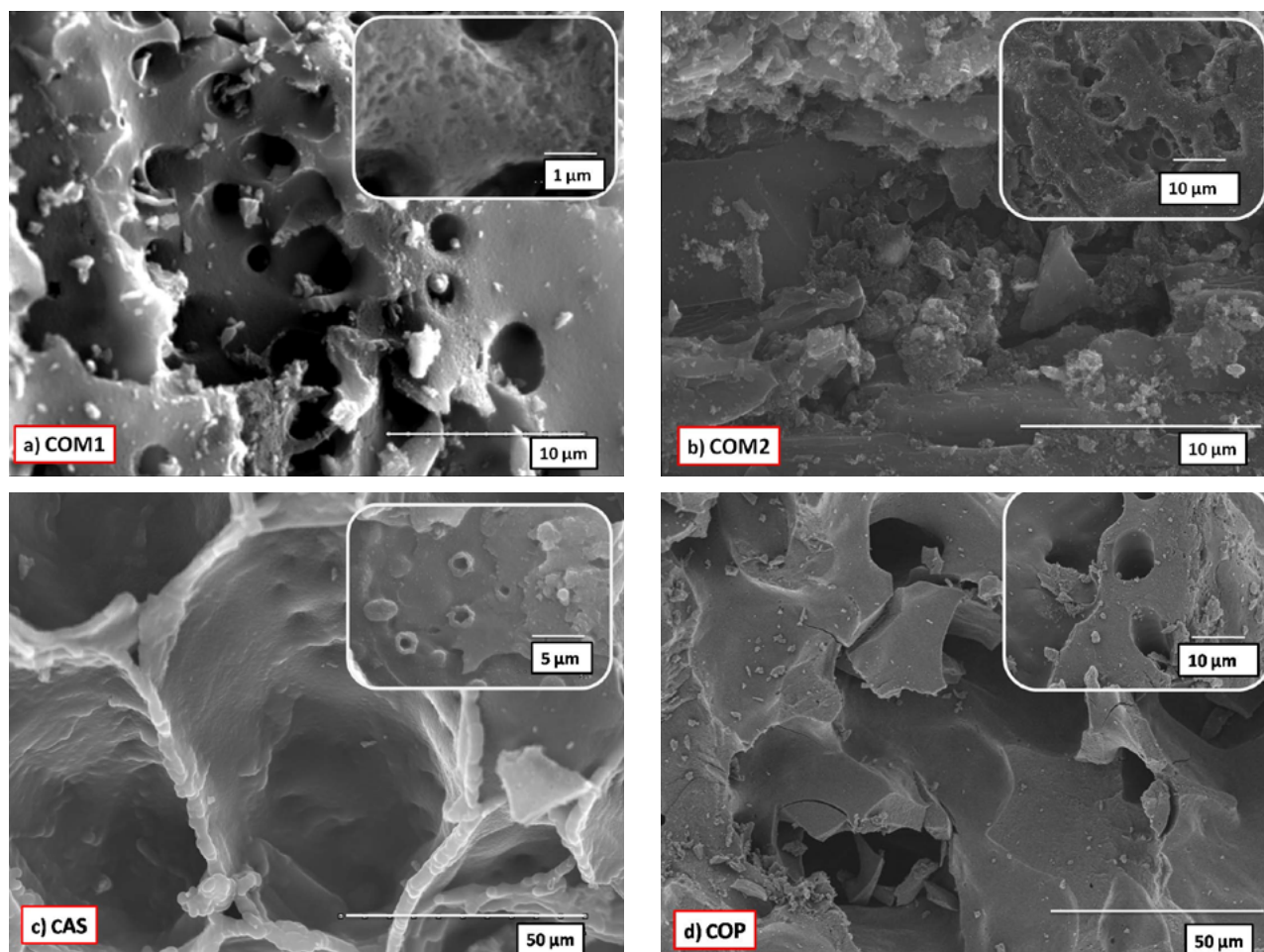
The comparison of N<sub>2</sub> and CO<sub>2</sub> as has been traditionally regarded as a powerful tool in order to improve the characterization of the smallest porosity, since the former gas can not get access to these pores under the working temperature; in this way, if  $V_{\text{miN}_2} < V_{\text{miCO}_2}$ , it is assumed that the solid has predominance of ultramicropores, while if the opposite occurs, then the solid is more likely to have large micropores and mesopores [12]. From Table 1, where the values of micropore volumes as determined from application of DR method to CO<sub>2</sub> adsorption data are presented, the predominance of ultramicropores for samples

COM1 and CAS can be confirmed.

It is remarkable that the difference between  $V_{\text{miCO}_2}$  and  $V_{\text{miN}_2}$  is largest for COM1, denoting its important contribution of ultramicropores. A detailed inspection of N<sub>2</sub> adsorption isotherms reveals that the knee of the curve at lower  $P/P_0$  is very abrupt, in coherence with this fact.

Figure 3 (a-d) displays the SEM micrographs made for the adsorbents at different magnifications. In general, all the samples present white particles on the surface, which can be attributed to sintering of the precursor inorganic matter during the heating treatment; these particles become more clearly visible for samples COM1 and COM2.

Besides, it is evident that the differences on the precursor as well as the processing methodology influence the surface appearance of adsorbent. For example, carbon COM1 (Fig. 3a) stands out due to their cylindrical pores, while COM2 (Fig 3.b) is composed of macrometer-sized monolithic fragments with sharp edges. Regarding the manufactured ACs

**Figure 3.** SEM micrographs of ACs. Lower size image: magnification of 10000; larger image: magnification of 2000.**Figura 3.** Micrografías SEM de CAs. Imagen de menor tamaño: aumento de 1000; mayor tamaño: aumento de 2000.



(Fig. 3c and d), the pores resemble the cell walls of the original plant structures, exhibiting great opened cavities, which are beehive-shaped in the case of CAS and cylindrical for COP. In this latter case, the surface is less robust than in the other samples with a “*millefeuille*” appearance.

On the other hand, the ACs differed on their surface functionalities. Table 2 compiles the analyses of the total amounts of acidic/oxygen and basic groups and groups, and PZC values. A greater presence of acidic surface groups followed the sequence COP>COM2>CAS>COM1. The opposite tendency is found for basic groups, as well as for the PCZ.

In the case of manufactured ACs, the surface chemistry is consistent with the preparation methodology; while for COP, H<sub>3</sub>PO<sub>4</sub> treatment caused the development of oxygen functionalities, for CAS, the high temperatures used during steam treatment (1123 K) were enough to remove most of temperature-sensitive functionalities, such as carboxylic acids [13].

**Table 2.** Point of zero Charge (PZC) and Surface functional groups (m<sub>equiv</sub> g<sup>-1</sup>): Total Basic Groups (TBGs) and Total contents of acidic/polar oxygen functional groups (TOFGs)

**Tabla 2.** Punto de carga cero y grupos funcionales superficiales (m<sub>equiv</sub> g<sup>-1</sup>). Grupos básicos totales y contenido total de grupos funcionales ácidos/oxígeno polar

	COM1	COM2	CAS	COP
PZC	12.2	5.8	10.6	5.5
TBGs	0.69	0.20	1.52	0.19
TOFGs	0.88	1.02	0.92	1.46

### 3.2. Nitrate adsorption

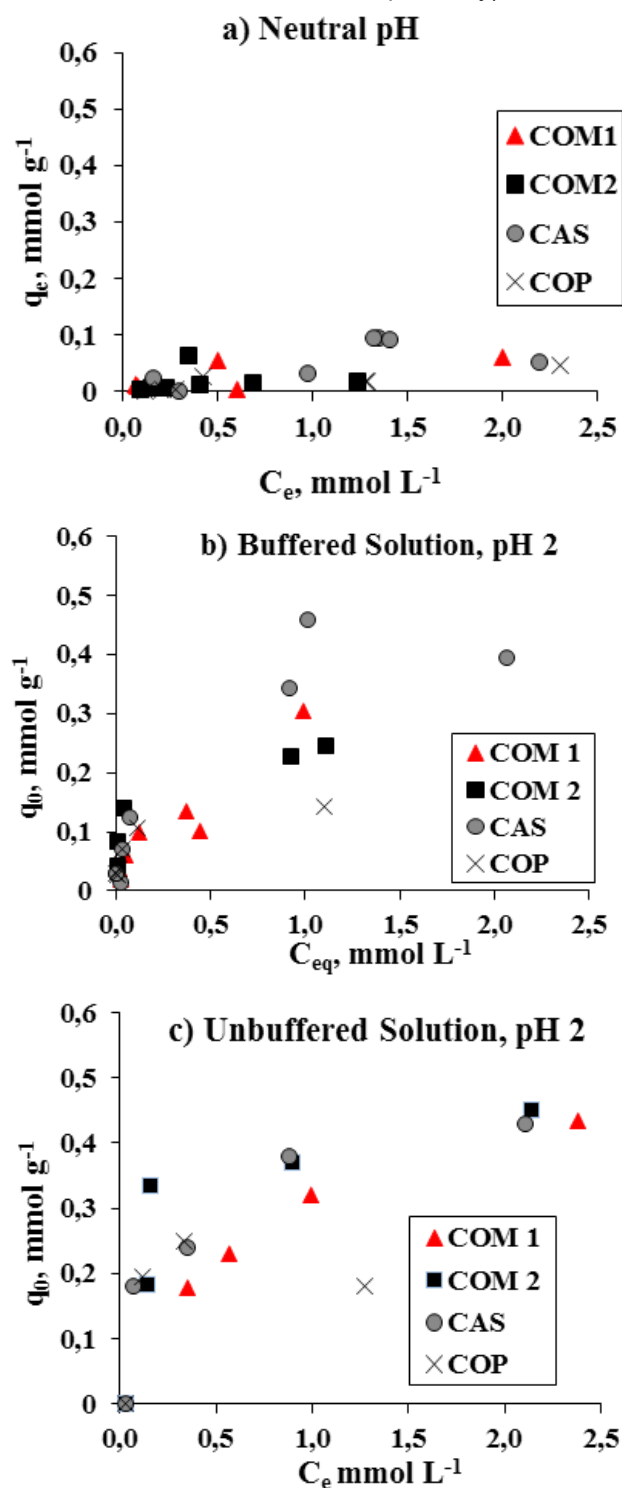
Nitrate adsorption studies were made at neutral (non-adjusted) pH and at pH 2 (with and without buffer solution added). All adsorption isotherms are collected in Figure 4 (a, b and c).

Firstly, the experiments made at neutral pH showed very unsatisfactory results in all cases, as compared with pH 2 experiments; Fig. 4.a displays adsorption isotherms with very low adsorption uptake values, especially at lower equilibrium concentrations, denoting a poor adsorption affinity in all cases. These results give evidence about the complexity of adsorption processes, where both dispersive and specific forces are involved, and where the porosity and chemistry of adsorbent and adsorbate, as well as other system features do have importance [14].

An initial explanation for the results obtained at neutral pH might be related to the adsorption media. In this way, OH<sup>-</sup> present in solution might compete with nitrate anions for the surface adsorption sites, reducing the extent of adsorption [15].

Another important factor relates to electrostatic interactions, provided that the adsorbate has a negative charge. The ACs used in this work differ in their surface acidity, and this in turn brings out a dissimilar modification in surface charges, once they get in contact with the neutral solution. In the case of basic adsorbents (COM1 and CAS) a migration of negative charges towards the bulk on the solution is expected, and in consequence the carbon surface will be positively charged, which might favour

the participation of electrostatic attractive forces. Similarly, in acid adsorbents the movement of protons from the adsorbents surface would lead to a negatively charged surface, and thus electrostatic repulsions could be expected. The migration of charges was confirmed by measuring the solution pH in equilibrium for a given initial nitrate concentration (3 mmol L<sup>-1</sup>); a pH drop was found for basic adsorbents (9.5 and 10.1, for COM1 and CAS runs, respectively), whereas a rise on it was detected for acid ones (6.1 and 5.9 for COM2 and COP, respectively).



**Figure 4.** Nitrate adsorption isotherms for commercial and home-made ACs.

**Figura 4.** Isotermas de adsorción de nitrato para CAs comerciales y fabricados en el laboratorio.

On the other hand, there is another source of influence of the surface chemistry on the adsorption of nitrate

**Table 3.** Models parameters for nitrate adsorption data**Tabla 3.** Parámetros de los modelos para los datos de adsorción de nitrato

		Unbuffered solution				Buffered solution			
		COM1	COM2	CAS	COP	COM1	COM2	CAS	COP
Lang.	$q_0$ , mmol g <sup>-1</sup>	0.449	0.410	0.438	0.305	0.418	0.256	0.896	0.191
	mmol <sup>-1</sup>	2.32	19.92	6.77	35.49	2.71	12.41	1.20	20.29
Model	R <sup>2</sup>	0.989	0.998	0.999	0.999	0.884	0.989	0.805	0.925
Freund.	$K_f$ (mmol <sup>-1</sup> )(Lmmol <sup>-1</sup> ) <sup>1/n</sup>	0.280	0.342	0.327	0.263	0.291	0.223	0.346	0.183
	n	3.06	5.77	4.88	9.30	1.67	3.69	2.01	2.85
Model	R <sup>2</sup>	0.858	0.613	0.874	0.852	0.877	0.665	0.871	0.834

ions; in ACs, the random ordering of the aromatic sheets causes a variation in the arrangement of electron clouds in the carbon skeleton, which results in the creation of unpaired electrons and incompletely saturated valences that would undoubtedly influence the adsorption behaviour. In the particular case of nitrate ions, the availability of unpaired electrons in the adsorbent surface can be unfavourable, hindering the process. It is well established that acid surface groups are bounded at the edge of aromatic sheets and therefore tend to localize these unpaired electrons [16]. For this reason, the presence of acidic surface groups might be considered to be positive for the particular adsorption of nitrate ions.

If the participation of electrostatic interactions was relevant at neutral pH, an improvement should be expected for basic adsorbents. From our results, the influence of such contributions does not seem to have a very significant role. Also, the convenience of using acid adsorbents due to their lower availability of unpaired electrons was not verified. In summary, at neutral pH conditions nitrate adsorption is likely to be hindered, independently of the adsorbent used.

With the aim of improving such results, the reduction of the pH at a value of 2 was studied, since previous pieces of research have found that nitrate adsorption is influenced by pH, improving under acidic conditions [16]. Figures 4.b and 4.c shows the nitrate adsorption isotherms corresponding to pH 2 under unbuffered and buffered conditions. From the plots, it is seen that decreasing the pH has a positive effect on nitrate adsorption for all ACs. However, more attentive analysis reveals some differences between the results obtained with and without buffer. In order to better analyze these effects, Langmuir and Freundlich models were applied to adsorption data. Table 3 collects characteristic parameters obtained from these models. Although the fitting of the experimental data to these models was not very satisfactory in some cases (especially for Freundlich model), the analysis of the characteristic parameters can help the comparison of results. Firstly, from the adsorption isotherms for unbuffered solutions (Fig. 4.b), low nitrate uptake values are found at low equilibrium concentrations, then increasing gradually at higher values of equilibrium concentration, showing a behaviour typical of porous solids with low affinity towards the adsorbate (COM2 is an exception in this regard). Despite this effect, nitrate adsorption values up to 0.4 mmol L<sup>-1</sup> are observed. Another interesting issue is that for unbuffered solutions there are no significant differences between the adsorption values achieved in the plateau for the different ACs, nor the values of  $q_0$  as determined from Langmuir

model. Thus, the influence of both chemical and textural features might not be very relevant, as it was found at neutral pH. The improvement at pH 2 might be rather related to the lower competitiveness NO<sub>3</sub><sup>-</sup>/OH<sup>-</sup> in solution. The migration of protons to the carbon surface and thus the enhanced electrostatic attractions might be also postulated. The analysis of the pH after adsorption equilibrium showed, as in the previous case, a rapid change as a consequence of the contact AC/solution, achieving values of 7.2, 4.4, 7.6 and 3.9 for COM1, COM2, CAS and COP, respectively. On the other hand, from Figure 4.c it can be inferred that using a buffer can enhance (CAS) or decrease (COM1, COM2 and COP) the ACs' uptake capacity.

Also, if a buffered pH 2 solution is used, the surface chemistry of the adsorbents acquires a relevant role. As deduced from Figure 4.c, basic adsorbents show the best results. According to their expected higher protonation, a significant prominence of electrostatic attractive forces might be responsible for this effect. Moreover, the greater the difference between the carbon PZC and pH, the greater the density of positive charge on the adsorbent surface.

This effect was decisive, providing the best results for ASC ( $q_0 = 0.896$  mmol g<sup>-1</sup>), even despite this adsorbent had the lowest surface area. Likewise, low levels of nitrate removal attained with COP were in line with the acidic characteristics of this activated carbon. For other adsorbates, and especially for non-polar ones, the adsorption capacity is very closely related to the textural characteristics of the adsorbent [17]. Dissimilarly, in this case, the key factors governing nitrate adsorption are the solution pH and the carbon surface chemistry.

#### 4. Conclusions

Activated carbons (ACs) with different textural and surface chemistry characteristics were evaluated with the aim of getting insights about the most interesting features for improving nitrate adsorption.

Regarding home-made ACs, they were prepared from orange peel (OP) and almond shell (AS) by chemical and physical activation, respectively. These treatments conferred dissimilar features to the adsorbents: while OP carbon (COP) was very mesoporous and had a predominancy of acid functionalities, AS carbon (CAS) was markedly microporous and had a basic surface. Similar trends were observed for the commercial ACs.

Nitrate adsorption studies revealed that the solution's pH had a very significant influence on the process, in such a way that it was enhanced at pH 2, which

was associated to the minimization of adsorption competition between nitrate and OH<sup>-</sup> ions. At this pH, the surface chemistry of the adsorbent was found to have a relevant role on the adsorption effectiveness; the more basic the AC, the greater the adsorption affinity towards this adsorbate, even although pore volumes were higher for acid adsorbents. This effect is remarkable and gives evidence about the need of testing any application before making a decision.

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