Conversion of biomass from an invasive species into activated carbons for removal of nitrate from wastewater

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ARTICLE INFO

ABSTRACT

Development of activated carbons targeted at nitrate ion removal is investigated by chemical activation of sawdust from the invasive species Parkinsonia aculeata wood. Phosphoric acid and potassium hydroxide are comparatively used as activating agent. Its effect on main physico-chemical properties and on the effectiveness of the activated carbons in nitrate removal is compared with those determined for a commercial sample. Activated carbons developed with the base show the best effectiveness in nitrate removal, as determined from application of the Langmuir model to the experimental isotherms. The behavior is consistent with the development of surface basic groups and the more basic character of these carbons. Noticeable improvement in nitrate uptake for all the carbons is attained after treatment with a saturated urea solution, with removal levels of ~80–90%, despite reductions in porous structures. Nitrate adsorption onto the urea-treated carbons is in direct correlation with their enhanced contents of elemental nitrogen.

1. Introduction

Nitrate contamination in surface and ground water has become a growing problem worldwide. Discharge of nitrogen containing compounds into the environment can cause severe damages. They include eutrophication of rivers and deterioration of water bodies, where pollution is caused by heavy algal growth, as well as hazards to human health. Concentrations of nitrate in drinking water exceeding the tolerance limits lead to the formation of nitrosoamine. This compound is related to cancer and increases the risk of diseases, such as methemoglobinemia, also known as cyanosis or blue baby syndrome, in new born infants [1–4]. Accordingly, removal of nitrate from water is of utmost importance from health and environmental viewpoints.

High levels of nitrate in water may result from human and animal wastes, and from the excessive use of chemical fertilizers. Nitrates are extremely soluble in water and can move easily through soil into drinking water supplies [4–6]. Different physico-chemical and biological methods have been investigated for the removal of nitrate in water and wastewaters, including adsorption, biological denitrification, enhanced ultrafiltration, and electrodialysis. Among them, adsorption is very feasible because it allows simple and economical operation [7], although it requires highly efficient adsorbents. Due to

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their versatility and spread range of applications, activated carbons (ACs) in powder or granular forms are widely used in the removal of several different organic and inorganic pollutants from water. However, effectiveness of ACs in nitrate uptake is quite poor and has been scarcely investigated, mostly using commercial samples [1,2,8–12].

On the other hand, it is still necessary to search for easily available, renewable bioresources as inexpensive precursors for sustainable manufacture of ACs [13]. In particular, use of *Parkinsonia aculeata* wood, a major invasive species in several regions worldwide, could represent an interesting option for ACs' production, simultaneously contributing to control the spread of this species through its conversion into a valuable product intended for wastewater treatment. *P. aculeata* forms dense thickets, preventing access for humans, native animals and livestock to waterways. It grows easily on most types of soils, withstands a great deal of heat, and survives in dry areas for prolonged spells. Moreover, seeds remain viable for many years and the seedpods float. The plant spreads by dropping pods into water or pods are washed downstream by seasonal flooding [14].

Within this context, the present study examines the development of ACs from *P. aculeata* wood sawdust, as unexplored precursor, for specific use in nitrate ion removal. The chemical activation process is applied. The effect of the chemical reagent used in the impregnation stage on main physico-chemical characteristics of *P. aculeata*-derived ACs and on their effectiveness in nitrate adsorption is investigated, comparatively using solutions of phosphoric acid and potassium hydroxide. Furthermore, modification of the ACs via post-treatment with saturated urea solutions is also explored in order to examine whether it leads to improve nitrate uptake. It should be mentioned that most works in the literature have been devoted to modify ACs by acid treatments in order to enhance the effectiveness of ACs in the removal of cationic species [8,15].

2. Experimental

2.1. Materials

P. aculeata wood was obtained from trees growing in a rural area placed in Buenos Aires province, Argentina. It is located at km 30.5 of route 215 (35° 4′ 24″ S, 58° 7′ 41″ W, 22.33 m elevation). Trunk's pieces of approximately 0.3 m length and 0.15 m cross-section diameter from a vertical distance of 1 m above ground were cut by our team with the help of some farmworkers using chainsaws. The pieces were *in situ* debarked and transported to our lab by road. Then, they were sun dried until constant weight was attained. Afterward, they were crushed, milled, and screen-sieved. Fractions of average particle diameter of 750 μm and 1500 μm were selected for preparation of the ACs with H_3PO_4 acid and KOH solutions, respectively. The samples were then washed and dried at 333 K up to constant weight.

2.2. Preparation of the activated carbons

2.2.1. Activation with H_3PO_4 acid
For phosphoric acid activation, sawdust fractions were impregnated with a 50% H_3PO_4 acid solution, using an acid/

precursor weight ratio of 2. The impregnated samples were first dried in an oven at 383 K for 2 h. Afterward, they were placed in a horizontal, fixed-bed reactor externally heated by an electric furnace, and thermally treated at a heating rate of 3 K min^{-1} up to 723 K under a self-generated atmosphere. Temperature selection was based on previous findings which demonstrate that maximum porosity development for ACs obtained by phosphoric acid activation from different ligno-cellulosic precursors is attained at 673–773 K [16–18]. Once the selected temperature was reached, it was held for 0.5 h. Then, the samples were allowed to cool down to reach ambient temperature. Further details of the equipment and procedure used have been reported earlier for other precursors [19]. To remove the excess of acid, the ACs were extensively rinsed with distilled hot water until neutral pH in the wash water was attained. Afterward, they were dried in an oven to constant weight.

2.2.2. Activation with KOH
The process involving carbonization of the precursor followed by subsequently KOH activation was applied since it reportedly leads to higher yields of ACs with higher surface areas and moderate ash content than those obtained by the one-step activation process [20]. A similar procedure to the one reported by Moreno Castilla et al. [21] was followed for ACs preparation.

Before proceeding to activation, carbonization of the precursor was carried out. For this purpose, 60 g of the precursor were heated under air flow (150 cm^3 min^{-1}) at a rate of 10 K min^{-1} up to 623 K. Once this temperature was attained, it was held for 1 h. Then, the carbonized precursor was mixed with a 13.4 mol dm^{-3} KOH solution using an impregnation weight ratio of 1. The latter is given by the ratio between the weight of KOH in solution and the weight of the carbonized precursor. The slurry was dried in an oven at 353 K up to constant weight. Afterward, it was placed in the same reactor used for acid activation, and heated under N$_2$ flow (150 cm^3 min^{-1}) at a rate of 10 K min^{-1} up to 573 K for 2 h. Then, the temperature was raised at the same heating rate to 1073 K, and it was held for 2 h, keeping the same N$_2$ flow rate. Finally, the sample was cooled down to ambient temperature maintaining the N$_2$ flow, and subsequently washed with 0.1 mol dm^{-3} HCl acid solution and with distilled water until absence of chloride ions in the washing water. The washed samples were then dried at 383 K to constant weight.

Yields in both cases were evaluated from weight differences. The ACs developed through chemical activation by using H_3PO_4 acid and KOH, are designated as ACA and ACB, respectively. For the sake of comparison, a commercial activated carbon (ACC) obtained by phosphoric acid activation of a woody precursor was also used and characterized.

2.3. Urea post-treatment of the activated carbons

The ACs obtained with both chemical reagents and the commercial sample were impregnated for 24 h at 383 K with a saturated urea solution, following a procedure similar to that reported previously [22]. An urea/ACs weight ratio of 2 was used since preliminary experiments showed that it led to enhance elemental N content of the derived ACs

compared to the one arising from a weight ratio of 1. The impregnated samples were heated under a self-generated atmosphere at 50 K min^{-1} to 623 K, held at this temperature for 3 h, and allowed to cool down to reach ambient temperature. The so-treated samples were washed several times with hot distilled water. The washed samples were then dried at 383 K until constant weight was attained. The ACs after being subjected to the urea treatment are labeled as ACA-UT, ACB-UT, and ACC-UT, for those obtained by activation with the acid, the base, and for the commercial sample, respectively.

2.4. Characterization of the activated carbons

2.4.1. Chemical characterization and point of zero charge
Chemical characteristics of the precursor, the developed ACs, as obtained and further subjected to the urea treatment, and the commercial sample were determined by proximate and elemental analyses. The former were performed according to American Society of Testing and Materials (ASTM) standards with a thermal analyser TA instrument SDT Q-600. Elemental compositions of the samples were assessed using a Carlo Erba EA1108 elemental analyser.

The total and individual amounts of acidic/polar oxygen functional groups on the surface of the derived ACs and the commercial sample were determined following a modified procedure based on Boehm's method. It enables to quantify carbonyls, phenols, lactones, and carboxyl groups by titration with a series of bases of different strength. The procedure applied has been earlier reported in detail [19,23]. Likewise, the content of basic surface groups was determined by contacting 0.5 g of each activated carbon with 50 cm^3 of 0.05 mol dm^{-3} HCl acid solutions. The slurries were stirred for 24 h and afterward filtered. A 10 cm^3 aliquot of the resulting solutions was subsequently titrated with 0.05 mol dm^{-3} NaOH. Values are expressed as millimol per gram of sample, in all cases.

The point of zero charge (pH$_{zc}$) of each sample, providing information about the nature of the carbon surface, was estimated from the pH of a concentrated dispersion as described elsewhere [24].

2.4.2. Textural characterization
N$_2$ adsorption–desorption isotherms at 77 K for the precursor, the derived ACs, and the commercial sample were determined with an automatic Micromeritics ASAP-2020 HV volumetric sorption analyzer. Prior to gas adsorption measurements, the samples were outgassed at 393 K overnight. Textural properties were assessed from the isotherms, according to conventional procedures depicted in detail in own previous studies [19]. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was determined by the standard BET procedure. Total pore volumes (V_t) were estimated from the amount of nitrogen adsorbed at the relative pressure of 0.95 ($p/p_0 = 0.95$). The mean pore widths (W) were calculated from $W = 4\, V_t/S_{BET}$. Pore size distributions (PSD) of the activated carbons were calculated from N$_2$ adsorption data using the DFT Plus Software (Micromeritics Instrument Corporation), based on the non-local density functional theory, that assumes slit pore shape [17].

2.5. Nitrate adsorption assays

Batch experiments were performed in order to examine the effectiveness of the ACs developed with both chemical reagents and the commercial sample in the removal of nitrate ion from model dilute solutions. For this purpose, a stock solution (16.1 mmol dm^{-3}) was first prepared by dissolving the necessary amount of analytical grade sodium nitrate in distilled water. Afterward, the stock solution was diluted as required to obtain standard solutions of concentrations ranging between 0.08 and 6 mmol dm^{-3}. Concentrations of nitrate ion in solution were determined by means of a UV–visible spectrophotometer (Shimadzu UVmini-1240) at $\lambda = 201$ nm [7]. All the adsorption experiments were carried out at a constant temperature of 298 ± 1 K, using particles of 375 μm-average size. Equilibrium was thoroughly verified for all the investigated systems from preliminary experiments performed for different prolonged contact times.

In order to investigate the effect of the solution's pH on the equilibrium adsorption of nitrate ions for the developed and commercial ACs, the pH of the solution in contact with each adsorbent was adjusted to different values comprised within the range 2–12 by using dilute NaOH or HCl solutions. For these assays, doses of 10^{-2} g cm^{-3}, and initial nitrate ion concentration of 1.61 mmol dm^{-3} were employed. Capped glass flasks containing the slurries were kept in a shaker at 0.2 s^{-1} and 298 K, thermostatically controlled with an external circulating bath, until equilibrium was attained. To check for any significant pH drift during the tests, the pH was recorded at the start and at the end of each experiment. No variations were determined with pH values maintained within 0.2 units. Once equilibrium was attained, the slurries were filtered through 0.45 μm membranes and nitrate concentrations in solution were determined as described above. Nitrate removal percentages were calculated as follows:

$$\text{Removal (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

where C_0 and C_e are the initial and equilibrium nitrate concentrations in solution, respectively.

Adsorption isotherms of nitrate onto the ACs developed with both reagents and the commercial carbon were determined by contacting 0.5 g of each sample with 50 cm^3 of nitrate solution of varying initial concentrations (0.1–6 mmol dm^{-3}). The general procedure depicted above was followed, keeping the same experimental conditions ($T = 298$ K, pH = 2, 0.2 s^{-1}). The amount of nitrate adsorbed at equilibrium per mass of activated carbon, q_e (mmol g^{-1}), was calculated as follows:

$$q_e = \frac{(C_e - C_0)}{D} \tag{2}$$

where D is the dose of sample used (g cm^{-3}).

All the experiments were performed at least twice. Fractional differences between replicates ($\Delta = (q_{e1} - q_{e2})\, q_{e2}^{-1}$) were less than 2% in all of the cases. Average values are reported. Furthermore, solute and adsorbent blanks were simultaneously run for control in all the assays under the corresponding conditions.

In order to represent the experimental data, the conventional two-parameter model of Langmuir was applied. It is described by the following equation:

$$q_e = \frac{K_L X_{mL} C_e}{1 + K_L C_e} \qquad (3)$$

Model characteristic parameters were estimated by non-linear regression analysis for a 5% significance level, by minimizing the following objective function:

$$O.F = \sum \left(q_{ei,\text{exp}} - q_{ei,\text{calc}} \right)^2 \qquad (4)$$

The appropriateness of the model to represent the experimental data was examined from the standard deviation (s), which was estimated according to:

$$s = 100 \left[\frac{\sum_{i=1}^{N} \left(q_{ei,\text{exp}} - q_{ei,\text{est}} \right)^2}{N - P} \right]^{1/2} \qquad (5)$$

3. Results and discussion

3.1. Yields and characteristics of the activated carbons

Table 1 reports chemical characteristics of P. aculeata wood, the developed ACs, and the commercial sample. Overall yields for the derived ACs are also listed in the same table. The results in Table 1 indicate that noticeable changes in the precursor occurred due to the activation process, in turn depending on the reagent used. Compared with the precursor, the ACs obtained with both reagents showed enhanced contents of ash, C, and N, as well as reductions in amounts of volatile matter, H, and O.

As seen in Table 1, H_3PO_4 acid activation led to higher yields, more than twice than those attained when KOH was used. The trend agrees with published results for ACs prepared from other precursors via chemical activation comparatively using H_3PO_4 acid and basic impregnants, and has been attributed to different chemical mechanisms. The acid reportedly intervenes in the initial stages of carbonization of the precursor, which begin at lower temperatures, while the basic agents only react after the precursor has been at least partially carbonized at higher temperatures [25]. H_3PO_4 acid promotes bond cleavage reactions of the constituent biopolymers and formation of new bio-phosphate ester cross-links within the precursor structure. This leads to a rigid matrix that restricts shrinkage of the precursor and limits volatile matter loss upon heating, thus resulting in a higher yield [16,26,27]. On the contrary, with basic agents, significant volatilization of the organic compounds formed as a result of low-temperature thermal decomposition of the precursor apparently occurs before the subsequent chemical reactions involving the activating agent become thermodynamically feasible at higher temperatures, and consequently, lower yields are attained [25,28,29].

The total and individual contents of surface acidic-polar oxygen functional groups of the derived ACs and the commercial carbon are illustrated in Fig. 1. As observed, the development of these functionalities on the carbons' surface strongly depends on the reagent used. The contents of ACA were similar to results reported for ACs derived from other lignocellulosic precursors by H_3PO_4 acid activation under similar conditions [19,24,30]. The ACA exhibited a higher total content of acidic groups than the ACB. Likewise, the total content of the acidic functionalities of the ACC was similar to that of the ACA. All the samples showed a major contribution of phenols and lactones, although the contents of these functionalities for the ACA and ACC were higher than that for the ACB. The latter was also characterized by the lack of carboxylic groups, whereas the ACs developed with the acid
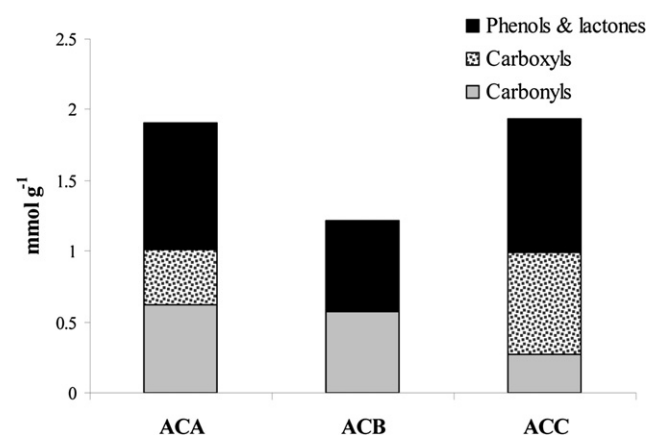
Table 1 – Yield and chemical characteristics of _Parkinsonia aculeata_ wood sawdust used as a precursor, the activated carbons developed with phosphoric acid (ACA) and potassium hydroxide (ACB), and the commercial sample (ACC).

	Parkinsonia aculeata	ACA	ACB	ACC
Proximate analysis	g kg^{-1} (dry basis)			
Volatile matter	774	57	32	9
Fixed carbon[a]	212	860	932	933
Ash	14	83	36	58
Elemental analysis	g kg^{-1} (dry-ash free basis)			
C	480	770	747	863
H	57	25	5	21
N	2	3	5	6
O[a]	461	202	243	110
Total content of surface groups	mmol g^{-1}			
Acidic		1.9	1.2	1.9
Basic		0.1	0.7	—
pH$_{zc}$	—	5.1	6.8	4.2
Yield (%)	—	47.0	19.8	—

a Estimated by difference.

Fig. 1 – Total and individual quantities of acidic surface functional groups determined for the activated carbons developed from _Parkinsonia aculeata_ wood sawdust, using phosphoric acid (ACA) and potassium hydroxide (ACB) as activating agents, and the commercial activated carbon (ACC).

and the ACC presented minor proportions of carboxyls, likely because they become unstable at the temperatures used in the thermal treatment stage. Nevertheless, the content of carboxyls for the ACC was higher than the one for the ACA. Temperature-sensitive surface functionalities, such as carboxylic groups, on ACs obtained by H_3PO_4 acid activation reportedly arise from acidic hydrolysis of the raw precursor, and begin to decompose at relatively low temperatures (>523 K) [31].

The results also evidenced that only the ACs developed with KOH possessed an appreciable amount of basic groups (0.7 mmol g^{-1}). In turn, the ACA presented a low content of basic functionalities (0.1 mmol g^{-1}), whereas no basic groups were detected for the commercial sample. Basic properties of the ACs are generally ascribed to delocalized π electrons in the basal planes of the carbon matrix, which act as Lewis base, and also to the presence of functional groups with basic nature, such as pyrones. ACs with basic properties are expected to have potential for adsorption of species with net negative charge, at low pH [13].

On the other hand, pH_{ZC} values determined for the ACA and the ACC (Table 1) indicate that they were acidic. Likewise, the pH_{ZC} value for those samples developed with KOH points to an almost neutral character of the surface of the ACB. The results were consistent with the total contents of acidic and basic surface functionalities determined for the three samples (Table 1).

Textural parameters evaluated from N_2 adsorption–desorption isotherms for the developed ACs and the commercial carbon are reported in Table 2. They indicate that the acid activation led to ACs of higher BET surface area and total pore volume than those obtained with KOH, although the commercial sample showed the highest values. ACB presented the highest contribution of micropores to the total pore volume, whereas predominance of mesopores characterized the porous structures of the ACA and ACC.

Reasons for the differences in pore width of ACs obtained with H_3PO_4 acid and KOH have been analyzed elsewhere [25]. For H_3PO_4 acid activation, the larger pore width has been attributed to cross-linking, eventual formation of folded graphitic-like structures, as well as to relatively large gaps between the precursor molecules at the lower temperatures where bond cleavage and formation reactions

start. These factors could induce a relatively open and scarcely ordered packing of the graphitic-like structures, which could make densification more difficult at high temperatures. Besides, the presence of large phosphate or polyphosphate species could also prevent the graphitic-like layers from adopting an oriented dense structure [29]. In turn, the chemical reactions involved in the development of ACs with basic impregnants might not lead to such a significant level of cross-linking. On the contrary, they could remove C atoms which should impede reorientation of the growing graphitic-like structures [25].

3.2. Effect of the solution pH on nitrate adsorption

Fig. 2 shows the effect of the solution pH on nitrate removal at equilibrium for the developed ACs and the commercial sample from solutions of nitrate initial concentration of 1.61 mmol dm^{-3}. It can be appreciated that nitrate uptake was highly dependent on the solution pH in all cases. The removal of nitrate ions pronouncedly decreased as the solution pH increased. The trend may be attributed to differences in the degree of surface protonation of the carbons' surface with varying pH. Electrostatic attraction forces between nitrate anions and the positively charged surface should favor nitrate uptake at low pH values. As the pH increases, the carbon surface becomes progressively more negative charged and the gradually unfavorable higher concentration of hydroxyls in solution, that compete with nitrate anions for the surface adsorption sites, seem to predominate leading to reduce the extent of adsorption. Similar trends have been reported in the literature for some other commercial granular activated carbons used for nitrate uptake [1,12].

3.3. Nitrate adsorption isotherms

Fig. 3 shows the experimental nitrate adsorption isotherms onto both the developed ACs and the commercial sample.
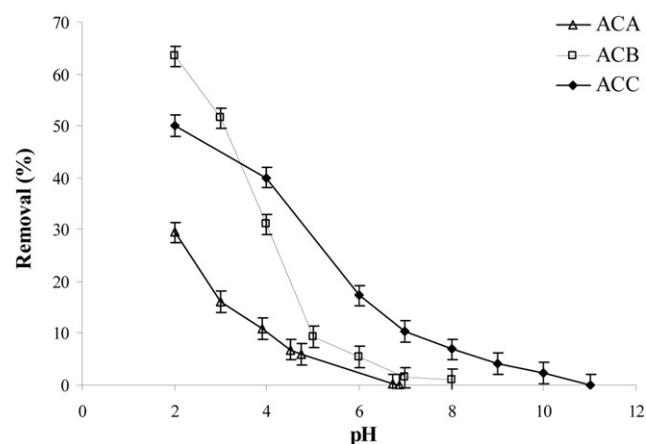

Fig. 2 – Effect of the solution pH on nitrate ion removal for the activated carbons developed from *Parkinsonia aculeata* wood sawdust with phosphoric acid (ACA) and potassium hydroxide (ACB), and for the commercial sample (ACC). Experimental conditions: $C_0 = 1.61$ mmol dm^{-3}; $D = 10^{-2}$ g cm^{-3}; T = 298 K; agitation speed = 0.2 s^{-1}.

Table 2 – Textural properties of the activated carbons developed from *Parkinsonia aculeata* wood sawdust by chemical activation with phosphoric acid (ACA) and potassium hydroxide (ACB), and the commercial sample (ACC).

Sample	S_{BET} [a] (m^2 g^{-1})	V_t [b] (cm^3 g^{-1})	V_μ [c] (cm^3 g^{-1})	W [d] (nm)
ACA	968	0.70	0.18	2.9
ACB	768	0.37	0.27	1.9
ACC	1424	1.08	0.28	3.0

a BET surface area.
b Total pore volume.
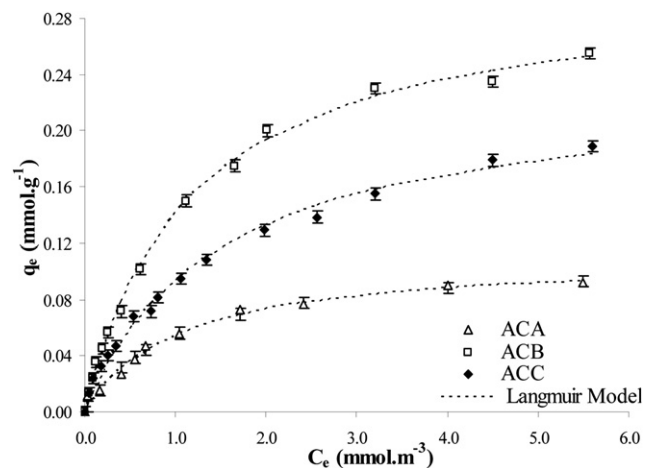c Micropore volume determined by the DFT method.
d Mean pore width.

Fig. 3 – Adsorption isotherms of nitrate ion onto the activated carbons developed from *Parkinsonia aculeata* wood sawdust with phosphoric acid (ACA) and potassium hydroxide (ACB), and onto the commercial sample (ACC). Comparison between the experimental data (points) and predictions of the Langmuir model (line). Experimental conditions: $D = 10^{-2}$ g cm^{-3}; $T = 298$ K; agitation speed $= 0.2$ s^{-1}; pH $= 2$; range of nitrate initial concentrations $= 0.1–6$ mmol dm^{-3}.

The estimated characteristic model parameters along with the corresponding values of the correlation coefficient (R^2) and the standard deviation are summarized in Table 3. As may be appreciated, the Langmuir model enables to represent properly the data for all the systems with R^2 values ≥ 0.990. It should be mentioned that the Freundlich model was also applied, but it led to a less adequate description of the results, as revealed by lower values of R^2.

The results in Table 3 indicate the highest maximum adsorption capacity (X_{mL}) for the ACB, followed in decreasing order by the ACC and the ACA. The found trend points to a combined effect of the surface chemistry and the characteristics of the porous structure of the ACs. Taking into account that the ACB showed the lowest development of porous networks, as judged from the estimated textural properties (Table 2), the surface chemistry of the carbon seems to play a prevalent role. The ACB was the only sample characterized by an appreciable content of basic

functionalities and the lowest amount of acidic groups, in comparison with the ACA and the ACC.

Furthermore, at the pH employed for determination of the nitrate isotherms (pH $= 2$), the surface of all the samples should be positively charged. Basic oxygen-containing functional groups (pyrones or chromenes), protonated amino groups (in case of nitrogen-rich carbons), and graphitic-like layers acting as Lewis bases and forming electron donor–acceptor complexes with water molecules have been ascribed as possible sources responsible for the development of surface positive charge of ACs [32]. Since the present investigated ACs without the subsequent urea treatment showed a low content of elemental N (Table 1), basic surface functionalities and graphitic-like layers, where most of the surface area resides [32], should mainly contribute to the positive charge of the samples' surface. Accordingly, the higher surface area of the ACC, associated with the presence of graphitic-like layers, could explain the higher X_{mL} estimated for this sample in comparison with that for the ACA. The results also suggest a relatively more important contribution of surface basic functionalities than of the graphitic-like layers to the development of the surface charge and, consequently, to nitrate ion uptake, as inferred from the highest X_{mL} value determined for the ACB.

3.4. Effect of the urea post-treatment on characteristics of the activated carbons and on their effectiveness in nitrate ion adsorption

To further explore the effect of the surface chemistry of the ACs on their performance in the uptake of nitrate ions, the samples developed with both reagents and the commercial sample were subjected to the urea treatment described in Section 2.3. Chemical and textural characteristics for the urea-treated ACs are summarized in Table 4. Comparison of the results in Table 4 with those reported in Table 1 indicates that the urea treatment of the ACs induced pronounced variations in their proximate analyses, elemental compositions, pH$_{zc}$ values, and total contents of surface functionalities. Main modifications included marked increases in N content for all the carbons, accompanied by decreases in C contents. Content of N increased between 25 and 33 times, with the ACB-UT possessing the highest one. Besides, relatively higher pH$_{zc}$ values and appreciable contents of basic functionalities for the three ACs, as well as reduced total amounts of surface acidic groups were determined for all the samples, pointing to enhancements in their basic character.

Comparison of textural properties of the developed ACs and the commercial sample before and after the urea treatment (Tables 2 and 4) points to noticeable alterations in their porous structures. The results in Table 4 indicate that the urea treatment led to pronouncedly reduce BET area and total pore volume for all the samples. Likewise, changes in pore size distributions took place. The ACA-UT showed a marked increase in micropores contribution to the total pore volumes, that almost duplicated that determined for the untreated sample. On the contrary, reduction in micropore volume with respect to the untreated carbons for the urea-treated ACB and ACC was found, even though it was more pronounced for the latter. The trends were reflected in the PSD of the urea-treated

Table 3 – Langmuir model parameters estimated for nitrate ion adsorption isotherms onto the activated carbons developed with phosphoric acid (ACA) and potassium hydroxide (ACB), and the commercial activated carbon (ACC).

Sample	X_{mL} (mmol g^{-1})	K_L (m^3 mmol^{-1})	R^2	s (%)
ACA	0.11	0.98	0.992	0.003
ACB	0.30	0.87	0.997	0.510
ACC	0.23	0.64	0.990	0.010

Table 4 – Chemical-textural characteristics of the activated carbons developed with phosphoric acid (ACA-UT) and potassium hydroxide (ACB-UT), and the commercial sample (ACC-UT) after the urea treatment.

	ACA-UT	ACB-UT	ACC-UT
Proximate analysis	g kg^{-1} (dry basis)		
Volatile matter	139	119	68
Fixed carbon[a]	841	870	912
Ash	20	11	20
Elemental analysis	g kg^{-1} (dry-ash free basis)		
C	675	737	733
H	32	16	16
N	131	148	101
O[a]	162	99	150
Total content of surface groups	(mmol g^{-1})		
Acidic	1.5	0.8	1.5
Basic	0.4	0.4	0.6
pH$_{ZC}$	5.7	6.9	6.1
Textural properties			
S$_{BET}$[b] (m^2 g^{-1})	308	191	776
V$_t$[c] (cm^3 g^{-1})	0.17	0.09	0.61
V$_\mu$[d] (cm^3 g^{-1})	0.09	0.05	0.08
W[e] (nm)	2.2	2.0	3.1

a Estimated by difference.
b BET surface area.
c Total pore volume.
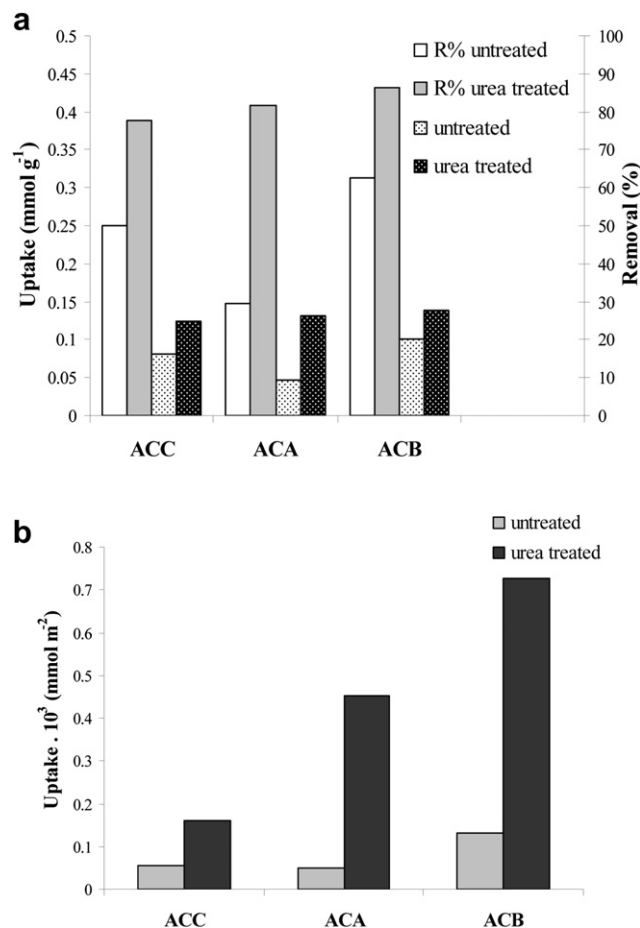d Micropore volume determined by the DFT method.
e Mean pore width.

Fig. 4 – Effectiveness of the activated carbons developed from *Parkinsonia aculeata* wood sawdust with both reagents and of the commercial sample in nitrate ion removal at equilibrium before and after the urea treatment expressed as: a) mmol of nitrate removed per unit mass of sample and percentages of removal (%); b) mmol of nitrate removed per unit surface area of sample. Conditions: $D = 10^{-2}$ g cm^{-3}; $T = 298$ K; agitation speed $= 0.2$ s^{-1}; pH = 2; $C_0 = 1.61$ mmol dm^{-3}.

samples (not shown) and were evidenced by a smaller pore width for the ACA and larger pore widths for the ACB and ACC (Table 4). Nitrogenation treatments of ACs affect not only the surface chemistry, but also their porous structures, depending on the original activated carbon, the chemical reagent, and treatment conditions.

The effectiveness of the urea-treated ACs in nitrate adsorption at equilibrium from solutions of initial concentration of 1.61 mmol dm^{-3}, expressed per mass unit of each sample at pH = 2, is shown in Fig. 4-a. For the sake of comparison, values attained before the urea treatment are included in the same figure, as well as percentages of nitrate removal. As seen, removal levels of around 80–90% were attained after the urea treatment. Furthermore, in order to account for the pronounced reduction in the pore structures of the samples, earlier discussed, part b) of Fig. 4 illustrates nitrate ion uptakes normalized by the corresponding surface area of the untreated and urea-treated samples. A similar proposal has been recently reported for other ACs – adsorbate systems [33]. It should be stressed that total amounts of surface basic functional groups for the urea-treated ACs, also expressed per unit of surface area, noticeably increased with respect to the virgin ACs, being at least one order of magnitude greater.

As may be appreciated in Fig. 4(a–b), nitrate uptakes by the treated ACs were higher than those attained by the untreated ones, in agreement with the higher contents of elemental N and basic functionalities, and pH$_{zc}$ values of the former ones. However, the differences were pronouncedly larger for the normalized nitrate uptakes (Fig. 4-b), their extent being in

direct correlation with the elemental N content of the ACs. The greater the N content of the sample, the higher the uptake of nitrate anion. The results suggest that, as mentioned above for N-enriched ACs [32], protonated amino functionalities could additionally contribute to an enhanced development of the surface positive charge in the urea-treated activated carbons, which should facilitate the uptake of nitrate ions. Incorporation of N-based groups, such as amidine and/or amino groups, supplied by the urea treatment might enable the formation of a chelate complex with nitrate anion at low pH, that could contribute to favor nitrate uptake [34]. Present results are in accordance with other findings recently reviewed for ACs subjected to different nitrogenation treatments. It has been pointed out that, despite widely differing in size, surface charge or polarity, nitrogenated ACs generally show higher adsorption capacities compared with the virgin samples [15].

4. Conclusions

Effective activated carbons for removal of nitrate anions have been developed by chemical activation of wood sawdust from the invasive species *P. aculeata* using either phosphoric acid or potassium hydroxide, and further post-treated with saturated urea solutions. Nevertheless, taking into account that phosphoric acid activation involves only a single thermal treatment stage at milder operating conditions, and leads to higher yields than activation with KOH, the former process followed by the subsequent urea treatment seems more convenient.

Acknowledgments

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