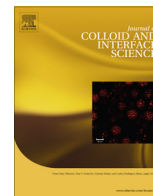




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Nitrate uptake improvement by modified activated carbons developed from two species of pine cones

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ABSTRACT

Activated carbons from two species of pine cones (*Pinus canariensis* and *Cupressus sempervirens*) were prepared by phosphoric acid activation and tested for the removal of nitrate ions from aqueous solution. To investigate the feasibility of improving their nitrate adsorption capacity, two different post-treatments – a thermal treatment and a treatment with saturated urea solution – were also applied to the prepared activated carbons. Comparison of the treated and untreated activated carbons showed that both post-treatments improved the nitrate adsorption performance more than twice. The maximum adsorption capacity, as evaluated from determination of the adsorption isotherms for the *P. canariensis* based carbons, and their proper representation by the Langmuir model, demonstrated that the post-treatment with the urea solution led to activated carbons with increased nitrate removal effectiveness, even superior to other reported results. Enhancements in their adsorption capacity could be mainly ascribed to higher contents of nitrogen and basic functional groups, whereas porous structure of the activated carbons did not seem to play a key role in the nitrate uptake.

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1. Introduction

Pollution of groundwater by nitrate leaching is a common problem worldwide. The principal nitrate contamination would come from industrial ammonium synthesis via fertilizers and from animal manures, whereas landfill has rapidly grown to become the second largest source of groundwater nitrate, affecting groundwater quality in urban areas [1–8]. Nitrate induces eutrophication and it has been linked to the outbreak of infectious diseases. Consumption of water with high concentrations of nitrate may cause methaemoglobinemia in infants, with symptoms of cyanosis and asphyxia, and stomach cancer in adults [9,10]. Methaemoglobin levels >50% can quickly lead to coma and death if the condition is not recognized and treated [11]. Due to the above health hazards associated with this contaminant in water, strict limits have been recommended [12,13].

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Several methods have been used for the removal of nitrate from water including ion-exchange resin, chemical reduction, electrodiagnosis, biological denitrification, reverse osmosis, nanofiltration [3,9,14–21]. However, such methods usually suffer from low treatment efficiency and high operation costs. Adsorption is an attractive option as it allows simple and economical operation. Adsorption by activated carbons (ACs) has proven to be very efficient in the removal of a wide variety of contaminants and has become one reliable method in the field of water treatment. Nevertheless, only few works have been devoted to examine nitrate uptake by ACs, with results indicating very low removal levels [3,22,23].

The adsorption ability of ACs depends on the precursor, the activation process and the operating conditions used for their preparation, that have a pronounced effect upon their physicochemical characteristics. Different materials, such as coal, lignocellulosic biomasses, bones, and some polymers, have been employed as precursors by applying physical or chemical activation processes. In particular, the use of agricultural, agro-industrial and /or forestry wastes has been emphasized since they represent a very attractive option due to their renewable character, low cost, and abundance [24–27]. On the other hand, some studies have also

Nomenclature

C_0	initial nitrate concentration (mmol/L)	R^2	correlation coefficient
C_e	equilibrium nitrate concentration (mmol/L)	s	standard deviation (Table 4) (%)
D	sample's dose (g/mL)	X_{mL}	maximum adsorption capacity in the Langmuir model (Tables 4 and 5) (mmol/g)
K_F	Freundlich constant (Table 4) (mmol/g (L/mmol) ^{n_F})	X_{mLF}	maximum adsorption capacity in the Langmuir–Freundlich model (Table 4) (mmol/g)
K_L	energy of adsorption in the Langmuir model (Table 4) (L/mmol)		
K_{LF}	Langmuir–Freundlich constant (Table 4) (L/mmol)		
n_F	Freundlich adsorption intensity (Table 4)	<i>Subscripts</i>	
n_{LF}	Langmuir–Freundlich model parameter (Table 4)	calc	calculated value
N	number of experimental points	exp	experimental value
P	number of parameters estimated		
q_e	amount of nitrate adsorbed at equilibrium per unit mass of carbon (mmol/g)		

focused their attention on post-treatments involving modifications in physicochemical properties of ACs in order to improve their performance in the uptake of a particular pollutant [17,28,29]. However, in the case of nitrate removal, this kind of approaches has not conducted to completely satisfactory results [3,22,30]. Therefore, further research is still needed to improve ACs performance toward adsorption of this priority pollutant.

Within this scenario, the main goal of the present work was to develop activated carbons of enhanced performance for the removal of nitrate ions from wastewater. For this purpose, conversion of pine cones from two different unexplored species (*Pinus canariensis* and *Cupressus sempervirens*) by phosphoric acid activation was studied. The precursors were selected due to their availability in huge amounts, easy collection, and renewable character [31]. Nitrate adsorption effectiveness of the developed ACs was evaluated and application of two different post-treatments, namely thermal treatment under nitrogen flow and a treatment with saturated urea solution, was also investigated in order to improve their performance. Chemical and textural characteristics of the developed activated carbons before and after modifications were determined, and their influence on nitrate adsorption capacity of the ACs was discussed.

2. Experimental

2.1. Characterization of the precursors

P. canariensis cones (PC) were collected from Pinamar, Buenos Aires province, Argentina, whereas *C. sempervirens* cones (CS) were obtained from the campus of University of Buenos Aires. Both were collected between December and January. The cones were washed repeatedly with distilled water to remove adhering dirt and soluble impurities, and dried at 60 °C. Chemical characteristics of raw pine cones were assessed. Soluble extractives contents were determined according to TAPPI T204 om-88 standards. Klason lignin (insoluble lignin) was determined from extractive-free samples, according to TAPPI 222 om-02 procedure. All the experiments were performed at least twice. Differences between replicates were less than 0.5% in all of the cases. Average values are reported. The amount of holocellulose (cellulose + hemicellulose), expressed on dry basis and extractive-free, was determined according to:

$$\text{Holocellulose (\%)} = 100 - \text{Lignin (\%)} \quad (1)$$

2.2. Preparation of the activated carbons

The dried cones were crushed, milled, and screen-sieved. Sample fractions of average particle diameter of 750 μm were impregnated

with a 50% H₃PO₄ acid solution, using an acid/precursor weight ratio of 2. The impregnated samples were first dried in an oven at 110 °C for 2 h, and then placed in a tubular reactor to be thermally treated at a heating rate of 3 °C/min up to 450 °C under a self-generated atmosphere. 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 [32,33]. 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 until constant weight. The ACs obtained from *P. canariensis* and *C. sempervirens* cones are labeled as PC-P and CS-P, respectively.

2.3. Post-treatments of the activated carbons

2.3.1. Thermal post-treatment

Fractions of the ACs from both precursors were placed separately in porcelain capsules positioned inside a horizontal tubular reactor externally heated by an electric furnace. They were thermally treated at a heating rate of 50 °C/min up to 800 °C under flowing N₂ (purity 99.99%; flow rate 500 mL/min). The samples were held at this temperature for 1 h and then cooled down to ambient temperature keeping the same nitrogen flow. The ACs obtained from both precursors after this thermal treatment were labeled as PC-PT and CS-PT, respectively.

2.3.2. Urea post-treatment

Fractions of the ACs obtained from both precursors were impregnated with a saturated urea solution for 24 h at 110 °C, following a procedure similar to that reported in a previous work [32]. The impregnated samples were then thermally treated under a self-generated atmosphere, at 50 °C/min to 350 °C, held at this temperature for 3 h, and allowed to cool down to ambient temperature. The so-treated samples were washed several times with hot distilled water and then dried at 110 °C until constant weight. The ACs obtained after this urea treatment were labeled as PC-PU and CS-PU, respectively.

2.4. Characterization of the ACs

2.4.1. Chemical characterization

Chemical characteristics of the ACs were determined by proximate and elemental analyses. The former was performed according to American Society of Testing and Materials (ASTM) standards with a thermal analyzer TA instrument SDT Q-600. Elemental compositions of the samples were assessed using a Carlo Erba EA1108 elemental analyzer.

The total contents of acidic oxygen functional groups (OFG) on the surface of the derived ACs were determined following a modified procedure based on Boehm's method [32–34]. 0.5 g of each sample was suspended in 50 mL of a 0.05 N solution of sodium ethoxide. The slurries were stirred for 24 h and afterward filtered. A 10 mL aliquot of the resulting solutions was added to 15 mL of a 0.05 N HCl acid solution and subsequently back-titrated with 0.05 N NaOH. Likewise, the content of basic surface groups was determined by contacting 0.5 g of each activated carbon with 50 mL of 0.05 M HCl solutions. The slurries were stirred for 24 h and afterward filtered. A 10 mL aliquot of the resulting solutions was sequentially titrated with 0.05 N NaOH solution. Values were expressed as milliequivalents per gram of sample.

The pH of the carbons was measured according to the following procedure: 1 g of carbon was contacted with 100 mL of distilled water and the mixture was boiled for 5 min. The suspension was cooled down to ambient temperature and the pH was measured to the nearest 0.1 pH unit.

The point of zero charge, pH_{ZC} , namely the pH at which the surface has a net neutral charge, provides information about the nature of the carbon surface. When the pH of the solution is lower than pH_{ZC} , the acidic water donates more protons than the surface groups, and so the adsorbent surface is positively charged. Conversely, above pH_{ZC} , the surface is negatively charged. Determination of pH_{ZC} was carried out according to a method previously reported by Carrott et al. [35]. 0.6 g of each activated carbon was added to 10 mL of a 0.1 M $NaNO_3$ solution. The suspensions were kept in a shaker at 25 °C, until equilibrium was attained. The pH at point of zero charge, pH_{ZC} , was determined as the pH of the concentrated dispersion filtered with 0.45 μm nylon membranes.

2.4.2. Textural characterization

N_2 adsorption–desorption isotherms at (–196 °C) for the precursors and the derived ACs were determined with an automatic Micromeritics ASAP-2020 HV volumetric sorption analyzer. Prior to gas adsorption measurements, the samples were outgassed at 120 °C overnight. Textural properties were assessed from the isotherms, according to conventional procedures depicted in detail in our previous studies [32,36]. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was determined by the standard BET procedure. Total pore volume (V_t) was 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 isotherm data using the DFT Plus Software (Micromeritics Instrument Corporation), based on the non-local density functional theory, and assuming slit pore shape.

2.5. Nitrate adsorption assays

In order to examine the effectiveness of the developed ACs in the removal of nitrate, batch experiments were first performed using a model dilute solution. Adsorption experiments were carried out at pH = 2, according to preliminary results. Capped glass flasks containing 0.5 g of adsorbent and 50 mL of nitrate solution (1.61 mmol/L) were kept in a shaker, at 300 rpm, thermostatically controlled with an external circulating bath at 25 ± 0.5 °C. Once equilibrium was attained, the slurries were filtered through 0.45 μm pore diameter nylon membranes and nitrate concentrations in solution were determined by means of a UV–visible spectrophotometer (Shimadzu UVmini-1240 model) at $\lambda = 201$ nm. Nitrate uptake percentages were calculated as follows:

$$\text{Uptake (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

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

Adsorption isotherms of nitrate onto the developed ACs were further determined for the raw and treated samples that attained the best effectiveness. 0.5 g of each sample were contacted with 50 mL of nitrate solution of varying initial concentrations (0.1–8 mmol/L), keeping otherwise the above mentioned conditions (300 rpm, 25 °C and pH = 2). Samples were filtered through 0.45 μm nylon membranes, and nitrate concentrations in solution were determined as described above. The amount of nitrate adsorbed at equilibrium per mass of activated carbon, q_e (mmol/g), was calculated as follows:

$$q_e = \frac{(C_0 - C_e)}{D} \quad (3)$$

where D is the dose of adsorbent used (g/mL). All the experiments were performed at least twice. Differences between replicates were less than 3% in all cases. Average values are reported. Furthermore, solute and adsorbent blanks were simultaneously run for control in all the assays under the corresponding conditions.

3. Results and discussion

3.1. Characteristics of the precursors and the developed raw and post-treated ACs

Chemical characteristics of the pine cones species used as ACs precursors are listed in Table 1. Contents of volatile matter and fixed carbon as well as percentages of C, H, N, and O, were similar for both precursors. Values were also similar to those previously reported in the literature for pine cones from other species [37,38]. Pine cones from CS presented higher contents of ash and lignin than the ones obtained from PC. The higher content of lignin for the former precursor could be responsible for the higher yields attained in the preparation of the ACs derived from CS (49%) compared to that obtained from PC (41%). This trend has also been reported by other authors [39] as comparing yields attained in ACs preparation from different lignocellulosic precursors. BET surfaces areas of both precursors were similar and almost negligible (~ 1 m²/g).

Table 2 shows chemical characteristics of the ACs derived from both precursors before and after the post-treatments applied. As can be seen, phosphoric acid activation promoted similar modifications on the chemical characteristics of both precursors. The derived ACs presented noticeable less content of hydrogen and oxygen than the corresponding precursors (Table 1), due to dehydration and volatile matter release taking place during the

Table 1
Chemical characteristics of *Pinus canariensis* cones (PC) and *Cupressus sempervirens* cones (CS) used as ACs precursors.

	PC	CS
<i>Proximate analysis</i>	<i>(wt%, dry basis)</i>	
Volatile matter	69.1	65.5
Fixed carbon ^a	30.0	31.0
Ash	0.9	3.5
<i>Elemental analysis</i>	<i>(wt%, dry-ash free basis)</i>	
C	52.9	47.8
H	6.0	5.7
N	0.6	0.9
O ^a	40.5	45.6
<i>Biopolymer content</i>	<i>(wt%, dry and extractive free basis)</i>	
Lignin	37.6	44.6
Hollocellulose ^a	62.4	55.4

^a Calculated by difference.

Table 2

Chemical characteristics of the ACs derived from *Pinus canariensis* (PC-P) and *Cupressus sempervirens* cones (CS-P), and of the thermally post-treated (PC-PT; CS-PT) and urea post-treated (PC-PU; CS-PU).

	Samples					
	PC-P	PC-PT	PC-PU	CS-P	CS-PT	CS-PU
Ash (wt%, dry basis)	4.1	5.3	1.6	9.5	12.4	5.0
Elemental analysis	(wt%, dry-ash free basis)					
C	88.2	93.3	67.0	80.0	89.7	66.7
H	3.4	0.8	2.3	2.8	0.9	2.6
N	0.4	0.3	13.0	0.6	0.5	13.8
O ^a	8.0	5.5	17.6	16.6	8.9	16.9
pH	3.8	5.3	4.5	3.6	4.0	6.0
pH _{ZC}	5.1	7.4	6.0	4.3	6.4	6.2

^a Estimated by difference.

thermal stage of the activation process. Instead, contents of ash and carbon for the ACs were higher than those of the precursors. The ACs derived from CS possessed higher ash content than those obtained from PC, in agreement with the higher contents of ash and oxygen of the former precursor. The high oxygen content of CS might lead to an intensified oxygenated self-generated atmosphere during the thermal treatment of the impregnated precursor that could favor ash formation. The thermal post-treatment produced a reduction in hydrogen and oxygen contents for both ACs, and enhancements in the pH of the resulting ACs. This trend could be attributed to the thermal decomposition of some acidic oxygen functional groups present on the ACs surfaces. The ACs obtained after the urea treatment showed a noticeable higher contents of nitrogen than that of the respective untreated samples, as well as an increment in pH and pH_{ZC} values, whereas a reduction in ashes and carbon contents were evidenced for those ACs.

The total contents of surface acidic oxygen functional groups and basic functionalities of the derived ACs are illustrated in Fig. 1. As observed, cones from both species led to activated carbons with similar quantities of acidic oxygen functional groups and absence of basic functionalities. In turn, both treatments applied induced the formation of basic functionalities and reductions in total contents of acidic oxygen functional groups present on ACs surfaces. Particularly, the thermal treatment promoted a noticeable reduction in the total content of acidic oxygen functionalities. This result is in accordance with other studies reporting that some acidic functional groups are unstable at high temperatures and decompose to carbon monoxide and carbon dioxide, leaving highly reactive sites on the carbon surface, which have free-radical character to some relatively small extent. After cooling to room temperature, they can react with oxygen present in air,

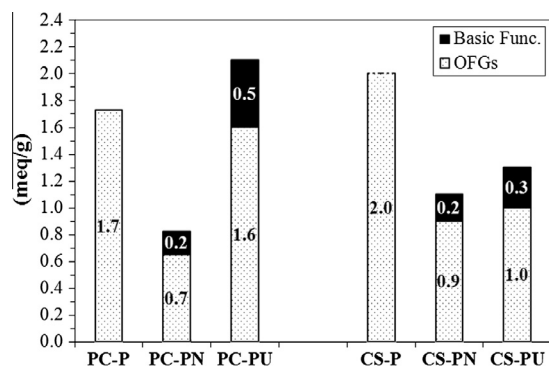


Fig. 1. Total quantities of acidic oxygen (OFGs) and basic surface functional groups determined for the raw ACs derived from *Pinus canariensis* (PC-P) and *Cupressus sempervirens* cones (CS-P), the thermally post-treated (PC-PT; CS-PT) and the urea post-treated (PC-PU; CS-PU) samples.

giving new surface oxide, which can be assigned to some carbon-yls, pyrone, and chromene-type structures [40–45]. These groups have a basic character, and could be responsible of basic properties of the samples. The greatest increase in the content of basic functionalities was determined for the urea treated samples. It could be linked to the presence of nitrogen functional groups such as amidine and/or amino groups [46,47].

Parts (a) and (b) of Fig. 2 shows N₂ adsorption/desorption isotherms for the ACs derived from PC and CS before and after both treatments applied, whereas those corresponding to pore size distributions are illustrated in parts (c) and (d). N₂ adsorption isotherms for the prepared ACs (Fig. 2a and b) presented similar shapes showing intermediate characteristics between type I and IV, according to the IUPAC classification, which are associated with the presence of both micropores and mesopores. The isotherms for the ACs obtained after both post-treatments revealed less N₂ adsorbed volumes at higher relative pressures than the respective untreated activated carbons, indicating a major contribution of micropores in those samples. Nevertheless, the reduction was more pronounced for the urea post-treated ACs. All the isotherms showed a hysteresis loop of type IV associated with monolayer-multilayer adsorption followed by capillary condensation in mesopores. The pore size distribution of the ACs (Fig. 2c and d), ascertained by the density functional theory (DFT) model, evidenced that all the samples had similar pore size distributions, with most of the pores ranging in-between 1.5 nm and 5 nm. Textural characteristics of the raw and post-treated activated carbons are listed in Table 3. The results in Table 3 indicate that the activated carbons derived from PC presented slightly higher surface area and total pore volume than those obtained from CS. Both post-treatments applied induced a noticeable reduction in the specific surface area of the activated carbons. Nevertheless, the reduction was more pronounced after the urea treatment, likely due to the incorporation of some nitrogen species to the edges of graphitic-like layers that could produce steric hindrances and partially blocking the access of nitrogen molecules to some small pores [48].

3.2. Effectiveness of the untreated and post-treated ACs in nitrate uptake

Fig. 3 shows nitrate uptake by the derived ACs before and after applying both treatments. As can be seen from Fig. 3, ACs derived from PC cones presented a better nitrate removal efficiency than those obtained from CS cones. Both post-treatments applied led to enhancements in nitrate adsorption performance of the activated carbons. Basic functionalities (Fig. 1) and the introduction of nitrogen into the carbons matrix by the urea treatment (Table 2) seem to be mainly responsible for the improved performance of the post-treated carbons in the adsorption of nitrate from water,

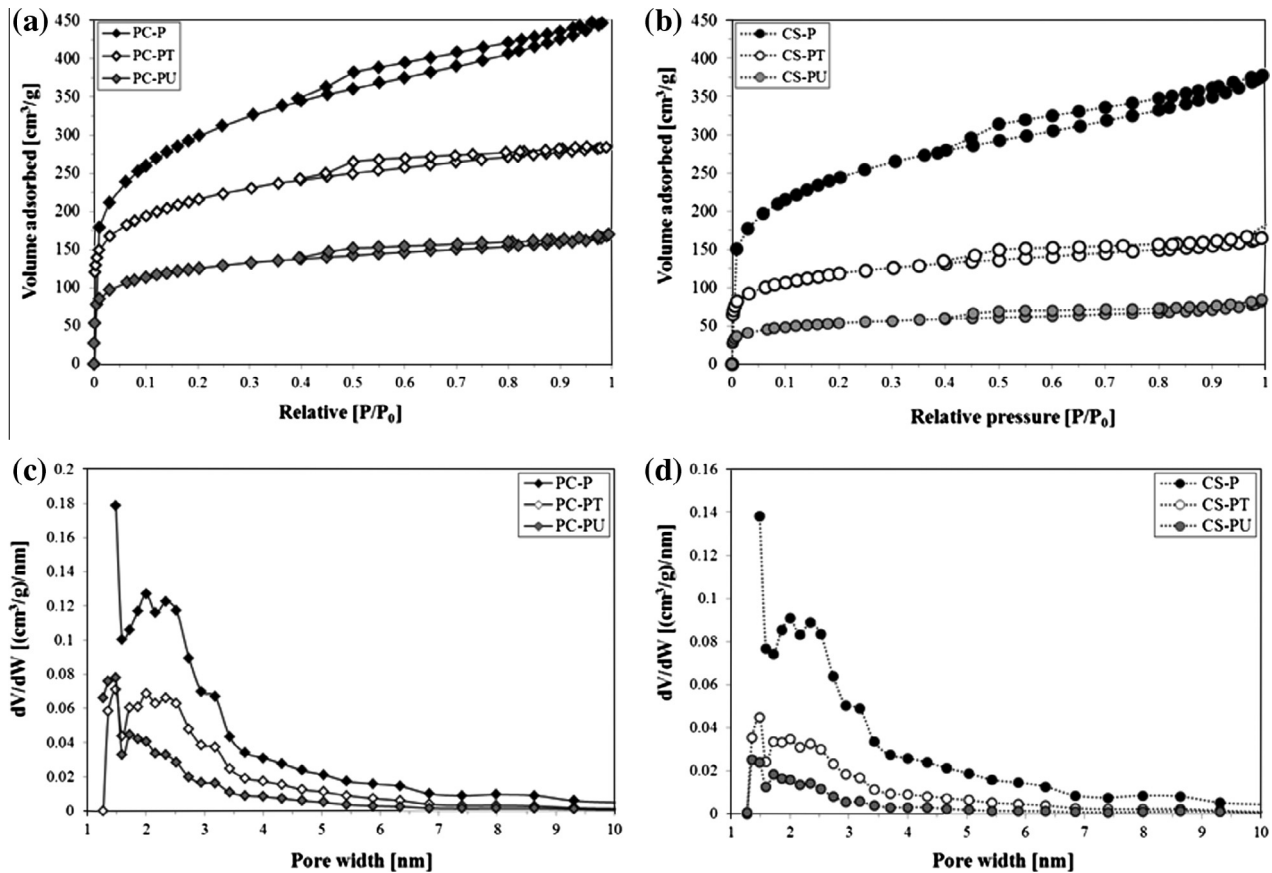


Fig. 2. N_2 adsorption–desorption isotherms (a and b), and pore size distribution (c and d) for the raw ACs derived from *Pinus canariensis* (PC-P) and *Cupressus sempervirens* cones (CS-P) samples, the thermally post-treated (PC-PT; CS-PT) and the urea post-treated ACs (PC-PU; CS-PU).

Table 3

Textural characteristics of the raw ACs derived from *Pinus canariensis* (PC-P) and *Cupressus sempervirens* cones (CS-P), the thermally post-treated (PC-PT; CS-PT) and the urea post-treated (PC-PU; CS-PU) samples.

	Sample					
	PC-P	PC-PT	PC-PU	CS-P	CS-PT	CS-PU
S_{BET}^a (m^2/g)	1082	772	449	881	428	192
V_t^b (cm^3/g)	0.7	0.4	0.2	0.6	0.2	0.1
W^c (nm)	2.5	2.3	2.2	2.5	2.3	2.4

^a BET Surface area.

^b Total pore volume.

^c Mean pore width.

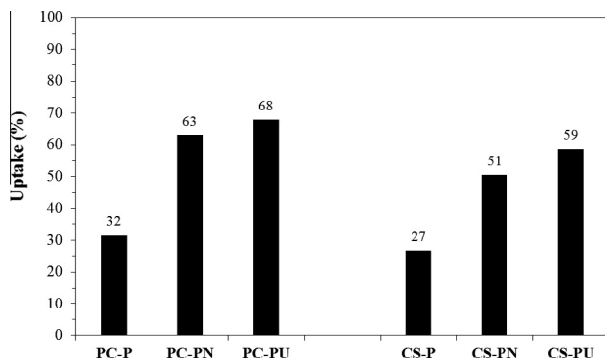


Fig. 3. Nitrate uptake for the raw ACs derived from *Pinus canariensis* (PC-P) and *Cupressus sempervirens* cones (CS-P), the thermally post-treated (PC-PT; CS-PT) and the urea post-treated samples (PC-PU; CS-PU).

despite both post-treatments induced noticeable reductions in BET surface areas and total pore volumes of the ACs (Table 3).

Due to the better removal efficiency evidenced for the PC cones-based ACs, nitrate adsorption isotherms were determined for these samples, in order to assess the influence of both post-treatments onto nitrate maximum adsorption capacities. For this purpose, three commonly used isotherm models were applied to the experimental data: the Langmuir, Freundlich and Langmuir–Freundlich models [49,34]. The model characteristic parameters were estimated by non-linear regression analysis for a 5% significance level, by minimizing the following objective function (O.F) = $\sum(q_{ei,\text{exp}} - q_{ei,\text{calc}})^2$. The appropriateness of the model to represent the experimental data was examined from the standard deviation (s) = $100\{\sum(q_{e,\text{exp}} - q_{e,\text{calc}})^2/(N - P)\}^{1/2}$.

In order to determine whether the adsorption is favorable, a dimensionless constant separation factor (R_L) was estimated. It is defined according to $R_L = 1/(1 + K_L C_0)$, where C_0 is the initial concentration of nitrate (mmol/L). According to R_L values, the type of isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [50].

The experimental data obtained for the nitrate adsorption isotherm onto the raw AC derived from the PC cones and onto these samples further subjected to the post-treatments, and model predictions are shown in Fig. 4. The estimated characteristic model parameters along with the corresponding values of the correlation coefficient (R^2) and the standard deviation are listed in Table 4. As can be seen from Fig. 4, the three models applied properly described the experimental data obtained with quite similar high correlation coefficients (Table 4). The values of R_L for the adsorption of nitrate onto the activated carbons, ranged between

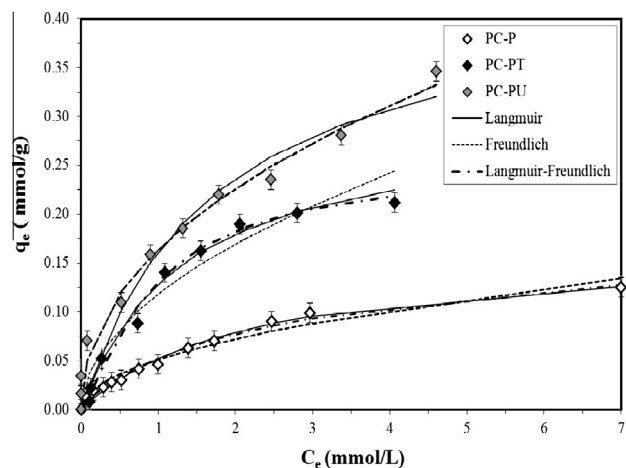


Fig. 4. Nitrate adsorption isotherms for the untreated ACs derived from *Pinus canariensis* cones (PC-P), the thermally post-treated (PC-PT) and the urea post-treated (PC-PU) samples. Comparison between experimental data and models predictions. Conditions: $D = 0.5$ g/50 mL; $T = 25$ °C, 300 rpm, pH = 2, $C_0 = 0.1$ – 8 mmol/L.

Table 4

Model characteristic parameters estimated for nitrate adsorption isotherms onto the untreated ACs derived from *Pinus canariensis* (PC-P), and the thermally post-treated (PC-PT) and the urea post-treated (PC-PU) samples.

Model	Parameters	PC-P	PC-PT	PC-PU
Langmuir $q_e = \frac{K_L X_{mL} C_e}{1 + K_L C_e}$	X_{mL} (mmol/g)	0.16	0.30	0.45
	K_L (L/mmol)	0.47	0.76	0.55
	s (%)	0.4	0.8	2.0
	R^2	0.990	0.995	0.973
Freundlich $q_e = K_F (C_e)^{n_F}$	n_F	0.50	0.52	0.49
	K_F [(mmol/g)/(L/mmol) n_F]	0.05	0.12	0.16
	s (%)	0.6	1.2	1.4
	R^2	0.974	0.970	0.981
Langmuir–Freundlich $q_e = \frac{K_{LF} X_{mLF} (C_e)^{n_{LF}}}{1 + K_{LF} (C_e)^{n_{LF}}}$	X_{mLF} (mmol/g)	0.20	0.25	0.56
	K_{LF} (L/mmol) $^{n_{LF}}$	0.36	1.08	0.42
	n_{LF}	0.84	1.29	0.77
	s (%)	0.4	0.7	1.8
	R^2	0.990	0.994	0.980

Table 5

Comparison of nitrate maximum adsorption capacities (X_{mL}) obtained in this work with other previously reported from different raw and post-treated ACs.

Sample	X_{mL} (mmol/g)	Reference
– Commercial AC Filtrasorb 400 (Cargon-Mitsubishi) (F400)	0.14	Ota et al. [3]
– F400 oxidized with HNO ₃ and outgassed at 800 °C	0.13	
– F400 oxidized with HNO ₃ and outgassed at 1000 °C	0.18	Ota et al. [3]
– F400 oxidized with HNO ₃ and outgassed at 350 °C (F400-Ox)		
– F400-Ox heat treated at 600 °C	0.02	
– F400-Ox heat treated at 900 °C	0.21	
– F400 activated with CO ₂ at 900 °C	0.12	
– F400 activated with steam at 1000 °C	0.16	Cho et al. [23]
– Granular activated carbon made from lignite (Jarcarbon, Korea)	0.23	
– Cationic polymer-modified granular activated carbon (CPMG)	0.44	Mahmudov and Huang [22]
– Commercial AC Filtrasorb 400 (F400), pH = 4	0.29	
– AC derived from sugar beet baggase	0.15	Demiral and Gündüzoğlu [51]
– AC derived from coconut shell	0.03	
– AC posttreated with ZnCl ₂	0.16	Bhatnagar et al. [30]
– Commercial powdered AC derived from plants	0.07	
– Commercial AC (Nacalai tesque Model 079–39, Japan)	0.01	
– Bamboo powder charcoal obtained at 900 °C	0.02	Della Rocca et al. [52]
– AC derived from <i>Pinus canariensis</i> cones (PC-P)	0.16	
– PC-P thermally post-treated (PC-PT)	0.30	Present work
– PC-P posttreated with urea solution (PC-PU)	0.45	

0.17 and 0.26, indicating that the ACs adsorption behavior was favorable for all the systems studied. The maximum adsorption capacities, evaluated according to the Langmuir model (X_{mL}), for the post-treated carbons increased around 88% for the thermally treated sample, and 181% for the urea treated one, in comparison with that of the untreated sample.

Taking into account the textural characteristics of the samples (Table 3) and their nitrate adsorption capacity (Table 4), it could be observed that in spite of the highest BET surface area of PC-P, this untreated AC adsorbed lower quantities of nitrate than the post-treated samples. In turn, the urea post-treated carbons, despite its lowest surface area, exhibited the highest adsorption capacity toward nitrate (Fig. 2), evidencing that the specific surface area of the AC did not have a significant effect on the nitrate adsorption capacity. Therefore, the present results highlight the relevance of the surface chemistry of the adsorbent material on the nitrate adsorption performance of the activated carbons. Particularly, some basic oxygen species as well as N-based groups, such as amidine and/or amino groups, could act as selective adsorption sites for nitrate ions. Furthermore, basic sites generated from π -electrons on the graphitic like layers could accommodate certain protons resulting in a pronounced increase in the adsorption capacity [3].

On the other hand, maximum nitrate adsorption capacities obtained in the present work, as evaluated according to the Langmuir model, were similar or even higher than most of those recently reported by other researchers for different ACs (Table 5).

4. Conclusions

Present results demonstrate the feasibility of converting two different species of pine cones into activated carbons directed to nitrate adsorption from polluted water. Modifications applied to the developed activated carbons, including a thermal treatment at 800 °C in nitrogen atmosphere, and a urea treatment followed by a consecutive heat treatment at 350 °C, had a positive effect on the removal of nitrate ions from water, despite of the detrimental effect produced upon their surface areas. Nitrate maximum adsorption capacities for the activated carbon derived from *P. canariensis*, as judged from representing the experimental adsorption isotherms by the Langmuir model, was 0.16 mmol/g for the untreated sample, whereas values of 0.30 and 0.45 mmol/g were obtained for the thermal treated and the urea treated samples, respectively. The enhancement in nitrate uptake was mainly attributed to a noticeable increment in nitrogen functionalities and to the incorporation of basic groups into activated carbons matrix. The maximum adsorption capacity of the modified activated carbons from *P. canariensis* cones developed in this work was in most cases pronouncedly higher than that previously reported in the open literature for other activated carbon samples.

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References

- [1] T.S. Anirudhan, T.A. Rauf, J. Ind. Eng. Chem. 19 (2013) 1659–1667.
- [2] B. Gu, Y. Ge, S.X. Chang, W. Luo, J. Chang, Global Environ. Change 23 (2013) 1112–1121.
- [3] K. Ota, Y. Amano, M. Aikawa, M. Machida, Appl. Surf. Sci. 276 (2013) 838–842.
- [4] A. Zghibi, J. Tarhouni, L. Zouhri, J. Afr. Earth Sc. 87 (2013) 1–12.
- [5] I. García-Garizábal, J. Causapé, R. Abrahao, J. Hydrol. 442–443 (2012) 15–22.
- [6] A. Kurunc, S. Ersahin, B.Y. Uz, N.K. Sonmez, I. Uz, H. Kaman, G.E. Bacalan, Y. Emekli, Agric. Water Manag. 98 (2011) 1013–1019.
- [7] F.M. Anayah, M.N. Almasri, Appl. Geogr. 29 (2009) 588–601.
- [8] M.N. Almasri, Environ. Impact Assess. Rev. 27 (2007) 220–242.
- [9] P. Loganathan, S. Vigneswaran, J. Kandasamy, J. Environ. Manage. 131 (2013) 363–374.
- [10] M.H. Ward, Rev. Environ. Health 24 (2009) 357–363.
- [11] L. Knobeloch, B. Salna, A. Hogan, J. Postle, H. Anderson, Environ. Health Perspect. 108 (2000) 675–678.
- [12] WHO, Guidelines for Drinking-water Quality, fourth ed. World Health Organization, 2011.
- [13] EPA, National Primary Drinking Water Standards. <<http://water.epa.gov/drink/contaminant/index.cfm#list>>, 2009.
- [14] S. Bagherifam, S. Komarneni, A. Lakzian, A. Fotovat, R. Khorasani, W. Huang, J. Ma, S. Hong, F.S. Cannon, Y. Wang, Appl. Clay Sci. 95 (2014) 126–132.
- [15] S. Kilpimaa, H. Runtti, T. Kangas, U. Lassi, T. Kuokkanen, Chem. Eng. Res. Des. (2014), <http://dx.doi.org/10.1016/j.cherd.2014.03.019>.
- [16] R. Mukherjee, S. De, J. Membr. Sci. 466 (2014) 281–292.
- [17] A. Bhatnagar, W. Hogland, M. Marques, M. Sillanpää, Chem. Eng. J. 219 (2013) 499–511.
- [18] A. Keränen, T. Leiviskä, B. Gao, O. Hormi, J. Tanskanen, Chem. Eng. Sci. 98 (2013) 59–68.
- [19] A. Olgun, N. Atar, S. Wang, Chem. Eng. J. 222 (2013) 108–119.
- [20] A. Bhatnagar, M. Sillanpää, Chem. Eng. J. 168 (2011) 493–504.
- [21] P.C. Mishra, R.K. Patel, J. Environ. Manage. 90 (2009) 519–522.
- [22] R. Mahmudov, C.P. Huang, Sep. Purif. Technol. 77 (2011) 294–300.
- [23] D. Cho, C. Chon, Y. Kim, B. Jeon, F.W. Schwartz, E. Leed, H. Songe, Chem. Eng. J. 175 (2011) 298–305.
- [24] P. Nowicki, R. Pietrzak, H. Wachowska, Catal. Today 150 (2010) 107–114.
- [25] P. Nowicki, H. Wachowska, R. Pietrzak, J. Hazard. Mater. 181 (2010) 1088–1094.
- [26] P. Nowicki, M. Skrzypczak, R. Pietrzak, Chem. Eng. J. 162 (2010) 723–729.
- [27] P. Nowicki, R. Pietrzak, Bioresour. Technol. 101 (2010) 5802–5807.
- [28] H. Treviño-Cordero, L.G. Juárez-Aguilar, D.I. Mendoza-Castillo, V. Hernández-Montoya, A. Bonilla-Petriciolet, M.A. Montes-Morán, Ind. Crops Prod. 42 (2013) 315–323.
- [29] R. Pietrzak, T.J. Bandoz, Carbon 45 (2007) 2537–2546.
- [30] A. Bhatnagar, M. Ji, Y. Choi, W. Jung, S. Lee, S. Kim, G. Lee, H. Suk, H. Kim, B. Mine, S. Kim, B. Jeon, J. Kang, Sep. Sci. Technol. 43 (2008) 886–907.
- [31] M. Momčilović, M. Purenović, A. Bojić, A. Zarubica, M. Randelović, Desalination 276 (2011) 53–59.
- [32] G.V. Nunell, M.E. Fernández, P.R. Bonelli, A.L. Cukierman, Biomass Bioenergy 44 (2012) 87–95.
- [33] J. de Celis, N.E. Amadeo, A.L. Cukierman, J. Hazard. Mater. 161 (2009) 217–223.
- [34] M.E. Fernandez, G.V. Nunell, P.R. Bonelli, A.L. Cukierman, Bioresour. Technol. 106 (2012) 55–62.
- [35] P.J.M. Carrott, J.M.V. Nabais, M.M.L. RibeiroCarrott, J.A. Menéndez, Microporous Mesoporous Mater. 47 (2001) 243–252.
- [36] M.E. Ramos, P.R. Bonelli, S. Blacher, M.M.L. RibeiroCarrott, P.J.M. Carrott, A.L. Cukierman, Colloids Surf. A: Physicochem. Eng. Aspects 378 (2011) 87–93.
- [37] A.E. Ofomaja, E.B. Naidoo, Chem. Eng. J. 175 (2011) 260–270.
- [38] R. Font, J.A. Conesa, J. Moltó, M. Muñoz, J. Anal. Appl. Pyrol. 85 (2009) 276–286.
- [39] Suhas, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Bioresour. Technol. 98 (2007) 2301–2312.
- [40] J. Rivera-Utrilla, M. Sánchez-Polo, V. Gómez-Serrano, P.M. Álvarez, M.C.M. Alvim-Ferraz, J.M. Dias, J. Hazard. Mater. 187 (2011) 1–23.
- [41] N. Wibowo, L. Setyadhi, D. Wibowo, J. Setiawan, S. Ismadi, J. Hazard. Mater. 146 (2007) 237–242.
- [42] C.Y. Yin, M.K. Aroua, W.M. Ashr, W. Daud, Sep. Purif. Technol. 52 (2007) 403–415.
- [43] P. Chingombe, B. Saha, R.J. Wakeman, J. Colloid Interface Sci. 297 (2006) 434–442.
- [44] P.C.C. Faria, J.J.M. Órfao, M.F.R. Pereira, Water Res. 38 (2004) 2043–2052.
- [45] F. Kapteijn, J.A. Moulijn, S. Matzner, H.-P. Boehm, Carbon 37 (1999) 1143–1150.
- [46] R. Pietrzak, H. Wachowska, P. Nowicki, Energy Fuels 20 (2006) 1275–1280.
- [47] F. Adib, A. Bagreev, T.J. Bandoz, Langmuir 16 (2000) 1980–1986.
- [48] A. Bagreev, J.A. Menendez, I. Dukhno, Y. Tarasenko, T.J. Bandoz, Carbon 42 (2004) 469–476.
- [49] S.K. Singh, T.G. Townsend, D. Mazyck, T.H. Boyer, Water Res. 46 (2012) 491–499.
- [50] E. Lorenc-Grabowska, G. Gryglewicz, M.A. Diez, Fuel 114 (2013) 235–243.
- [51] H. Demiral, G. Gündüzoğlu, Bioresour. Technol. 101 (2010) 1675–1680.
- [52] C. Della Rocca, V. Belgiorno, S. Meriç, Desalination 204 (2007) 46–62.