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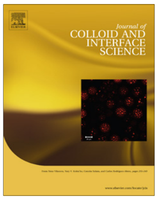

Nitrate uptake improvement by modified activated carbons developed from two species of pine cones

G.V. Nunell[a,b], M.E. Fernandez[a,b], P.R. Bonelli[a,b], A.L. Cukierman[a,b,c,*]

[a] *Programa de Investigación y Desarrollo de Fuentes Alternativas de Materias Primas y Energía (PINMATE), Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón de Industrias, Intendente Güiraldes 2620, Ciudad Universitaria, C1428BGA Ciudad Autónoma de Buenos Aires, Argentina*

[b] *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Rivadavia 1917, C1033AAJ Buenos Aires, Argentina*

[c] *Cátedra de Farmacotecnia II, Departamento de Tecnología Farmacéutica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Junín 956, C1113AAD Ciudad Autónoma de Buenos Aires, Argentina*

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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.

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].

Several methods have been used for the removal of nitrate from water including ion-exchange resin, chemical reduction, electrodialysis, 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, lignocelullosic 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

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[*] Corresponding author at: Programa de Investigación y Desarrollo de Fuentes Alternativas de Materias Primas y Energía (PINMATE), Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón de Industrias, Intendente Güiraldes 2620, Ciudad Universitaria, C1428BGA Ciudad Autónoma de Buenos Aires, Argentina. Fax: +54 11 45763366.

E-mail address: analea@di.fcen.uba.ar (A.L. Cukierman).

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Nomenclature

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

Subscripts

calc	calculated value
exp	experimental value

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:

$$\text{Hollocellulose}\ (\%) = 100 - \text{Lignin}\ (\%) \tag{1}$$

2.2. Preparation of the activated carbons

The dried cones were crushed, milled, and screen-sieved. Sample fractions of average particle diameter of 750 mm 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 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 N_2 (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.