

# Affinity for Anions Developed in Charcoal by Acid Treatment

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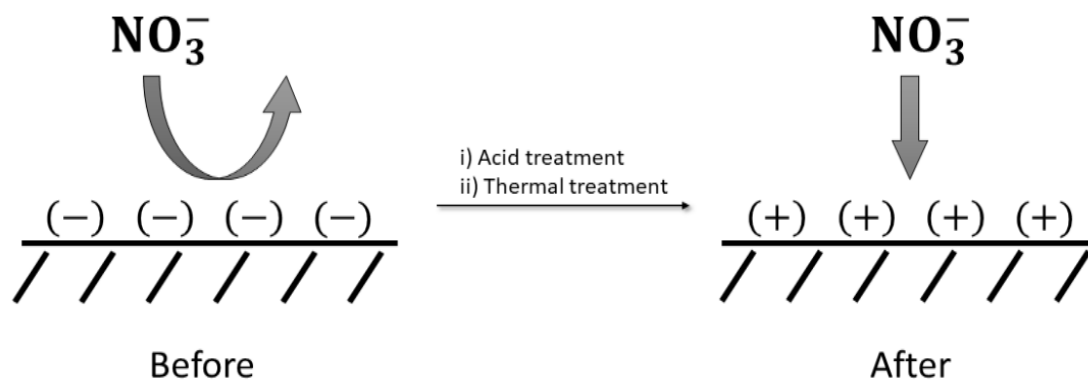
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## Graphical Abstract



## Abstract

In this study, we report a two-step method that creates at the surface of charcoal acidic groups that remove nitrate from an aqueous solution. The process used in this work with charcoal includes first an acid treatment followed by a heat treatment in a non-oxidizing atmosphere—a simple method to perform this treatment in a standard laboratory furnace is additionally presented—. As a control group, we use a process that omits the acid treatment and includes only the heat treatment. The precursors and products of the investigated processes were characterized in terms of (a) surface chemistry (zero charge point, Boehm titration), (b) structure (scanning electron microscopy, X-ray diffraction, nitrogen adsorption, Hg porosimetry), and (c) composition (CHN elemental analysis, thermal gravimetric analysis, Energy Dispersive X-ray Fluorescence). Acid-thermal treatment of charcoal creates Lewis acid groups that remove nitrate anions from an aqueous solution. The nitrate-removing Lewis acid groups were absent in the starting material as well as in the material obtained in the control group. The creation of these surface groups occurs without significant damage to the macropore structure of the charcoal particles. A simple process can generate chemical groups with an affinity for anions in an aqueous solution on the charcoal surface.

**Key Words:** Charcoal; Lewis acidity; removal of nitrate; water decontamination; anion affinity;

## Highlights

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## 1. Introduction

Charcoal obtained from wood and other vegetal components is a widely researched material in the filtration of water pollutants. Wood and parts of vegetables are available at low cost in areas where potable water is scarce. Urban pruning residues or industrial by-products are examples of locally available sources of biomass that can be converted into charcoal.

The conversion of biomass to charcoal (carbonization) can be done with well-established technological processes. Wood carbonization is essentially a chemical reaction that removes mainly hydrogen and oxygen elements from cellulose, hemicellulose and lignin that form wood, but preserves the internal structure due to the plant cell walls. The carbonized cell walls are the macropore walls present in charcoal. In addition, mesopores ( $2 < d < 50$  nm) and micropores ( $d < 2$  nm) can form in these walls, which significantly increase the specific surface area of charcoal. Although most laboratory-scale biomass carbonization is performed with complex and expensive processes that produce about a gram of charcoal, a simple and inexpensive carbonization process that produces two orders of magnitude more carbon was recently reported [1].

Upon contact with charcoal particles, a remaining aqueous solution interacts with both the outer surface and the inner surface. The inner surface can interact with the solution because the open pore structure allows the transfer of matter to and from the charcoal particles.

The surface of charcoal possesses functional groups that have affinity for cations dissolved in water. Those groups locate on both the external and internal surfaces of charcoal particles. The inner surface is accessible to cations because water can move through the network of open pores that permeate the charcoal particles. These properties make charcoals valuable in water decontamination.

Although charcoal has been investigated in the removal of contaminants from water, most of the work has been done on the removal of species that behave as Lewis acids such as metal cations in aqueous solution. In contrast, little work has been reported on the removal of basic Lewis species such as anions from solution.

In this work, we report a simple process that confers charcoal the ability to remove anions such as nitrate from water.

## 2. Materials and Methods

### 2.1 Chemicals

Distilled water. HNO<sub>3</sub> (65% p/p,  $\delta_{\text{HNO}_3} = 1,39$  g/mL, Cicarelli). Eucalyptus wood. NaNO<sub>3</sub> (Biopack). NaOH (Cicarelli). HCl (Cicarelli). NaHCO<sub>3</sub> (Biopack), Na<sub>2</sub>CO<sub>3</sub> (Mallinckrodt).

### 2.2 Charcoal

#### 2.2.1 Synthesis

The conversion of eucalyptus wood into *charcoal* (**C**) was carried out according to a simple and economical process previously described by us [1].

#### 2.2.2 Posttreatments

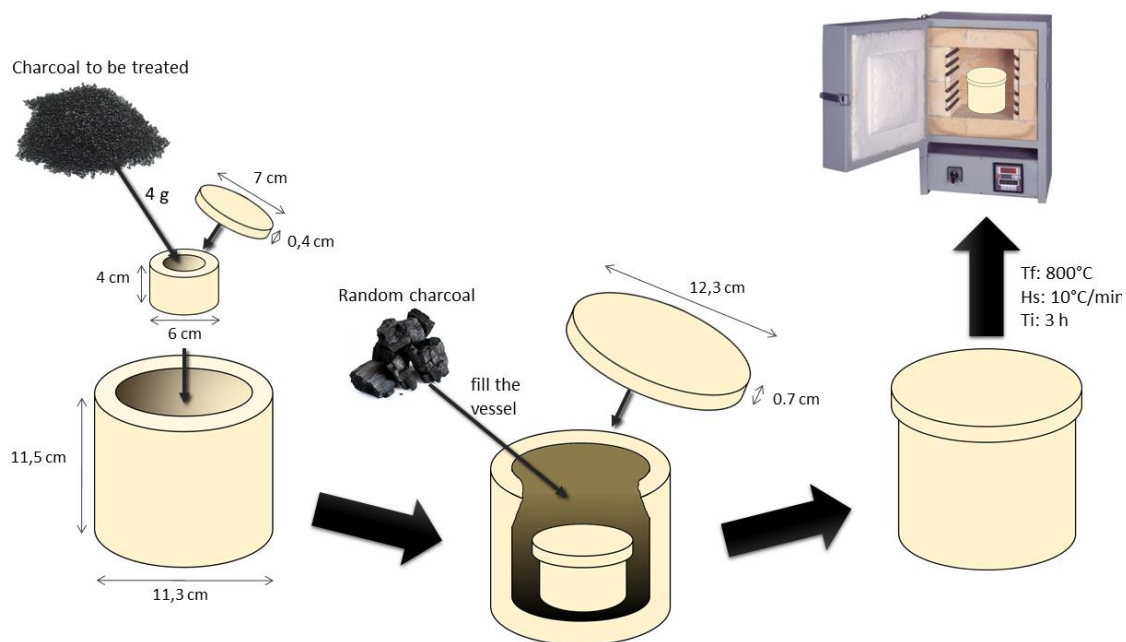
**Chemical-thermal Treatment.** The dry **C** underwent a two-step post-treatment: (a) acid treatment and (b) heat treatment. This is how the *chemically-thermally treated carbon* (**C\*800**) was prepared.

The chemical treatment was carried out as follows:

- **C** (34.1 g) dispersed in concentrated nitric acid solution (225 mL, 1:10 dilution in distilled water) was heated in a 500 mL beaker covered with a watch glass at 80 °C for 3 h (the dispersion was stirred with a glass rod every 30 min) and cooled to room temperature for 24 h.
- The dispersion was filtered to recover the charcoal, which was washed with distilled water (ca. 2 L) and then oven dried (60 °C, 72 h).

The heat treatment was performed as follows:

- The chemically treated **C** (ca. 4 g) was heat treated (RT - 800 °C, 10 °C.min<sup>-1</sup>; 800 °C, 3 h; oven cooled to RT) in a self-made vessel (see construction in SI) as shown in Figure 1.



**Figure 1.** Schematic description of the thermal treatment of charcoal in a non-oxidizing atmosphere.

**Thermal Treatment (Control Group).** As a control group, a charcoal was prepared that was only *heat-treated* (**C800**). This material was prepared by thermally treating dry **C** (*i.e.*, chemical treatment was omitted).

### 2.3 Nitrate Removal in Batch System

The ability to remove nitrates from solution of **C**, **C800** and **C\*800** materials was investigated in batch systems at 10 and 30 g.L<sup>-1</sup> solid-liquid ratio starting at 100 ppm of nitrate. 10 g.L<sup>-1</sup> solid-liquid ratio systems were obtained by adding 10 mg of charcoal in 10 mL of nitrate solution on a 15 mL plastic conical centrifuge tube with screw cap. 15 g.L<sup>-1</sup> solid-liquid ratio systems were obtained by adding 15 mg of charcoal in 5 mL of nitrate solution on the same tubes. Closed tubes were mechanically agitated (Decalab Rotolab-25, 25 °C) for 24 h. After filtration, the concentration of nitrate in aqueous solution was determined spectrophotometrically (HP 8453, 220 nm). All experiments were done in triplicate.

### 2.4 Characterization of Charcoal

The surface chemistry, structure and composition of **C\*800** and **C800** were characterized as follows.

## 2.4.1 Surface Chemistry

**Point of Zero Charge (PZC) Measurements.** The addition method used to obtain the PZC of the black powder has been described previously [2]. Briefly, ten flasks (10 mL, glass, screw cap) were filled with aqueous NaNO<sub>3</sub> solution (0.01 M). The pH values were adjusted with either HNO<sub>3</sub> (1 M, 0.1 M, and 0.01 M solutions) or NaOH solution (1 M, 0.1 M, and 0.01 M solutions) to values 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11. The pH measurements were performed with a calibrated glass electrode (ALPHA, Glass electrode PY-41). The electrode was calibrated with standard solutions of pH = 4, 7 and 10. Charcoal was added to each flask (ca. 50 mg measured with ±1 mg precision), and closed flasks were mechanically agitated (Decalab Rotolab-25, 24 h, room temperature ca. 25 °C). After the solid was separated by centrifugation (1500 rpm), the pH of the liquid was measured.

PZC of both **C\*800** and **C800** were determined from ΔpH (pH values of solution before and after contact with charcoal) vs. initial pH. All experiments were done in triplicate.

**Boehm Titration.** The oxygen-containing acidic and basic surface functional groups of **C** and **C\*800** were determined using the Boehm titration method [2].

Titrations were performed as follows. First, charcoal (0.2500 g) was mixed with 50 mL of either 0.01 N NaOH, or 0.01 N NaCO<sub>3</sub> or 0.01 N NaHCO<sub>3</sub>. Added volumes were weighted with ± 0.001 g precision. Charcoal suspensions were shaken in tightly closed containers for 72 h. Then, 10 mL of supernatant —filtered with a syringe attached to a disc filter— were mixed with 20mL of 0.01 N HCl. All added volumes were also weighted with ± 0.001 g precision. Finally, the solution was back-titrated with 0.01 M NaCO<sub>3</sub> using an automatic Schott titrator.

Surface acidity was calculated with the following assumptions. First, solution of NaHCO<sub>3</sub> neutralizes only functional groups with pKa less than 6.4. This is the strongest acid fraction where we find acid carboxylic groups. Second, solution of Na<sub>2</sub>CO<sub>3</sub> neutralizes acid functional groups with pKa less than 10.3. This fraction including carboxyl, lactones, and phenols groups. Last, solution of NaOH neutralizes acid functional groups with pKa less than 15.7 We consider that it neutralizes all acid functional groups (carboxyl, lactones, phenols, carbonyls, and any other acidic. Equations (Eq. 1, 2 and 3) were used to calculate the mmol of acidic surface groups per gram of solid.

$$n_1 \left[ \frac{\text{mmol}}{g_{\text{charcoal}}} \right] = \frac{((V_1 - V_2)[\text{mL}] \times C_{\text{Na}_2\text{CO}_3} \left[ \frac{\text{meq}}{\text{mL}} \right] \times 2 \left[ \frac{\text{mmol}}{\text{meq}} \right])}{W [\text{g}] \times \frac{m_a}{m_i}} \quad (\text{Eq. 1})$$

$$n_2 \left[ \frac{\text{mmol}}{\text{g}_{\text{charcoal}}} \right] = \frac{((V_3 - V_4)[\text{mL}] \times C_{\text{Na}_2\text{CO}_3} \left[ \frac{\text{meq}}{\text{mL}} \right] \times 2 \left[ \frac{\text{mmol}}{\text{meq}} \right])}{W [\text{g}] \times \frac{m_a}{m_i}} - n_1 \quad (\text{Eq. 2})$$

$$n_3 \left[ \frac{\text{mmol}}{\text{g}_{\text{charcoal}}} \right] = \frac{((V_5 - V_6)[\text{mL}] \times C_{\text{Na}_2\text{CO}_3} \left[ \frac{\text{meq}}{\text{mL}} \right] \times 2 \left[ \frac{\text{mmol}}{\text{meq}} \right])}{W [\text{g}] \times \frac{m_a}{m_i}} - (n_1 - n_2) \quad (\text{Eq. 3})$$

$n_1$ ,  $n_2$  and  $n_3$  are the fraction of carboxylic, lactones and phenols groups respectively.  $V_1$  and  $V_2$  are the spent titrant volume for the titration of the carbon-treated and untreated with  $\text{NaHCO}_3$  base.  $V_3$  and  $V_4$  are the spent titrant volume for the titration of the carbon-treated and untreated with  $\text{Na}_2\text{CO}_3$  base.  $V_5$  and  $V_6$  are the spent titrant volume for the titration of the carbon-treated and untreated with  $\text{NaOH}$  base.  $W$  is charcoal weight added.  $m_a/m_i$  is the fraction of measured base. All experiments were done in quadruplicate and the uncertainty was expressed in standard deviation.

## 2.4.2 Structure

**Scanning Electron Microscopy (SEM).** Images were obtained from the powders obtained after sieving (JEOL JCM-6000 Neo Scope, High-vacuum, PC-High 15 kV).

**X-ray Diffraction.** Diffractograms were obtained from dried powders (Philips PW-3710; Cu-K $\alpha$  radiation  $\lambda=0.154$  nm, 35 kV, 40 mA, step  $0.04^\circ$ , 2 s.step $^{-1}$ ). Reflexes were assigned after comparing the diffractogram with reflexes from a database (Open Crystallographic Database, <http://www.crystallography.net/cod/>, software X'Pert HighScore).

**Nitrogen Sorption.** Nitrogen sorption isotherms were measured with a 3 Flex Micromeritics instrument at 77 K. Specific surface areas were determined from the adsorption branch with the Brunauer- Emmett-Teller (BET) method using the 3Flex Micromeritics software. Prior to measurement, the samples were activated at 200 °C for 6 h.

**Hg Porosimetry.** The powder was dried (110 °C, 24 h) before measuring Hg porosimetry isotherms (Pascal-Thermo Fisher Module 440 & Module 140). Accumulated specific pore volumes were calculated (SOL.I.D software) between 10 nm and 100  $\mu\text{m}$ . The pore size distribution was calculated from the derivative of the accumulated specific pore volume. Macropore volume was estimated directly from the intrusion isotherm curve.



### 2.4.3 Composition

**CHN Analysis.** The dried powder was analyzed with Elemental Analysis equipment (CE 440 – Exeter). Calibration was carried out with acetanilide patron. Results was expressed in element percentage. The fraction of “%Other” represents the difference between the 100% of the sample and the percentage of all element.

**Thermal Gravimetric Analysis (TGA).** Measurements were performed on dried charcoal (Rigaku Thermo Plus II; drying 100 °C 2 h, 100 to 1000 °C at 10 °C.min<sup>-1</sup> under airflow).

**Energy Dispersive X-ray Fluorescence (EDX).** The dried powder was analyzed with EDX (JEOL JCM-6000 Neo Scope) to obtain an elemental composition and mapping of elements.

### 2.5 Statistical Analysis

*Mean Values.* Mean values were expressed as mean value ± confidence interval (CI) obtained from ANOVA.

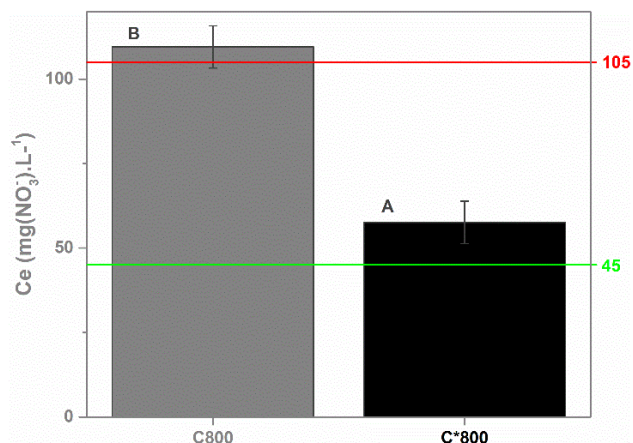
*Comparison of Mean Values with ANOVA.* Analysis of variance (ANOVA) of point of ΔpH and Ce of nitrate was conducted (InfoStat version 2020; Centro de Transferencia InfoStat, FCA, Universidad Nacional de Córdoba, Argentina) ( $\alpha = 0.05$ ). Data normality was verified with a Q-Q plot. Variance homogeneity was verified with the scatter plot of residuals of variables (see SI section D).

*Pair-wise Comparison of Mean Values with Tukey Test.* Comparisons among multiple means were made by the Tukey test ( $\alpha = 0.05$ ).

## 3. Results

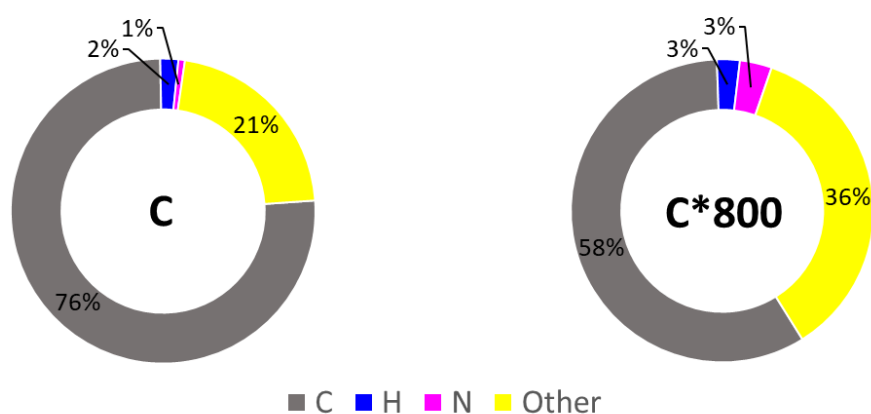
### 3.1 Nitrate Removal by C800 and C\*800 in Batch Systems

The ability of C800 and C\*800 to remove nitrate can be seen in Figure 2. Acid treatment followed by heat treatment produces C\*800 which significantly reduces the nitrate concentration in the aqueous phase. In contrast, heat treatment only produces C800 which does not significantly remove nitrate from T. Similar behavior was observed with batch systems with S/L 10 g/L instead of 30 g/L (**Figure 9**). Thus, acid treatment modifies the surface chemistry of charcoal and creates chemical groups that adsorb nitrate.



**Figure 3.** Nitrate concentration (error bars are confidence interval of ANOVA) in the liquid phase of a batch system (S/L = 30) after 24 h of contact between either **C\*800** (black) or **C800** (gray) and a nitrate solution (initial concentration 105 ppm). Nitrate concentration in solution exposed to **C\*800** is significantly lower than solution exposed to **C800** (ANOVA,  $p < 0.0001$ ; Tukey’s test; see SI), but the concentration of nitrate in solution before and after treatment with C800 shows no significant difference.

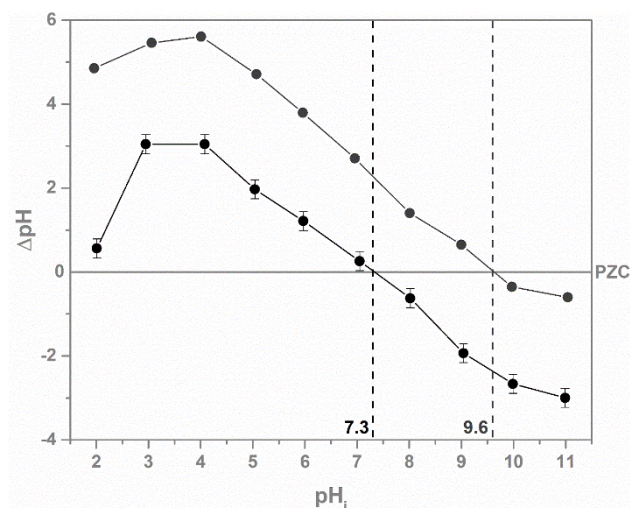
### 3.2 Effect of Chemical-thermal Treatment on Surface Chemistry



**Figure 2.** CHN Analysis of C a C\*800.

The percentage mass of the elements C, H, and N present in C and C\*800 is shown in **Figure 2**. These results reveal two important trends caused by the application of acid treatment followed by heat treatment. On the one hand, the final solid product contains significantly less C. Its carbon content lowered from 76% in C to 58% in C\*800. On the other hand, the final product increases the mass of other elements. While elements H and N increased their mass by 1% and 2%, other elements increased their mass from 21% in C to 36% in C\*800.

The  $\Delta\text{pH}$  in the solution 24 h after dispersing the solid to form batch systems are shown in Figure 3. This figure shows that **C\*800**, which removes nitrate from aqueous solution, has an isoelectric point at  $\text{pH} = 7.3$ . In contrast, **C800**, which does not remove nitrate from water, has an isoelectric point near  $\text{pH} = 10$ .



**Figure 4.**  $\Delta\text{pH}$  values (error bars are standard deviations) versus  $\text{pH}$  obtained for **C\*800** (black) and **C800** (gray) allow to know the point of zero charge (PZC) of the solid in solution.  $\text{PZC}_{\text{C}^*800} = 7.3$ ;  $\text{PZC}_{\text{C}800} = 9.6$ .

The presence of acid groups on the charcoal surface was characterized by a Boehm titration, which reports acid groups with  $\text{pK}_a$  in the intervals  $<6.4$ ,  $6.4 - 10.3$ , and  $10.3 - 15.7$ . The surface density of acid groups with  $\text{pK}_a$  within  $6.4 - 10.3$  significantly increased after the acid-thermal treatment from **C** to **C\*800** (see table 1). But the surface density of acidic groups with  $\text{pK}_a$  within the other studied intervals did not significantly change. In contrast, the analysis of experiments performed with **C800** was inconclusive because the amount of acid consumed in the titrations of the added bases ( $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaOH}$ ) was greater than that of the added base.

**Table 1.** Surface density of chemical groups (mmol.g<sup>-1</sup>; uncertainty is standard deviation) with pKa < 6.4 (column 2), pKa between 6.4 and 10.3 (column 3), and pKa between 10.3 and 15.7 (column 4) estimated with Boehm titration.

Material	pKa		
	< 6.4	6.4 – 10.3	10.3 – 15.7
<b>C</b>	-0.2 ± 0.02	0.03 ± 0.03	0.09 ± 0.04
<b>C800</b> <sup>§</sup>	-	-	-
<b>C*800</b>	-0.05 ± 0.03	0.29 ± 0.08	0.2 ± 0.1

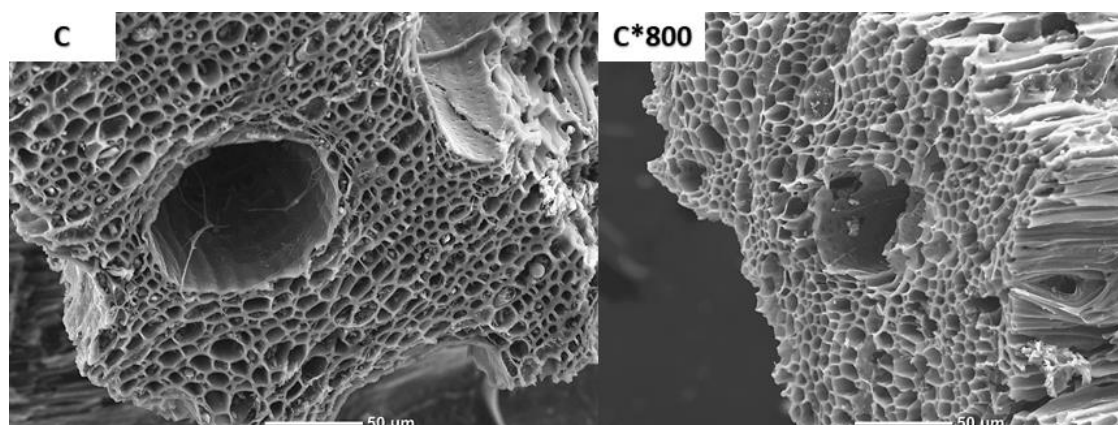
Ka = acidity constant of surface groups

pKa = - log<sub>10</sub> Ka

§ Inconclusive results

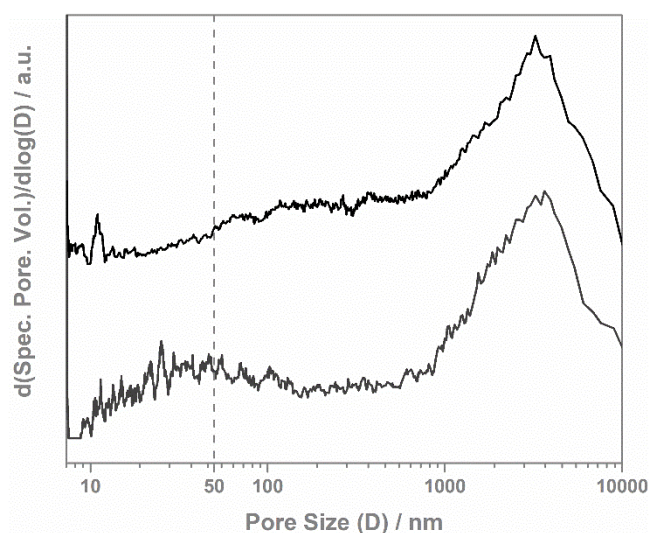
### 3.3 Structure and Composition of C800 and C\*800

SEM-images of C and C\*800 can be viewed in Figure 4. These images show that C\*800 retains after acid and heat treatment the macropore structure. Similarly, C800 (Figure 10) also preserves the macropore structure.



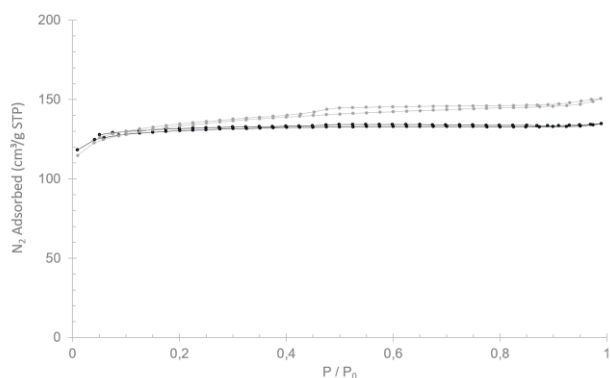
**Figure 5.** Scanning electron microscopy images of **C** (left) and **C\*800** (right) show that the carbonaceous walls of the macropores—which form the internal structure of the carbon particles—persist after chemical-thermal treatment.

The estimated pore size distribution of Hg porosimetry for C800 and C\*800 can be seen in Figure 5. These curves show that both materials possess a significant amount of macropores with mean pore size centered at about 4 microns. Despite the small difference observed between the two materials for the smallest macropores (50 - 1000 nm), the results indicate that both heat treatment alone and chemical treatment followed by heat treatment produce a material with a macropore structure.



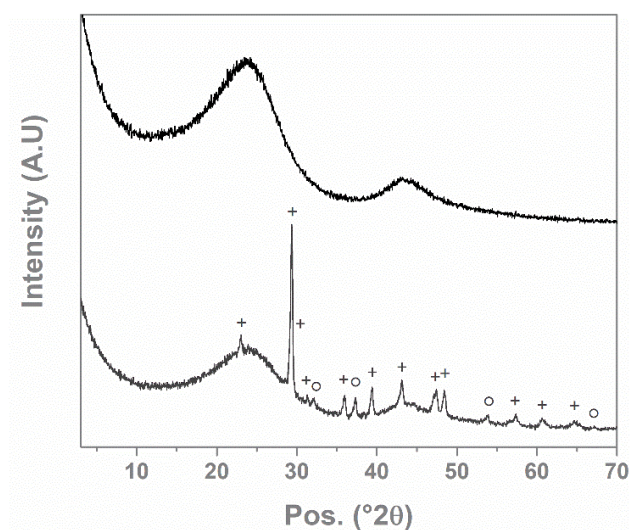
**Figure 6.** Pore size distribution calculated from Hg intrusion porosimetry for **C800** (gray) and **C\*800** (black). The vertical dashed line represents the boundary between mesopores and macropores.

$N_2$  sorption isotherms of **C800** and **C\*800** are shown in Figure 6. These isotherms indicate that **C800** and **C\*800** have similar micropore volume (ca.  $120 \text{ cm}^3 \cdot \text{g}^{-1}$ ). Moreover, that **C800** additionally possesses some mesopores that give rise to the slight increase of the isotherm at  $P/P_0 > 0.10$  and to the formation of hysteresis.



**Figure 7.** nitrogen adsorption isotherms obtained for **C800** (gray) and **C\*800** (black).

X ray diffractograms of **C800** and **C\*800** are shown in **Figure 7**. The diffractogram of **C\*800** lacks reflections originating from crystals. The two observed broad maxima originate from X-ray scattering. In contrast, **C800** has reflections that can be assigned to calcium carbonate and calcium oxalate crystals.



**Figure 8.** X-ray diffractograms obtained for C800 (gray, bottom) and C\*800 (black, top). Calcium carbonate (+); calcium oxide (o).

The content of inorganic material present in **C800** and **C\*800** was estimated from the ashes obtained after heat treatment in the air up to 1000 °C. **C800** leaves significantly more ash (6.9%) than **C\*800** (0.5%). Elemental analysis of the ashes with X-ray

fluorescence shows the presence of O (28.5%) and Ca (71.5%) in both materials. Light elements such as H cannot be detected with EDX.

## 4. Discussion

### 4.1 Chemical-thermal Treatment Develops Nitrate Removal Capability

Nitrate removal with charcoal after chemical-thermal treatment (**C\*800**) and charcoal after thermal treatment (**C800**) -control group- was studied in batch systems (Figure 2 & **Figure 9**). These experiments show that the acid-thermal treatment confers on the carbon the ability to remove nitrate from water. In contrast, neither **C** [1] nor **C800** remove nitrate from water. Thus, the acid treatment seems to play an essential role in the process that confers to charcoal the ability to remove nitrate anions from water.

The acid treatment of charcoals as a variable for modifying the ability to remove contaminants from water has been studied previously. However, much work has been done to increase the ability to remove cationic contaminants from water [3] [4] [5]. Therefore, the use of acid treatment of charcoals in order to provide anion removal capacity is a strategy that has apparently been little investigated.

From the point of view of the Lewis acid-base model, cations in solution are acidic chemical species that have an affinity for basic chemical groups on the surface of the charcoal. In contrast, anions in solution are bases that have an affinity for surface acids [6][7]. Therefore, nitrate removal experiments in batch systems suggest that heat treatment alone (**C800**) does not significantly modify the type of surface groups on the charcoal surface. However, acid treatment followed by heat treatment (**C\*800**) generates acidic chemical groups on the surface that have an affinity for the nitrate anion in the solution.

Experimental evidence suggests the absence of acidic groups at **C800** and their presence at **C\*800**. We, therefore, decided to characterize the presence of acidic groups on the charcoal surface.

### 4.2 The Chemical-Thermal Treatment Creates Acidic Surface-groups

We used two approaches to investigate the changes in acid-base chemistry at the charcoal's surface: (1)  $\Delta$ pH vs. pH, and (2) Boehm titration.

The  $\Delta$ pH vs. initial pH curves (**Figure 4**) reveal the acid-base behavior of **C800** and **C\*800** placed in contact with an aqueous solution. These curves indicate that **C800** has a chemical behavior similar to **C** [1], which does not remove anions from water. In

contrast, **C\*800** has a more acidic surface than **C**, which does remove nitrate from the solution. These curves suggest that the higher surface acidity **C\*800** would result in the ability to remove anions at  $\text{pH} > 7.3$ .

It is worth mentioning that the  $\Delta\text{pH}$  vs.  $\text{pH}$  curves indicate that charcoal also contains basic groups on its surface. These basic groups would be responsible for removing protons from the solution at  $\text{pH} < 7.3$ . Consequently, the picture that emerges of the **C\*800** surface is that of a heterogeneous surface with acidic and basic groups that, unlike the **C** and **C800** surfaces, possesses acidic groups that allow the removal of nitrate anions from an aqueous solution.

The titration of charcoal with Boehm's method made it possible to quantify the surface acid groups whose  $\text{pK}_a$  within ranges  $<6.4$ ,  $6.4 - 10.3$ , and  $10.3 - 15.7$ . These experiments suggest that the acid-thermal treatment creates new surface acid groups whose  $\text{pK}_a$  is between  $6.4 - 10.3$  (see Table 1). The acidic-thermal treatment can form new acid groups by incorporating oxygen atoms to the surface, including groups such as carboxylic acids. The formation of these groups is compatible with the observed decrease in the carbon element content and the increase of the hydrogen and oxygen elements. We infer an increment in oxygen content from the rise in mass corresponding to other elements (see **Figure 2**). The formation of these oxygenated acidic groups has also been reported in the literature [4] [8][5].

### 4.3 **C\*800** Keeps a Hierarchical Pore Structure

The influence of the chemical-thermal treatment on **C** was investigated with scanning electron microscopy (**Figure 5**), Hg porosimetry (**Figure 6**), X-ray diffraction (**Figure 8**), and nitrogen adsorption (**Figure 7**).

The charcoal particles retain the hierarchical macropore structure after chemical and thermal treatments. Also, the macropore walls of **C800** and **C\*800** seem to have similar amounts of micropores (ca.  $130 \text{ cm}^3 \cdot \text{g}^{-1}$ ). This value is somewhat higher than the  $80 \text{ cm}^3 \cdot \text{g}^{-1}$  calculated for **C**.

In addition, the acid treatment seems to remove the inorganic substances. While **C** and **C800** possess calcium carbonate and acetate crystals and leave 6.6 and 6.9% ash after combustion, **C\*800** lacks crystals according to X-ray diffraction and leaves only 0.5% ash.

Consequently, we could conclude that

1. **C**, **C800**, and **C\*800** have a similar pore structure, and
2. the acid treatment removes calcium compounds from the particles, and



## 5. Conclusion

In summary, in this work we show that a chemical treatment with nitric acid followed by a thermal treatment modifies the surface chemistry of carbon. As a result, weaker acidic chemical groups with a higher affinity for anions in solution arise. Modifying the surface chemistry lies the key to developing better vegetable carbons that remove anions from water.

## 6. Acknowledgments

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## 7. Authors' Contribution [9]

**Long A. Leonel:** Methodology, Formal analysis, Writing - Review & Editing.

**Arnal Pablo M.:** Conceptualization, Methodology, Investigation, Writing – Original Draft, Review & Editing, Supervision, Project administration, Funding acquisition.

## 8. References

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