OBTENCIÓN DE CARBÓN ACTIVADO A PARTIR DE CÁSCARA DE SANDIA Y NUEZ DEL NOGAL, Y SU APLICACIÓN EN LA ADSORCIÓN DE PLOMO Y CINC.

Elaborado por:

JONATHAN JULIAN MORENO BARBOSA

Para obtener el título en:

INGENIERÍA AMBIENTAL

Universidad de Los Andes
Facultad de Ingeniería
Departamento de Ingeniería Civil y Ambiental
Facultad de Ciencias
Departamento de Química
Grupo de Investigación de Sólidos Porosos y Calorimetría (GSPC)
Bogotá – 2011
UNIVERSIDAD DE LOS ANDES

OBTENCIÓN DE CARBÓN ACTIVADO A PARTIR DE CÁSCARA DE SANDIA Y NUEZ DEL NOGAL, Y SU APLICACIÓN EN LA ADSORCIÓN DE PLOMO Y CINC.

Elaborado por:

JONATHAN JULIAN MORENO BARBOSA

Directores

PH.D. JUAN CARLOS MORENO PIRAJÁN
MSC. ANDREA DEL PILAR MALDONADO ROMERO

Universidad de Los Andes
Facultad de Ingeniería
Departamento de Ingeniería Civil y Ambiental
Facultad de Ciencias
Departamento de Química
Grupo de Investigación de Sólidos Porosos y Calorimetría (GSPC)
Bogotá – 2011

Página 2 de 34
Agradecimientos

Señor en tus manos me pongo,
    haz de mi lo que quieras,
por todo lo que hagas de mi te doy gracias.
Estoy dispuesto a todo y lo acepto todo,
con tal de que tu voluntad se cumpla en mí y en todas las criaturas de la tierra.
No deseo nada más Dios mío pongo mi vida en tus manos,
te la doy Dios mío con todo el amor de mi corazón porque te amo y es para mí una
necesidad de darme, entregarme, sin medida y con absoluta confianza porque tu eres mi
padre.

Amén.

Gracias Dios por la vida, gracias papas por la confianza y ayuda, y gracias a mi hermano por el apoyo.

A Cata por ser tan linda y tan especial, por aguantarme, por todos los bellos momentos que compartimos en el laboratorio y fuera de él. Te amo cata y casate conmigo.

Por supuesto a todas las personas que contribuyeron y en especial a las personas del laboratorio. Gracias totales.
**Tabla de contenido**

Abstract ........................................................................................................................................... 7  
Introduction ........................................................................................................................................ 8  
Objectives ........................................................................................................................................ 11  
Materials and Methods ...................................................................................................................... 11  
  Raw Materials .................................................................................................................................. 11  
  Chemicals ....................................................................................................................................... 11  
  Preparation of the activated carbons ............................................................................................... 11  
  Characterization of the activated carbons. ....................................................................................... 12  
  Adsorption Experiments .................................................................................................................. 13  
Results and Discussion ....................................................................................................................... 15  
  Properties of the Activated Carbons ............................................................................................... 15  
  Nitrogen Adsorption Isotherms ...................................................................................................... 15  
  Scanning Electron Micrograph ...................................................................................................... 17  
  IR Spectroscopy ............................................................................................................................. 18  
  Thermo Gravimetric Analysis ......................................................................................................... 20  
  Point of Zero Charge and Boehm Titration .................................................................................... 21  
  Aqueous Adsorption Isotherms ...................................................................................................... 23  
  Langmuir and Freundlich isotherms ............................................................................................... 26  
Conclusions ...................................................................................................................................... 29  
Acknowledgements ............................................................................................................................ 30  
References ........................................................................................................................................ 30  
Recommendations: ............................................................................................................................. 34  

Página 4 de 34
Índice de Figuras

Figure 1 Nitrogen adsorption isotherms at -196°C for the GACW and GACN............15
Figure 2 Pore distribution of the GACW and GACN.....................................................17
Figure 3 SEM images at magnification of 500×. (a) GACN, (b) GACW, (c) GACW........18
Figure 4 IR images for activated carbons a) GACW and b) GACN................................18
Figure 5 TG analysis of GACW and GACN. Ramp temperature between 20°C and 900°C,
rate of heating of 10°C/min and N2 atmosphere. ..........................................................20
Figure 6 Point of Zero Charge for the GACN and GACW. ..............................................21
Figure 7 Adsorption isotherms in aqueous solution for a) zinc (II) and b) lead (II) at a
constant pH of 4,5 and 25°C ..........................................................................................23
Figure 8 Speciation distribution curves of a) zinc and b) lead as a function of pH at
25°C. ..................................................................................................................................25
Índice de Tablas

Table 1 Textural properties of the Activated Carbons GACW and GACN ........................ 16
Table 2 Results of Boehm titration (mmol/g) and pH of point of zero charge ........ 22
Table 3 The effect of initial concentration of adsorption of lead (II) and Zinc (II) onto GACW and GACN ............................................................................................................. 24
Table 4 Isotherms parameters for the sorption of metal ions on GACW and GACN 26
Table 5 RL values of Langmuir model for the sorption of metal ions on GACW and GACN ................................................................................................................................ 28
Abstract

Activated carbons from watermelon shell (GACW) and walnut shell (GACN) were synthesized through chemical activation with phosphoric acid 40% w/w, as an alternative low-cost adsorbent for the removal of lead (II) and zinc (II) ions from aqueous solutions. The yield of production was 85% and 80% for GACW and GACN respectively. To compare the differences and similarities between the two activated carbons the following tests were performed: surface and pore width with SEM, nitrogen adsorption isotherms at -196°C (77 K), IR spectroscopy, TGA, point of zero charge (PZC) and Boehm titration. The GACN has 10% more surface area (789 m²/g for GACN and 710 m²/g for GACW) and 13% more pore volume than GACW. Also, GACN has a better resistance to high temperatures than GACW (the loss of mass at 900°C was 20% for GACN, while for GACW was 31%). The effect of the initial concentration of lead (II) and zinc (II) ions on the adsorption process was studied in a batch process mode. To quantify the adsorption of lead and zinc adsorption isotherms of both metals in aqueous solution were performed for each carbon using analytic technique of atomic absorption. The adsorption isotherm data were better fitted by Langmuir model. Experimental results suggest that one gram of GACW adsorbs more milligrams of lead (II) and zinc (II) than one gram of GACN; it is suggest that the pore distribution is a significant variable in the adsorption process because GACW present mesopores and micropores, and GACN has only micropores. Also, the surface chemistry is an important variable in the adsorption process because GACW present a lower pH_{PZC} than GACN (3.05 for GACW and 4.5 for GACN) and the solution’s pH of each metal was adjust in 4.5, for that it could be suggested that the electrostatic interactions were increase between the ion and the carbon surface.

Keywords: Adsorption from solution, Activated carbon, watermelon, walnut, lead, zinc.
Introduction

The cost of activated carbon has been risen to over time. For that, it is necessary to find new process alternatives of production of the activated carbon using non-conventional and low cost methodologies in order to achieve a sustainable process. Also, the waste disposal has becoming an important issue for the society, and the problems of treatment and disposal of the waste need to be solved.

Lead and zinc are the most important heavy metals in the industry. However, they are well-known toxics and can find their ways to the aquatic environment through wastewater discharge (Depci, Kul and Onal 2012). Lead can threaten human life due to its toxicity, accumulation in food chains and persistence in nature. It is a general metabolic poison and enzyme inhibitor and can accumulate in bones, brain, kidney and muscles. World Health Organization (WHO) recommended the maximum acceptable concentration of lead in drinking water as 0.1 mg/L – 0.05 mg/L (Zhang, W.H. and Valix 2004). Zinc is one of the most important metals often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants. Zinc is not biodegradable and travels through the food chain via bioaccumulation. World Health Organization (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/L (Hawari, Rawajfih and Nsour 2009).

Treatment of industrial effluents containing heavy metals as zinc and lead is mainly based on precipitation, coagulation, ion exchange and electroplating. These processes are usually expensive and sometimes ineffective, especially when the concentration of heavy metals is low (Hawari, Rawajfih and Nsour 2009).

Adsorption has been universally accepted as one of the most widely used methods for removing heavy metals from aqueous solution. Commercial activated carbon has been studied as an adsorbent for removal of heavy metal ions from water for several years due to the great specific surface area and pore structure, but it is expensive (Depci, Kul and Onal 2012). To overcome this disadvantage, activated carbon can be produced from different raw
carbon sources like lignite, coal, and biomass available and low cost waste materials such as wood, sawdust, bagasse, and coconut shells (Gratuito, et al. 2007). The production of activated carbon from agricultural by-products is a research field of increasing interest as it deals with the problem of the disposal of agro-residues, at the same time producing an added-value product that can be used in a number of environmental applications. In the last years waste materials, agricultural mostly, have attracted considerable attention due to their wide availability, everywhere in the globe (Paraskeva, Kalderis and Diamadopoulos 2008) (Elizalde-Gonzalez and Hernandez-Montoya 2007) (B. Ash et al., 2006). Activated carbon made from agricultural by-products is a high added-value, ‘green’ product, made from renewable resources. Legislation in many countries and the ‘cash for trash’ concept favour the production of useful green products from agro-residuals. Development of economical processes for the production of activated carbon from agricultural by-products with good adsorbing capacities may result in economies of scale for wastewater treatment, especially in industries local to the production of by-products (Paraskeva, Kalderis and Diamadopoulos 2008). Used automobile tires and the pyrolytic carbon black are also investigated intensively given the environmental concerns associated with their disposal (Stavropoulos and Zabaniotou 2009).

Some successful examples of activated carbons produced from agricultural wastes are: 1. Waste Palm Shell Converted to High Efficient Activated Carbon by (Rahman, et al. 2012), 2. Activated carbon prepared from Van apple pulp for the adsorption of lead and zinc by (Depci, Kul and Onal 2012), and 3. The chemical activation of Cyperus alternifolius and the characterization the activated carbon produced by (Sun, et al. 2011).

Production of activated carbon can either be through physical or chemical activation. In physical activation, the material is carbonized under inert atmosphere and then activated at high temperature using either steam or carbon dioxide as the activating reagent, while in chemical activation; the precursor is treated with chemicals to help with the initial dehydration. In most cases, the chemical activation is preferred over physical activation, because the first one is commonly used for biomass precursor, for the reason that it

Página 9 de 34
achieves higher yield and larger surface areas. Also, it requires lower operating and energy costs as lower temperatures are used (Ahmedna, Marshall and Rao 1999).

In this study, the watermelon (*Citrullus lanatus*) shell and the walnut (*Juglans regia L.*) shell were collected from “Paloquemao” and “Corabastos”, market places located in Bogotá, Colombia. The solid residue, watermelon and walnut shell, were used as potential alternative precursor to obtained activated carbon (GACW and GACN) and their applicability as adsorbents for the uptake of lead and zinc from aqueous solution. Watermelon is one of the soft-core fruit and has very significant role for Colombian trade since Colombia won USD 618.000 in 2011 for exports to The United Kingdom, Canada, Germany and Ecuador (Parker 2011). Walnut shell is the most common type of soft abrasive for industrial use. It has excellent durability and is now widely used to blast clean and polish soft metals, glass, fiberglass, wood, plastic and stone.

Aforementioned, watermelon and walnut shell were used in the production of activated carbon, because they are low-cost and accessible raw materials and never have been used as precursors of activated carbons. This may be not only contributes the waste assessment, but also increases the strength of competition of these market places located in Bogotá.

The aim of this study is to produce activated carbon from agricultural waste; watermelon shell and walnut shell by chemical activation using $\text{H}_3\text{PO}_4$. The literature has many articles dealing with activated carbons produced from raw material using both the chemical and physical activation methods; however it has not yet been reported the chemical activation of watermelon shell with $\text{H}_3\text{PO}_4$. The major novelties of this work are: the production of two activated carbons from different precursors with the same activation technique, the comparison of physical and chemical properties of the activated carbons synthesized and the evaluation of the efficiency of adsorption of lead and zinc onto the activated carbons.

To perform this study the experimental tests carried out were: Scanning Electron Micrograph (SEM), nitrogen adsorption isotherms, IR spectroscopy, point zero of charge,
Boehm Titration, TGA and aqueous solutions adsorption isotherms of lead (II) and zinc (II).

**Objectives**

- Explorar la obtención de carbón activado a partir de cascara de sandia y nuez del nogal.
- Comparar la eficiencia de los carbones activados obtenidos en función del tipo de síntesis: Química y Física.
- Establecer la capacidad de adsorción de cada uno de los materiales sintetizados aplicados en la adsorción desde solución acuosa de iones plomo y cinc.
- Realizar la caracterización de los carbones obtenidos a partir de adsorción de N$_2$.

**Materials and Methods**

**Raw Materials**

The watermelon and walnut shell were obtained from the solid waste disposal of a market place located in Bogotá, Colombia and used without further treatments.

**Chemicals**

Standard stock solutions of Pb (II) and Zn (II) (1000 mg/L), as their respective chloride salts, (MERCK certified) were prepared in de-ionized double distilled water and appropriate concentrations of each heavy metal were fixed using the stock solutions for the adsorption studies. The exact concentration of all the prepared solutions was measured by atomic absorption (AAnalyst 400 PerkinElmer).

**Preparation of the activated carbons**

The preparation of the activated carbons produced from watermelon and walnut shells took four steps, I) The watermelon and walnut shells were dry in an oven, LINDBERG/BLUE Gravity One at 80°C per two weeks, II) The watermelon and walnut shells were crushed in
a mill, DM-200 Detsch, to get a grain size of 2 mm. III) phosphoric acid 40% w/w was added to the crushed shells at a ratio of 1:2 (g GAC/g H₃PO₄) to prepare the impregnate samples, these samples were carbonize in a furnace, (Carbolite HVT-1200), at 500°C -700°C for 1.12 h under nitrogen (N₂) flow of 120 mL min⁻¹ at a heating rate of 10 °C min⁻¹. IV) The carbonize sample (activated carbon) was washed several times with distilled water to remove the phosphoric acid, we checked the pH of the washing water until this value was constant; in the case of GACN the constant pH of the washing water was 5.5 and for GACW was 5.9. Then the activated carbons were dried in an oven, LINDBERG/BLUE Gravity One at 80°C per 24 hours.

The yield of production of each carbon was calculated as:

\[
\text{% Yield} = \frac{W_c}{W_o} \times 100
\]  

(1)

Where \( W_o \) is the mass of watermelon or walnut shell without any treatment (g) and \( W_c \) is the mass of activated carbon produced (g).

**Characterization of the activated carbons.**

The structure of surface and the pore width were determined with SEM by JEOL JSM-6060. The nitrogen adsorption/desorption isotherms at -196°C in the range of 10⁻⁶ to 1 relative pressures were conducted to determine the textural parameters, such as surface area (BET model), pore volume (DR) and pore size distribution (DFT). Prior to the measurement, the sample was degassed at 250°C for 2 h. These nitrogen adsorption isotherms were made by a surface analyzer Autosorb IQ2 (Quantachrome Inst., Boynton Beach, USA). The IR spectroscopy was made to the activated carbons by Nicolet 6700 (Thermoscientific, USA) in order to know the differences and similarities in functional groups between the precursors and the activated carbons, the IR spectrum was measured in the range of 400 cm⁻¹ to 4000 cm⁻¹. Also the TG analysis was made in Netzsch STA 409 TGA-DTA-DSC, in order to know the thermal stability of the GACW and GACN.
The point of zero charge (PZC) was measured in order to get information of the superficial charge of the carbon at the solution’s pH; this measurement was made with seven different weights (0 g, 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g and 0.6 g of carbon) of GACN and GACW in a solution of 0.1 M of NaCl, the quantity of solution used in each weight of carbon was 50 mL. These samples were shaken for 2 days and then the pH of each solution was measured (see Fig. 6), the point of zero charge of each carbon is the value when the pH is constant (Jaramillo, Álvarez and Gómez-Serrano 2010).

The amounts of acidic and basic surface groups were determined using a shortened version of the Boehm titration method (El-Sayed and Bandosz 2004), (Jaramillo, Álvarez and Gómez-Serrano 2010), (Boehm 2001) and (Giraldo and Moreno 2006); determination of carbonyl groups using sodium ethoxide was not carried out. 0.25 g of carbon sample was placed in 25 mL of the following 0.1 M solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. The vials were sealed and shaken for 5 days and filtrated, and then 5 ml of each filtrate was pipette and the excess of base or acid left in the solution was titrated with 0.05-ml increments of 0.1 M HCl or NaOH in an automatic titrator CG840B Schott, depending on the original titrant used. The amount of acidic sites of various types was calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na₂CO₃, carboxylic and lactonic; and NaHCO₃, only carboxylic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon.

**Adsorption Experiments**

The pH in all the solutions was adjusted (4.5) in order to ensure that the species adsorbed were Lead (II) and Zinc (II).

The effect of the initial concentration of lead (II) and zinc (II) ions was studied in a batch process mode at room temperature by shaking a series of bottles (50 mL) for two weeks. These bottles contain the desired dose of adsorbent (0.5 g) with different concentrations (10 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L, 500 mg/L) of lead (II) and zinc.
(II). Two weeks after GACN and GACW had contact with each one of the solution, 10 mL of each sample was taken and filtrated using Whatman no 42 filter paper; we obtain in total 14 samples (7 for GACN and 7 for GACW).

To quantify the removal of lead and zinc in aqueous solutions adsorption isotherms of both metals were performed for each carbon using analytic technique of atomic absorption (AAnalyst 400 PerkinElmer). It was made a calibration curve for each one of the heavy metals between 1 mg/L to 100 mg/L, the 14 samples taken were diluted by a factor of 1/10. The reproducibility during concentration measurements was assured by repeating the experiments three times under identical conditions and calculating the average values. In order to check the accuracy of the results, all adsorption experiments were duplicated.

The amount of Pb (II) and Zn (II) adsorbed on GACW and GACN, q (mg/g.) were calculated by the mass balance:

\[
q = \frac{(C_0 - C) \cdot V}{W} \quad (2)
\]

Where \( C_0 \) (mg/L) is the initial metal ion concentrations and \( C \) (mg/L) is unadsorbed metal ion concentrations in solution at time t, V(L) is the volume of the solution and W(g) is the weight of the dry activated carbon.
Results and Discussion

Properties of the Activated Carbons

The properties of the activated carbons which were studied in this work are: Surface area, Pore Volume and Pore Distribution by Nitrogen adsorption Isotherms, also the textural properties by Scanning Electron Micrograph, functional groups of the activated carbon by IR-spectroscopy and the loss of mass of the adsorbent material by TGA, the pH of the point of zero charge and the number of acidic and basic groups by Boehm titration.

Nitrogen Adsorption Isotherms

The nitrogen adsorption isotherm for each carbon is in Fig. 1, it can be appreciate that GACN presents an isotherm type I, accordance with the International Union of Pure and Applied Chemistry (IUPAC), this isotherm represents the presence of micropores (Kaneko 1994). The reversible Type I isotherm is concave to the p/p° axis and it approaches a limiting value as p/p° to 1. Type I isotherms are given by microporous solids having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites and certain porous oxides), the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area (IUPAC 1985).
The GACW present an isotherm type IV characteristic of mesoporous solids with a narrow distribution of pore diameters, this isotherm also exhibited type H4 hysteresis loops (Lopez Ramon, et al. 1999) and (Leofanti, et al. 1998) the type H4 loop is often associated with narrow slit-like pores. The initial part of the Type IV isotherm is attributed to monolayer-multilayer adsorption; type IV isotherms are given by many mesoporous industrial adsorbents (IUPAC 1985).

BET surface areas were determined from 35-point adsorption isotherms that were completed with a 0.1 g of sample. The activated carbon made from walnut shell (GACN) has 10% more surface area and 13% more pore volume than the activated carbon made from watermelon shell (GACW) (see Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GACW</td>
<td>710</td>
<td>0.263</td>
</tr>
<tr>
<td>GACN</td>
<td>789</td>
<td>0.304</td>
</tr>
</tbody>
</table>

Fig. 2 shows the pore size distributions of GACW and GACN. The GACN has pore sizes centered between 1.0 nm and 1.7 nm, contrary with the pore distribution of the GACW which has pore sizes centered between 0.5 nm and 4 nm. The GACN present a large pore volume but a short pore size distribution and the GACW present a low pore volume and a wide pore size distribution. The two carbons have the same conditions for the activation, for that it could be suggested that the responsible of the differences in the pore distribution of the two activated carbons is the precursor.
Scanning Electron Micrograph

Scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the GACW and GACN. Fig. 3 shows the SEM photographs with magnification of 500×. Pores of different size and different shape could be observed. It can be seen from the micrographs that the external surface of the chemically activated carbon is full of cavities.

In Fig. 3 can be seen that the carbons has a highly porous structure with sharp edges. The GACN has closed pores, which have geometry of slit-shaped pores or slit. On the other hand, the GACW has two types of pores, the open pore (center) and the pore closed (right image). In the open pore geometry is a slit-shaped pore or slit, while in the closed pore geometry can be seen cylindrical pores.
As is shown in Fig. 3 the external surface of the activated carbons has cracks, crevices, and some grains in various sizes in large holes. It can be concluded from SEM images taken during experiments performed at a carbonization temperature of 500 °C that porous structure was formed because of most of the organic volatiles were evolved (Saka 2012), leaving behind the ruptured surface of activated carbon with a small number of pores.

**IR Spectroscopy.**

IR spectrum of GACW and GACN is given in Fig. 4, this analysis provides information on the chemical structure of the adsorbent material. All spectra show a wide absorption band at 3200 cm\(^{-1}\) to 3600 cm\(^{-1}\) with a maximum at about 3429.94 cm\(^{-1}\). This band can be assigned to the O–H stretching mode of hydroxyl groups and adsorbed water. The position and asymmetry of this band at lower wave numbers indicate the presence of strong hydrogen bonds (Zawadki 1989).
A very small peak at 1560 cm\(^{-1}\) to 1555 cm\(^{-1}\) for GACW and GACN is usually assigned to C=O stretching vibrations of ketones, aldehydes, lactones or carboxyl groups. The weak intensity of this peak suggests that synthetic phosphoric acid activated carbons contain a small amount of carboxyl groups.

The spectra for GACN also show a strong band at 1600 cm\(^{-1}\) to 1580 cm\(^{-1}\) due to aromatic ring stretching vibrations (C=C) enhanced by polar functional groups. For GACW the spectra show a broad band between 1300 cm\(^{-1}\) and 900 cm\(^{-1}\) in all spectra, it has a maximum at 1159.42 cm\(^{-1}\). Absorption in this region is usually found in oxidized carbons (Zawadki 1989) and carbons activated with phosphoric acid (Puziy, et al. 2002).

Both Carbons (GACW and GACN) present bands at 1300 cm\(^{-1}\) to 1000 cm\(^{-1}\) and have been assigned to C-O stretching in acids, alcohols, phenols ethers and esters (Zawadki 1989). The absorption in the region 1300 cm\(^{-1}\) to 1000 cm\(^{-1}\) is also characteristic for phosphorus and phosphor-carbonaceous compounds (Bellamy 1954), (Zawadki 1989), (Puziy, et al. 2002), reported the appearance of a peak at 1190 cm\(^{-1}\) in carbons obtained from coal activated by phosphoric acid activation. This peak was assigned to phosphates (Puziy, et al. 2002). Solum (1995) also reported the appearance of a band at 1203 cm\(^{-1}\) due to the formation of phosphoric acid esters. Due to the overlap of absorption bands from many oxygen and phosphorus compounds in this region, an unambiguous assignment is difficult. However, based on reported data, the absorption at 1300 cm\(^{-1}\) to 900 cm\(^{-1}\) could be tentatively ascribed to the following phosphorus species: The peak at 1220 cm\(^{-1}\) to 1159 cm\(^{-1}\) for GACW may be assigned to the stretching mode of hydrogen-bonded P=O (Bellamy 1954), to O–C stretching vibrations in P–O–C linkage and to P=OOH (Corbridge 1956).

The peak of GACN at 1086 cm\(^{-1}\) to 1070 cm\(^{-1}\) may be ascribed to ionized linkage P–O in acid phosphate esters (Zawadki 1989) and to symmetrical vibration in a chain of P–O–P (polyphosphate) (Puziy, et al. 2002). For this carbon also at 1000 cm\(^{-1}\) to 990 cm\(^{-1}\) could be presence of P–O–C (aliphatic) stretching and P–O–C (aromatic) (Socrates 1994).
Thermo Gravimetric Analysis

The thermogravimetric analysis of the produced activated carbons as a function of temperature is shown in Fig. 5. It can be seen that GACW and GACN are stable at high temperatures.

![Thermo Gravimetric Analysis](image)

**Figure 5** TG analysis of GACW and GACN. Ramp temperature between 20°C and 900°C, rate of heating of 10°C/min and N2 atmosphere.

The loss of mass of the two carbons synthesized are very similar, the behavior is the same for both samples, however the GACW presents a higher loss of mass which can be appreciate in the Fig 5. The loss of mass between 27°C to 150°C could be attributed to the removal of physisorbed water initially present in the carbon pores (Sellin, Clacens and Coutanceau 2010); for GACW the weight loss is 20 wt.% and for GACN is 8 wt.% approximately. Between 151°C to 600°C no significant weight loss is observed for GACW and GACN, it is just 2 wt. % for each carbon. Finally, between 601°C to 900°C the loss step is 9 wt. % for GACW and 10 wt. % for GACN, the loss could be caused by conversion of residual lignin to carbon monoxide (Onal, et al. 2007) and also could be related to the pyrolysis of the material(Giraldo, et al. 2007). The total of weight loss is 31% for GACW and 20% for GACN.

Comparing the results obtained by TGA of the present work with the research of (Saka 2012) where the precursor was acorn shell and the activated carbon was synthesized by
chemical activation with zinc chloride (ZnCl$_2$), the GACW and GACN have a strong resistance to the loss of mass compare with this material; because the activated carbon obtained from acorn shell had a loss of mass of 85%; while, the loss of mass in GACW and GACN is 31% and 20% respectively. Therefore, the GACW and GACN had a better resistance with high temperatures compare with other activated carbons.

The Thermo gravimetric analysis suggested that in this case the loss of mass of the activated carbon synthesized depends on the precursor not on the activation method, because the activation method was the same for the two precursors.

**Point of Zero Charge and Boehm Titration**

The point of zero charge describes the condition when the electrical charge density on a surface is zero (Moreno Castilla, et al. 2007). The results for this test are shown in Fig.6, which shows that the carbon surface is acid with a pH of point of zero charge of 3.05 for GACW and 4.50 for GACN.

![Figure 6: Point of Zero Charge for the GACN and GACW.](image)

The distribution of charge in the surface with respect the pH of the solution is important because it helps to explain the ions adsorption. The point of zero charge is relevant in
surface science. For example, in the field of environmental science, it determines how easily a substrate is able to adsorb potentially harmful ions (Lopez Ramon, et al. 1999).

The activated carbon surface is positively charged for pH below the PZC, and negatively charged at pH above PZC (Valente Nabais, et al. 2011). This characteristic is important for the ACs applications because it determines the capacity of the carbon for ion exchange and liquid phase adsorption of ionic species that have electrostatic interactions as the main adsorption mechanism (Valente Nabais, et al. 2011). Aforementioned, the point of zero charge suggested that GACW in solutions with a pH above 3.05 it will have a carbon surface negatively charged, for GACN will be with a pH above 4.5.

| Table 2 Results of Boehm titration (mmol/g) and pH of point of zero charge. |
|-----------------------------|---------|--------|------|------|-------|-------|-------|
| Sample | pH\textsubscript{pzc} | Carboxylic | Lactonic | Phenolic | Acidic | Basic | Total |
| GACN   | 4.50   | 1.347  | 0.175  | 0.723  | 2.244  | 1.380  | 3.624  |
| GACW   | 3.05   | 1.847  | 0.225  | 0.782  | 2.854  | 1.357  | 4.211  |

The values of the content of surface groups and pH\textsubscript{pzc} obtained for GACW and GACN are set out in Table 2. It is seen that the composition of the carbon surface and hence its acidic–basic character and strength is similar for both carbons, it can be explained for the use of the same activation method (chemical activation with H\textsubscript{3}PO\textsubscript{4}). The Table 2 shows that most of acidic functional groups are carboxylic, followed by phenolic and lactonic in the two carbons. The total number of the surface basic sites was calculated to be 1.380 mmol/g and 1.357 mmol/g, for GACW and GACN respectively and it is smaller than the total number of the acidic surface sites (Momèiloviæ, et al. 2011).
Aqueous Adsorption Isotherms

The results of aqueous adsorption isotherms are presented in Fig. 7.

![Graph a)](image1)

*Figure 7 Adsorption isotherms in aqueous solution for a) zinc (II) and b) lead (II) at a constant pH of 4.5 and 25°C*

The removal of lead (II) and zinc (II) was compared between the two synthesized carbons as shown in Fig. 7. In Fig. 7-a it is observed that one gram of GACW adsorbs more milligrams of zinc (II) that one gram of GACN. For example, when the equilibrium concentration of the solution is 100 ppm Zn(II)/g GAC the concentration adsorbed per gram of GACW is 11 mg Zn (II)/g GACW, meanwhile the concentration adsorbed per gram of GACN is 6 mg Zn (II)/g GACN. It shows a higher adsorption capacity of Zinc (II) by GACW. Also, it is observed in Fig 7-b that one gram of GACW adsorbs more milligrams of lead (II) that one gram of GACN. For example, when the equilibrium concentration of the solution is 50 ppm Pb(II)/g GAC the concentration adsorbed per gram of GACW is 40 mg Pb (II)/g GAC, meanwhile the concentration adsorbed per gram of GACN is 25 mg Pb (II)/g GAC.
In the table 3 it can be explain the effect of the initial concentration in the adsorption of lead and zinc onto GACW and GACN, the left column shows the initial concentration used of each one of the solutions, it can be observe that the efficiency of adsorption depends on the initial concentration. For example, for an initial concentration of 300 mg/L the remaining concentration in the system of Pb$^{2+}$-GACW is 2.025 mg/L, meanwhile for an initial concentration of 500 mg/L the remaining concentration for the same system is 95 mg/L. Therefore, it can be inferred that the initial concentration has an influence in the adsorption process; at higher concentration (200 mg/L to 500 mg/L), the adsorption process is less efficient in the two carbons. It is suggested that this phenomenon could be attributed to the saturation of micropores and mesopores of the carbon.

The pH of the solution has a great influence in the adsorption capacity of a porous material. The acidity of solution affects seriously this capacity, because the superficial charge of the adsorbent is function of the solution’s pH (Moreno Castilla, et al. 2007). In aqueous solutions the cationic species depends on the pH of the solution and the total concentration of metal. Lead(II) and zinc(II) exist as ions until the pH of solution at 6.0 (Zhang, W.H. and Valix 2004). At pH 2, the activated carbon surface could have a positive charge, so electrostatic repulsion takes place between the same charge of the cations and the activated carbon (Depci, Kul and Onal 2012). All the solutions have a pH of 4.5 to ensure that the species adsorbed are lead (II) and Zinc (II). As shown in Fig. 8 the predominant species in the pH between 0 and 5 are Pb$^{2+}$ and Zn$^{2+}$.
Figure 8 Speciation distribution curves of a) zinc and b) lead as a function of pH at 25°C.

The adsorption of lead and zinc could be influenced by the interaction with the solid surface by: the textural or the electrostatic characteristics. The electrostatic characteristics are affecting by the existence of chemical surface groups and the pH of the solution (Moreno and Giraldo 2008). According with the point of zero charge and the Boehm titration, it can be inferred that the surface of GACW is negatively charged in the aqueous solutions of lead (II) and zinc (II), for this reason the electrostatic interactions will be favorable for the adsorption of Pb\(^{+2}\) and Zn\(^{+2}\) onto GACW. In the case of the Boehm titration the surface chemistry of both carbons are similar. However, GACW present more carboxylic groups which can increase the adsorption capacity of the carbon.

On the other hand, this phenomenon can be explained by the textural characteristics of GACW, being important the pore distribution. The GACW has micropores and mesopores, according to the IUPAC classification, increasing the active sites for adsorption of lead (II) and zinc (II), and the GACN has only micropores, decreasing the active sites for adsorption. Therefore, it can be suggested that the best activated carbon for adsorption of lead (II) and zinc (II) is GACW.

In order to explain why lead (II) presents a higher adsorption than zinc (II) one possible reason can be related with ionic potential, electronegativity and softness parameters (M. B. McBride 1989). The pauling electronegativity of Pb (II) is 2.33 and 1.65 for Zn (II) (Kalmykova, Stromvall and Steenari 2008). It is point out that electronegativity of Pb (II) is higher than Zn (II), so the adsorption capacity of Pb (II) is greater than Zn (II) (Depci, Kul and Onal 2012). The obtained results are compatible with the literature data (Minceva, et al.)
2008) and (M. B. McBride 1994), because the greater adsorption of lead (II) than zinc (II) in both carbons could be attributed to the higher electronegativity of this ion (Pb\(^{+2}\)).

**Langmuir and Freundlich isotherms**

The adsorption isotherm indicates how molecules of adsorbate are partitioned between the adsorbent and liquid phase at equilibrium as a function of adsorbate concentration. In this study, the equilibrium data obtained for the adsorption of lead (II) and zinc (II) ions onto GACW and GACN were analyzed by considering the Langmuir and Freundlich isotherm model.

The parameters of monocomponent Langmuir and Freundlich isotherms for lead and zinc solutions are present in Table 4.

**Table 4 Isotherms parameters for the sorption of metal ions on GACW and GACN**

<table>
<thead>
<tr>
<th>Adsorption System</th>
<th>Langmuir Isotherms</th>
<th>Freundlich Isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K_L) (L/mg)</td>
<td>(q_m) (mg/g)</td>
</tr>
<tr>
<td>Pb in GACW</td>
<td>0.942</td>
<td>40.984</td>
</tr>
<tr>
<td>Pb in GACN</td>
<td>0.289</td>
<td>32.362</td>
</tr>
<tr>
<td>Zn in GACW</td>
<td>0.499</td>
<td>11.312</td>
</tr>
<tr>
<td>Zn in GACN</td>
<td>0.293</td>
<td>6.079</td>
</tr>
</tbody>
</table>

In Langmuir model \(K_L\) is related to the energy of adsorption and \(q_m\) is the maximum monolayer adsorption capacity (mg g\(^{-1}\)) (Depci, Kul and Onal 2012). Therefore, it is observed in the Table 4 that the activated carbon which presents the higher energy of adsorption and higher maximum adsorption capacity in Pb\(^{+2}\) and Zn\(^{+2}\) is GACW; i.e., for Pb\(^{+2}\) the \(K_L\) and \(q_m\) in the GACW is 0.942 and 40.984 mg g\(^{-1}\), and for GACN 0.289 and 32.362 mg g\(^{-1}\) respectively. On the other hand, for Zn\(^{+2}\) the \(K_L\) and \(q_m\) in the GACW is 0.499 and 11.312 mg g\(^{-1}\), and for GACN 0.283 and 6.079 mg g\(^{-1}\) respectively. Also, the isotherms present in Fig. 7 for lead (II) and zinc (II) fit Langmuir Isotherms, because they
reach an asymptotical concentration in the two carbons with the two heavy metals (Moreno Castilla, et al. 2007), 6,079 mg Zn /g GACN, 11,312 mg Zn /g GACW, 32,362 mg Pb/g GACN, 40,984 mg Pb/g GACW.

The Langmuir adsorption isotherm quantitatively describes the deposition of a large layer of molecules on an adsorbent surface as a function of the concentration of the adsorbed material into the liquid which it is in contact (Depci, Kul and Onal 2012). A Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (Karagoz, et al. 2008). Langmuir isotherm is frequently evaluated by a separation factor, $R_L$, named as dimensionless separation factor and it is calculated to determine whether the adsorption system is favorable or not (Depci, Kul and Onal 2012). It is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0}$$

Where $R_L$ is a dimensionless separation factor, $C_0$ is the initial metal ion concentration and $K_L$ is Langmuir constant. The value of separation factor indicates the type of the isotherm and the nature of the adsorption process. The feasibility of the reactions are explained using the value of $R_L$ ($R_L > 1$ – unfavorable, $R_L = 1$ – linear, $0 < R_L < 1$ – favorable, $R_L = 0$ – irreversible) (Depci, Kul and Onal 2012). The values of $R_L$ were found in the range of 0.002–0.25, confirming the favorable adsorption process for all systems. The calculated values of $R_L$ are shown in the Table 5.
Table 5 RL values of Langmuir model for the sorption of metal ions on GACW and GACN

<table>
<thead>
<tr>
<th>Initial Concentration (mg/L)</th>
<th>Pb$^{2+}$ans</th>
<th>Zn$^{2+}$ans</th>
<th>Pb$^{2+}$and</th>
<th>Zn$^{2+}$and</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GACW</td>
<td>GACW</td>
<td>GACN</td>
<td>GACN</td>
</tr>
<tr>
<td>10</td>
<td>0.096</td>
<td>0.167</td>
<td>0.257</td>
<td>0.254</td>
</tr>
<tr>
<td>50</td>
<td>0.021</td>
<td>0.039</td>
<td>0.065</td>
<td>0.064</td>
</tr>
<tr>
<td>100</td>
<td>0.011</td>
<td>0.020</td>
<td>0.033</td>
<td>0.033</td>
</tr>
<tr>
<td>200</td>
<td>0.005</td>
<td>0.010</td>
<td>0.017</td>
<td>0.017</td>
</tr>
<tr>
<td>300</td>
<td>0.004</td>
<td>0.007</td>
<td>0.011</td>
<td>0.011</td>
</tr>
<tr>
<td>400</td>
<td>0.003</td>
<td>0.005</td>
<td>0.009</td>
<td>0.008</td>
</tr>
<tr>
<td>500</td>
<td>0.002</td>
<td>0.004</td>
<td>0.007</td>
<td>0.007</td>
</tr>
</tbody>
</table>

In Freundlich model $K_F$ (L/g) is the Freundlich constant, it is related to the distribution coefficients, and consequently to the degree of Pb$^{2+}$ or Zn$^{2+}$ affinity and mobility to the soil and $n$ is Freundlich exponent. These parameters are determined from a plot log $q_e$ versus log $C_e$ (Momèilovia, et al. 2011). A larger value for $1/n$ indicates a larger change in effectiveness over different equilibrium concentrations, when $1/n$ is >1.0, the change in adsorbed concentration is greater than the change in the solute concentration (Chilton, et al. 2002). In Table 4 it is shown values of $R^2$ lower than 0.8 indicating that the Freundlich model does not fit with the adsorption process in GACN and GACW. Therefore it could be inferred that the Freundlich model does not describes the adsorption of these heavy metals into the activated carbon synthesized.

According with the experimental results it could be suggest that the Langmuir model is the most appropriate model and the monolayer adsorption takes place in the system carbon-ion.
Conclusions

Watermelon and Walnut shell were tested as feedstock for activated carbon production because they are low-cost and accessible raw materials and the watermelon shell never has been used as precursor of activated carbon. Physical, chemical and adsorptive properties were studied finding good results: the yield of production was remarkable with 85 % for GACW and 80 % for GACN, the surface area is 710 m$^2$/g for GACW and 789 m$^2$/g for GACN with a well-developed pore structure and distribution (microporous for GACN and microporous and mesoporous for GACW). The activated carbon made from walnut shell has 13% more pore volume than the activated carbon made from watermelon shell. Also, GACN has a better resistance to high temperatures than GACW (the loss of mass at 900°C was 20 % for GACN, while for GACW was 31 %). The pH$_{PZC}$ is 3.05 for GACW and 4.5 for GACN; also, the carbons surfaces, their acidic–basic character and strength are similar for both carbons.

The adsorption isotherms of Pb (II) and Zn (II) on GACW and GACN are quite well consistent with the Langmuir model. The adsorption capacities of heavy metals in GACW was higher than GACN, Pb (II) in GACW (40,984 mg/g), Zn (II) in GACW (11,312 mg/g), Pb (II) in GACN (32,362 mg/g) and Zn (II) in GACN (6,079 mg/g). Therefore, it is suggested that between GACW and GACN the activated carbon with the higher adsorption of lead (II) and zinc (II) is the GACW; this could be explained since the GACW has a heterogeneous pore distribution which could avoid the pore blocking favoring the physisorption and the surface of GACW is negatively charged for this reason the electrostatic interactions will be favorable for the adsorption of Pb$^{2+}$ and Zn$^{2+}$. According with these results, the activated carbons produced in this work are an alternative low-cost adsorbent for the removal of lead (II) and zinc (II) ions from aqueous solutions. Furthermore, the superior adsorption capacity of the produced activated carbon suggests the process is potentially marketable.
Acknowledgements

The authors thank the Framework Agreement between Universidad de los Andes and Universidad Nacional de Colombia, as well as the Agreement Statement (Acta de Acuerdo) between the Departments of Chemistry of both Universities.

References


Sun, Yanyuan, Qinyan Yue, Baoyou Gao, Lihui Huang, Xing Xu, and Qian Li. "Comparative study on characterization and adsorption properties of activated carbons with H3PO4 and H4P2O7 activation employing Cyperus alternifolius as precursor." *Chemical Engineering Journal* 181-182 (2011): 790-797.


Recommendations:

- Realizar un control del pH, para garantizar que la especie que quiere ser removida se encuentra en el estado de oxidación deseado, y no se vea afectada la interacción del adsorbente con el adsorbato.
- Es importante realizar la medición del diámetro del poro cuando se realiza la prueba en el microscopio electrónico de barrido (MEB), ya que permite clasificar el poro de la muestra, ya sea en microporos, mesoporos y macroporos.
- Es primordial realizar un análisis elemental al precursor y al carbón sintetizado, para reconocer los cambios después de la activación.
### Identificación Autor(es) del Trabajo de Grado

<table>
<thead>
<tr>
<th>CÓDIGO</th>
<th>DOCUMENTO DE IDENTIDAD</th>
<th>APELLIDOS</th>
<th>NOMBRES</th>
<th>CORREO ELECTRÓNICO</th>
</tr>
</thead>
<tbody>
<tr>
<td>200611083</td>
<td>CC - 1032434146</td>
<td>Moreno Barbosa</td>
<td>Jonathan Julian</td>
<td><a href="mailto:lqou2048@gmail.com">lqou2048@gmail.com</a></td>
</tr>
</tbody>
</table>

**PROGRAMA**  Pregrado

**FACULTAD**  Facultad de Ingeniería

**DEPARTAMENTO**  Departamento de Ingeniería Civil y Ambiental

**ENTREGÓ FORMATO**
- SB-10 "Entrega trabajo de grado y autorización de uso a favor de la Universidad de los Andes": Documento con el cual, el autor permite su trabajo sea utilizado por la Universidad, para fines de consulta y de mencion en sus catálogos bibliográficos, tanto físicos como en línea.

### Identificación de Trabajo de Grado para Doblemente Título

**PROGRAMA**  No Aplica

**FACULTAD**  No Aplica

**DEPARTAMENTO**  No Aplica

**TESIS PARA DOBLEMENTE TÍTULO**
Si el trabajo de grado presenta aplicaciones para obtener dos títulos, por favor marque esta casilla y diga la información de esta sección.

### Información General del Trabajo de Grado

**Título del Trabajo de Grado:**
Obtención de carbón activado a partir de cáscara de sandía y hueso del nogal, y su aplicación en la adsorción de plomo y zinc

**Descripción Física**

<table>
<thead>
<tr>
<th>Número de páginas</th>
<th>Ilustraciones</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>8</td>
</tr>
</tbody>
</table>

**Material Acompañante (Camaldu):**
- Cassetes Audios
- Discos compactos
- Cassetes Video
- Depositas
- Dasquetes
- Otros ¿Cuáles?

**Fecha de elaboración**

<table>
<thead>
<tr>
<th>DD</th>
<th>MM</th>
<th>AAAA</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>01</td>
<td>2013</td>
</tr>
</tbody>
</table>

**Resumen del Trabajo de Grado.**

Activated carbons from watermelon shell (GACW) and walnut shell (GACN) were synthesized through chemical activation with phosphoric acid 40% w/w, as an alternative low-cost adsorbent for the removal of lead (II) and zinc (II) ions from aqueous solutions. The yield of production was 85% and 80% for GACW and GACN respectively. To compare the differences and similarities between the two activated carbons, the following tests were performed: surface and pore widths with SEM, nitrogen adsorption isotherms at -196°C (77 K), IR spectroscopy, TGA, point of zero charge (pzc) and Boehm titration. The GACN has 10% more surface area (789 m²/g for GACW and 710 m²/g for GACN) and 13% more pore volume than GACW. Also, GACN has a better resistance to high temperatures than GACW (the loss of mass at 900°C was 20% for GACW, while for GACN was 31%).

The effect of the initial concentration of lead (II) and zinc (II) ions on the adsorption process was studied in a batch process mode. To quantify the adsorption of lead and zinc adsorption isotherms of both metals in aqueous solution were performed for each carbon using an analytical technique of atomic absorption. The adsorption isotherm data were better fitted by Langmuir model. Experimental results suggest that 1 gram of GACN adsorbs more milligrams of lead (II) and zinc (II) than one gram of GAC; it is suggested that the pore distribution is a significant variable in the adsorption process because GAC present mesopores and micropores, and GACN has only micropores. Also, the surface chemistry is an important variable in the adsorption process because GACW present a lower pHPC than GACN (3.05 for GACW and 4.5 for GACN) and the solution's pH of each metal was adjust in 4.5, for that it could be suggested that the electrostatic interactions were increase between the ion and the carbon surface.
OBJETIVOS DEL TRABAJO DE GRADO.

Explorar la obtención de carbón activado a partir de cascara de sandía y nueces del rosal.
Establecer la capacidad de adsorción de cada uno de los materiales sintetizados aplicados en la adsorción desde solución acuosa de iones plomo y cinc.
Realizar la caracterización física y química de los carbones sintetizados.

METODOLOGÍA DEL TRABAJO DE GRADO

CONCLUSIONES DEL TRABAJO DE GRADO.

Watermelon and Walnut shell were tested as feedstock for activated carbon production because they are low-cost and accessible raw materials and the watermelon shell never has been used as precursor of activated carbon. Physical, chemical and adsorptive properties were studied finding good results: the yield of production was remarkable with 85 % for GACW and 80 % for GACN, the surface area is 710 m2/g for GACW and 789 m2/g for GACN with a well-developed pore structure and distribution (microporous for GACN and mesoporous for GACW). The activated carbon made from walnut shell has 13% more pore volume than the activated carbon made from watermelon shell. Also, GACN has a better resistance to high temperatures than GACW (the loss of mass at 900°C was 20 % for GACN, while for GACW was 31 %). The pHPC is 3.05 for GACU and 4.5 for GACN, also, the carbons surfaces, their acidic-basic character and strength are similar for both carbons.

The adsorption isotherms of Pb (II) and Zn (II) on GACW and GACN are quite well consistent with the Langmuir model. The adsorption capacities of heavy metals in GACW was higher than GACN, Pb (II) in GACW (40.984 mg/g), Zn (II) in GACW (11.312 mg/g), Pb (II) in GACN (32.362 mg/g) and Zn (II) in GACN (6.079 mg/g). Therefore, it is suggested that between GACW and GACN the activated carbon with the higher adsorption of lead (II) and zinc (II) is the GACW: this could be explained since the GACW has a heterogeneous pore distribution which could avoid the pore blocking favoring the physisorption and the surface of GACW is negatively charged for this reason the electrostatic interactions will be favorable for the adsorption of Pb2+ and Zn2+. According with these results, the activated carbons produced in this work are an alternative low-cost adsorbent for the removal of lead (II) and zinc (II) ions from aqueous solutions. Furthermore, the superior adsorption capacity of the produced activated carbon suggests the process is potentially marketable.

*PALABRAS CLAVES (TEMAS) DEL TRABAJO DE GRADO

Adsorption from solution, Activated carbon, watermelon, walnut, lead, zinc.

ACUERDOS DE CONFIDENCIALIDAD: ☋ NO TIENE ACUERDO(S) ☋ TIENE ACUERDO(S)

Si selecciona tener acuerdo de confidencialidad, por favor diligence el siguiente cuadro.

<table>
<thead>
<tr>
<th>Persona natural o jurídica</th>
<th>Desde</th>
<th>Hasta</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DD</td>
<td>AAAA</td>
</tr>
<tr>
<td></td>
<td>MM</td>
<td>AAAA</td>
</tr>
</tbody>
</table>

3. FIRMAS

AUTORES (Nombre completo)

FIRMA

Jonathan Julian Moreno Barbosa

FIRMA
DIRECTOR / ASOCIADO (Nombre completo)

Andrea Mulderado Rojas
Juan Carlos Moreno Piraján

JURADO / LECTOR (Nombre completo)

UNIVERSIDAD DE LOS ANDES
Facultad de Ingeniería
Departamento de Ingeniería Civil
y Ambiental

Las firmas de Autor y Director/Asesor son obligatorias. Si se manifiestan inconvenientes con el registro de la firma del Juzgado/Lector, deberá enjuiciar ante la respectiva Facultad la autorización para registrar las firmas de pares o un cédula que justifique la ausencia de la firma faltante.