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Removal of lead(II) and zinc(II) ions from aqueous solutions by adsorption onto activated carbon synthesized from watermelon shell and walnut shell

Jonathan Julián Moreno-Barbosa · Catalina López-Velandia · Andrea del Pilar Maldonado · Liliana Giraldo · Juan Carlos Moreno-Piraján

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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 $m^2 g^{-1}$ for GACN and 710 $m^2 g^{-1}$ 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 suggests 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, while GACN has only micropores. Also, the surface chemistry is an important variable in the adsorption process because GACW presents a lower pH_{PZC} than GACN (3.05 for GACW and 4.5 for GACN) and the solution's pH of each metal was adjusted in 4.5, for that it could be suggested that the electrostatic interactions were increased between the ion and the carbon surface.

Keywords Adsorption from solution · Activated carbon · Watermelon · Walnut · Lead · Zinc

1 Introduction

Over time, the cost of activated carbon has risen. For that reason, it is necessary to find new process alternatives of production of activated carbon using non-conventional and low cost methodologies in order to achieve a sustainable process. Keeping in mind that waste disposal has become an important issue, problems of waste treatment and disposal 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 et al. 2012). Lead can threaten

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J. J. Moreno-Barbosa · C. López-Velandia · A. d. P. Maldonado
Department of Civil and Environmental Engineering,
Universidad de los Andes, Cra 1 N° 18A-12, Bogotá, Colombia
e-mail: jj.moreno39@uniandes.edu.co

C. López-Velandia
e-mail: c.lopez37@uniandes.edu.co

C. López-Velandia
Department of Chemical Engineering, Universidad de los Andes,
Cra 1 N° 18A-12, Bogotá, Colombia

L. Giraldo
Department of Chemistry, Universidad Nacional de Colombia,
Cra 1 N° 18A-12, Bogotá, Colombia

J. C. Moreno-Piraján (✉)
Department of Chemistry, Universidad de Los Andes, Cra 1 N° 18A-12, Bogotá, Colombia
e-mail: jumoreno@uniandes.edu.co

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. The world health organization (WHO) recommended the maximum acceptable concentration of lead in drinking water as 0.1–0.05 mg L^{-1} (Zhang et al. 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 recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg L^{-1} (Hawari et al. 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 et al. 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 et al. 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, attracted considerable attention due to their wide availability everywhere in the globe (Paraskeva et al. 2008; Elizalde-Gonzalez and Hernandez-Montoya 2007; 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, as well as, 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 et al. 2008). The possibility of using automobile tires and 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) Activated carbon synthetized from waste palm shell by (Rahman et al. 2012), (2) Activated carbon prepared from Van apple pulp by (Depci et al. 2012), and (3) Activated carbon produced from *Cyperus alternifolius* (Sun et al. 2011).

The production of activated carbon can be performed either 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, due to the fact that the first one is commonly used for biomass precursor, because it achieves higher yield and larger surface areas; also, it requires lower operating and energy costs as lower temperatures are used (Ahmdnea et al. 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 precursors to obtain activated carbon (GACW and GACN) and their applicability as adsorbents for the uptake of lead and zinc from aqueous solutions. Watermelon is a soft-core fruit and has a significant role for Colombian trade, in fact, in 2011, exports of this fruits to The United Kingdom, Canada, Germany and Ecuador were of USD 618.000 (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 for activated carbons. This may not only contribute 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 H_3PO_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 H_3PO_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 adsorp -tion isotherms, IR spectroscopy, point zero of charge, Boehm titration, TGA and aqueous solutions adsorption isotherms of lead(II) and zinc(II).

2 Materials and methods

2.1 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.

2.2 Chemicals

Standard stock solutions of Pb(II) and Zn(II) (1,000 mg L^{-1}), 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).

2.3 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 dried in an oven, LINDBERG/BLUE Gravity One at 80 °C per 2 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 H_3PO_4) to prepare the impregnate samples, these samples were carbonized in a furnace, (Carbolite HVT-1200), at 500–700 °C for 1.12 h under nitrogen (N_2) flow of 120 mL min^{-1} at a heating rate of 10 °C min^{-1}. (IV) The carbonized 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 h.

The yield of production of each carbon was calculated as:

$$\% \text{ Yield} = \frac{W_c}{W_o} \times 100 \quad (1)$$

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).

2.4 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 400–4,000 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, 0.1, 0.2, 0.3, 0.4, 0.5 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 PZC of each carbon is the value when the pH is constant (Jaramillo et al. 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 et al. 2010; Boehm 2001; Giraldo et al. 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; Na_2CO_3, carboxylic and lactonic; and $NaHCO_3$, only carboxylic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon.

2.5 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 contained the desired dose of adsorbent (0.5 g) with different concentrations (10, 50, 100, 200, 300, 400, 500 mg L^{-1}) 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 obtained a total of 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). A calibration curve was made for each one of the heavy metals between 1 and 100 mg L^{-1}, 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^{-1}) were calculated by the mass balance:

$$q = \frac{(C_o - C) \times V}{W} \qquad (2)$$

where C_0(mg L^{-1}) is the initial metal ion concentrations and C(mg L^{-1}) 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.

3 Results and discussion

3.1 Properties of activated carbons

The properties of 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 SEM, functional groups of the activated carbon by IR-spectroscopy and the loss of mass of the adsorbent material by TGA, the pH of the PZC and the number of acidic and basic groups by Boehm titration.

3.1.1 Nitrogen adsorption isotherms

The nitrogen adsorption isotherm for each carbon is in Fig. 1, it can be appreciated that GACN presents an isotherm type I, according 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).

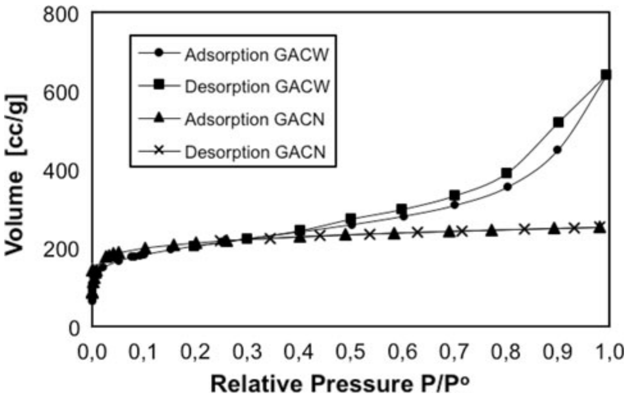

Fig. 1 Nitrogen adsorption isotherms at −196 °C for the GACW and GACN

Table 1 Textural properties of the activated carbons GACW and GACN

Sample	BET (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
GACW	710	0.263
GACN	789	0.304

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; 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).

Figure 2 shows the pore size distributions of GACW and GACN. The GACN has pore sizes between 1.0 and 1.7 nm, contrary with the pore distribution of the GACW which has pore sizes between 0.5 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.

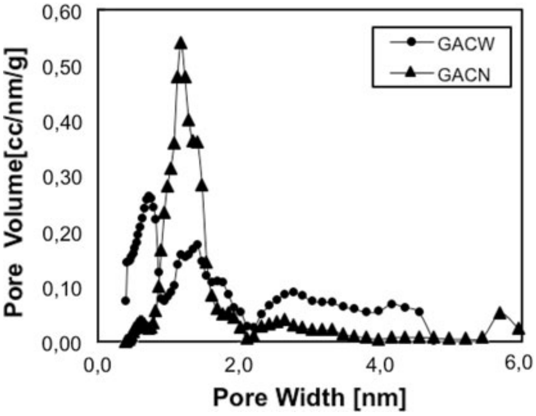

Fig. 2 Pore distribution of the GACW and GACN

3.1.2 *Scanning electron micrograph*

Scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the GACW and GACN. Figure 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.

Figure 3 shows that the carbons have 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.

3.2 IR spectroscopy

IR spectrum of GACW and GACN are given in Fig. 4, this analysis provides information on the chemical structure of the adsorbent material. All spectra show a wide absorption band at 3,200–3,600 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 indicates the presence of strong hydrogen bonds (Zawadki 1989).

A very small peak at 1,560–1,555 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 1,600–1,580 cm^{-1} due to aromatic ring stretching vibrations (C=C) enhanced by polar functional groups. For GACW the spectra show a broad band between 1,300 and 900 cm^{-1} in all spectra, it has a maximum at 1,159.42 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 between 1,300 and 1,000 cm^{-1} and have been assigned to C–O stretching in acids, alcohols, phenols ethers and esters (Zawadki 1989). The absorption in the region 1,300–1,000 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 1,190 cm^{-1} in carbons obtained from coal activated by phosphoric acid activation. This peak was assigned to phosphates (Puziy et al. 2002), and also was reported the appearance of a band at 1,203 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 1,300–900 cm^{-1} could be tentatively ascribed to the following phosphorus species: The peak at

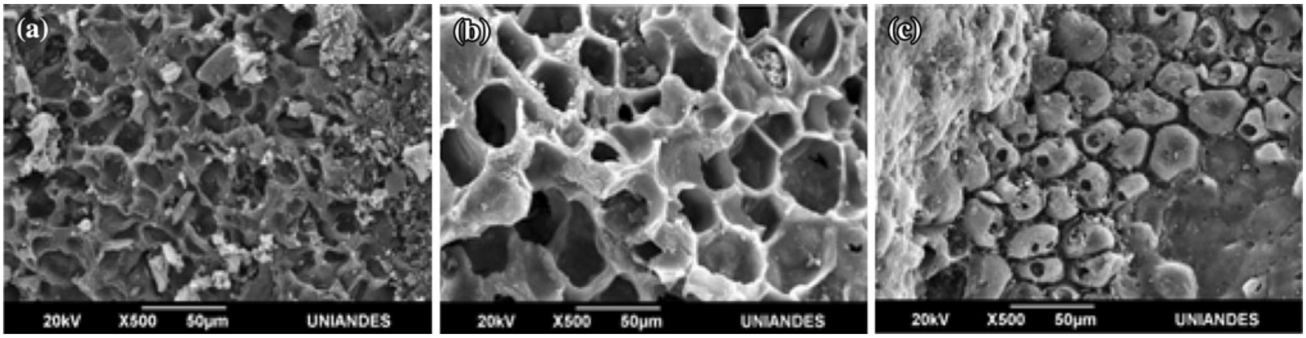

Fig. 3 SEM images at magnification of ×500. **a** GACN, **b** GACW, **c** GACW

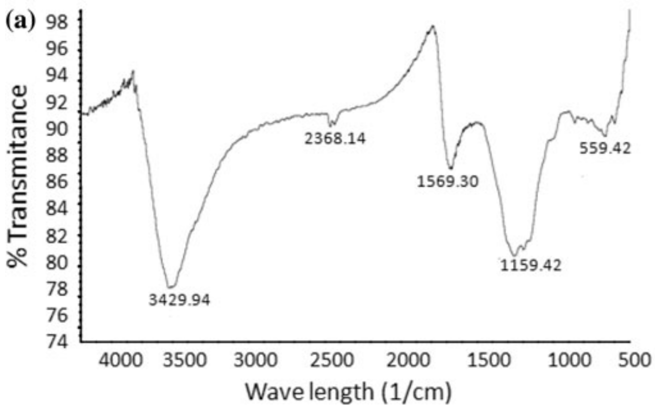

Fig. 4 IR images for activated carbons **a** GACW, **b** GACN

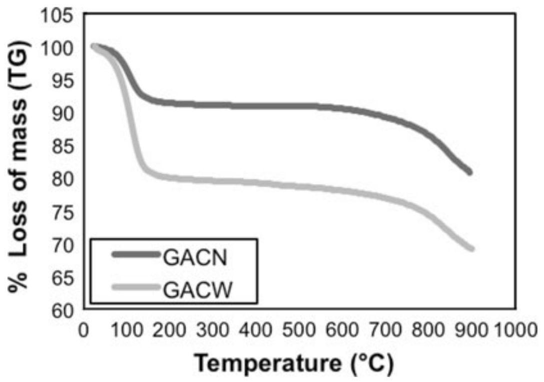

Fig. 5 TG analysis of GACW and GACN. Ramp temperature between 20 and 900 °C, rate of heating of 10 °C min^{-1} and N_2 atmosphere

1,220–1,159 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 1,086–1070 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 1,000–990 cm^{-1} could be presence of P–O–C (aliphatic) stretching and P–O–C (aromatic) (Socrates 1994).

3.2.1 *Thermo gravimetric analysis*

The thermo gravimetric 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.

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 appreciated in the Fig 5. The loss of mass between 27 and 150 °C could be attributed to the removal of physisorbed water initially present in the carbon pores (Sellin et al. 2010); for GACW the weight loss is 20 wt% and for GACN is 8 wt% approximately. Between 151 and 600 °C no significant weight loss is observed for GACW and GACN, it is just 2 wt% for each carbon. Finally, between 601 and 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 pyrolisis 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 stronger resistance to the loss of mass compared with this material, this, 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 have 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.

3.2.2 *Point of zero charge and Boehm titration*

The PZC 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 PZC of 3.05 for GACW and 4.50 for GACN.

The distribution of charge in the surface with respect the pH of the solution is important because it helps to explain

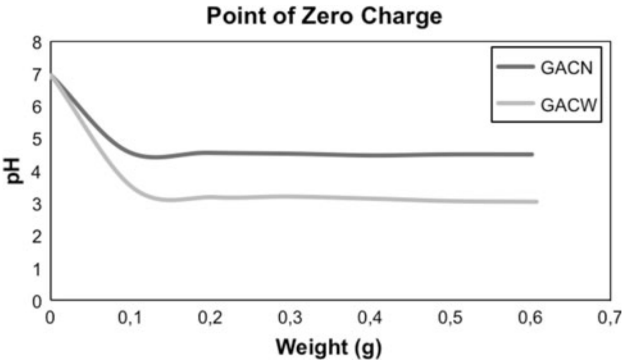

Fig. 6 Point of zero charge for the GACN and GACW

the ions adsorption. The PZC 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 (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 (Nabais et al. 2011). The above suggests that GACW in solutions with a pH above 3.05 will have a carbon surface negatively charged, while GACN will have a carbon surface negatively charged when the solution's pH is above 4.5.

The values of the content of surface groups and pH_{pzc} obtained for GACW and GACN are set out in Table 2. It can be observed that the composition of the carbon surface and hence its acidic–basic character and strength are similar for both carbons, it can be explained for the use of the same activation method (chemical activation with H_3PO_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 and 1.357 mmol g^{-1}, for GACW and GACN respectively and it is smaller than the total number of the acidic surface sites (Momèiloviæ et al. 2011).

3.3 Aqueous adsorption isotherms

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

The removal of lead(II) and zinc(II) was compared between the two synthesized carbons as shown in Fig. 7. In Fig. 7a is observed that one gram of GACW adsorbs more milligrams of zinc(II) than 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 7b that one gram of GACW adsorbs more milligrams of lead(II) than 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.

Table 3 explains 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 observed that the efficiency of adsorption depends on the initial concentration. For

Table 2 Results of Boehm titration (mmol g^{-1}) and pH of point of zero charge

Sample	pH_{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

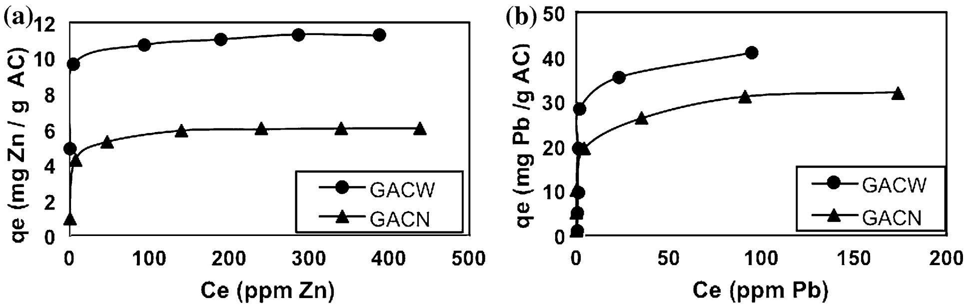

Fig. 7 Adsorption isotherms in aqueous solution for **a** zinc(II), **b** lead(II) at a constant pH of 4, 5 and 25 °C

Table 3 The effect of initial concentration of adsorption of lead(II) and zinc(II) onto GACW and GACN

Initial concentration (mg L^{-1})	Efficiency as a function of the initial concentration			
	Pb^{+2}-GACW (%)	Zn^{+2}-GACW (%)	Pb^{+2}-GACN (%)	Zn^{+2}-GACN (%)
10	94.8	98.3	100.0	98.4
50	98.0	99.6	100.0	85.1
100	98.8	94.8	99.9	53.2
200	99.4	52.9	97.8	29.6
300	99.3	36.8	88.3	20.0
400	94.3	28.2	77.2	15.1
500	81.0	22.5	65.3	12.1

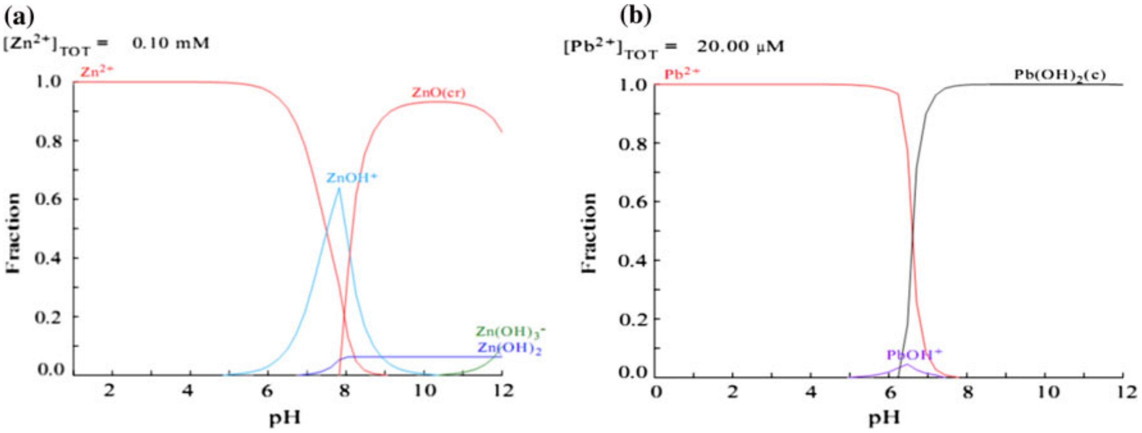

Fig. 8 Speciation distribution curves of **a** zinc, **b** lead as a function of pH at 25 °C

example, for an initial concentration of 300 mg L^{-1} the remaining concentration in the system of Pb^{+2}-GACW is 2.025 mg L^{-1}, meanwhile for an initial concentration of 500 mg L^{-1} the remaining concentration for the same system is 95 mg L^{-1}. Therefore, it can be inferred that the initial concentration has an influence in the adsorption process; at higher concentration (200–500 mg L^{-1}), 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 the 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 et al. 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 et al. 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}.

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 affected by the existence of chemical surface groups and the pH of the solution (Moreno and Giraldo 2008). From the PZC 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.

As to why lead(II) presents a higher adsorption than zinc(II) one possible reason can be related with ionic potential, electronegativity and softness parameters (McBride 1989). The pauling electronegativity of Pb(II) is 2.33 and 1.65 for Zn(II) (Kalmykova et al. 2008). It is important to 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 et al. 2012). The obtained results are compatible with the literature data (Minceva et al. 2008; 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}).

3.3.1 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.

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 et al. 2012; Mesquita et al. 2001; Mohan et al. 2006; Zhang 2011). 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 et al. 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

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

Adsorption system	Langmuir isotherms			Freundlich isotherms			
	K_L (L/mg)	q_m (mg g^{-1})	R^2	k_f (L g^{-1})	n	$1/n$	R^2
Pb in GACW	0.942	40.984	0.998	26.382	10.526	0.095	0.761
Pb in GACN	0.289	32.362	0.998	15.920	7.117	0.038	0.637
Zn in GACW	0.499	11.312	0.999	9.063	26.525	0.141	0.551
Zn in GACN	0.293	6.079	0.999	5.339	46.512	0.022	0.679

Table 5 R_L values of Langmuir model for the sorption of metal ions on GACW and GACN

Initial concentration (mg L^{-1})	R_L			
	Pb^{+2}-GACW	Zn^{+2}-GACW	Pb^{+2}-GACN	Zn^{+2}-GACN
10	0.096	0.167	0.257	0.254
50	0.021	0.039	0.065	0.064
100	0.011	0.020	0.033	0.033
200	0.005	0.010	0.017	0.017
300	0.004	0.007	0.011	0.011
400	0.003	0.005	0.009	0.008
500	0.002	0.004	0.007	0.007

determine whether the adsorption system is favorable or not (Depci et al. 2012). It is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_o} \quad (3)$$

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 et al. 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.

In Freundlich model K_F (L g^{-1}) 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 $\log C_e$ (Momèiloviæ 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 suggested that the Langmuir model is the most appropriate model and the monolayer adsorption takes place in the system carbon-ion.

4 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 $m^2 g^{-1}$ for GACW and 789 $m^2 g^{-1}$ 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^{-1}), Zn(II) in GACW (11,312 mg g^{-1}), Pb(II) in GACN (32,362 mg g^{-1}) and Zn(II) in GACN (6,079 mg g^{-1}). 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.

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