Understanding the adsorption of heavy metals on oxygen-rich biochars by using molecular simulation

A.K. Silos-Llamas^a, G. Durán-Jiménez^{a,b}, V. Hernández-Montoya^{a,*}, M.A. Montes-Morán^c,
N.A. Rangel-Vázquez

^aTecNM/Instituto Tecnológico de Aguascalientes, Av. Adolfo López Mateos No. 1801 Ote. C.P. 20256,
Aguascalientes, México.

^b Low Carbon Energy and Resources Technologies Research Group, Faculty of Engineering, University of
Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

^cInstituto Nacional del Carbón, INCAR-CSIC, Apartado 73 E-33080, Oviedo, Spain.

Abstract

The adsorption of heavy metals on biochars derived from *Carya illinoensis* biomass was studied using molecular simulation tools to understand the adsorption mechanism. The experimental conditions to obtain the best performing biochar were determined using a L_{16} orthogonal array of the Taguchi method and considering the removal of heavy metals from water as response variable. The studied factors were the mass of precursor, drying temperature, heating rate, maximum temperature of thermal treatment and holding time. Particularly, it was possible to obtain samples of biochar that were very efficient for the removal of Al^{3+} , Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} from water, using relatively low temperatures of carbonization (200-350 °C) and low processing times (20-50 min). The most influencing factor in the final properties of biochar was the maximum temperature of the thermal treatment. The biochars obtained were rich in oxygen functional groups (carboxylic and phenolic), which favored the removal of heavy metals from water by complexation and ionic exchange mechanisms. According with the data obtained by molecular simulation, the

*Corresponding author. Tel.: +52 449 9105002 Ext. 137

E-mail address: virginia.hernandez@yahoo.com.mx (Virginia Hernández-Montoya)

adsorption mechanism of heavy metals was controlled by the dipolar moment of the metallic cations, with Pb^{2+} being adsorbed more efficiently.

Key words: Adsorption, biochar, heavy metals, surface oxygen groups, molecular simulation.

1. Introduction

Biochar is a carbon-rich material usually obtained by thermal decomposition of biomass under oxygen-limited conditions. The textural characteristics and the surface chemistry of biochars depend on the thermal treatment used, the type of precursor (biomass) and the fabrication method [1]. The principal thermal treatments used for the preparation of biochar include fast pyrolysis, slow pyrolysis, flash carbonization, torrefaction, gasification, and more recently, hydrothermal carbonization [1-2]. Pyrolysis is the most common treatment to prepare biochar. In this treatment, the biomass is heated under inert atmosphere releasing the volatile matter from the raw material, yielding solid biochar and both condensable tar and gas fractions [3].

Biochar has received increasing attention due to its ability to store large amount of carbon, increase crop yield, reduce soil emission of greenhouse gases, improve soil quality, decrease nutrient leaching, and reduce irrigation and fertilizer requirements [4]. Other uses of biochar recently spotted include as fuel in carbon fuel cells to produce electricity, as catalyst in tar decomposition, for corncob hydrolysis and pyrolysis of waste engine oil [5]. Additionally, due to its porous structure and surface functional groups (e.g., carboxyl, carbonyl, and phenolic groups), biochar has been used as adsorbent of heavy metals in

aqueous solutions, and for the purification of gases [6-11]. For example, biochar resulting from the pyrolysis of wasted marine macro-algae in a conventional furnace has been used for the removal of heavy metals in aqueous solutions showing a maximum adsorption capacity of 98.6, 122.1 and 84.3 mg/g for Cu^{2+} , Cd^{2+} and Zn^{2+} , respectively [7]. Also, biochar obtained from sawdust of eucalyptus by combining hydrothermal carbonization and KOH activation has been used for the removal of hexavalent chromium in aqueous solution with a maximum adsorption capacity of 45.8 mg/g [12]. According with the data reported in the literature, biochars produced at lower temperatures of pyrolysis (300-400 °C) have higher amounts of oxygen functional groups, favoring the removal of heavy metals by complexation [1].

Biochar has been also tested for the adsorption of heavy metals from soils. For example, a manganese oxide-modified biochar composite was used in the adsorption of arsenic from red soil with arsenic retention increasing as the biochar content in the soil increased, mainly owing to an increase in soil pH [13]. Also, biochars derived from sewage sludge (BSS) and pruning trees (BPT) were studied for immobilizing metals (Cd^{2+} , Pb^{2+} and Zn^{2+}) in mine soils (acidic and basic soils). In acidic soils, BSS and BPT biochars performed very well, increasing the pH of porewater while decreasing metals concentration [14].

The purpose of the present work is to demonstrate that it is possible to obtain biochars for the removal of heavy metals (Al^{3+} , Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+}) from water by the optimization of the carbonization conditions using a L_{16} orthogonal array of the Taguchi method. Temperatures of thermal treatments and times of processing were kept relatively low (200-350 °C and 20-50 min, respectively), compared with other works [15]. Additionally, it is important to note that, in the present work, biochars tested were obtained

by direct carbonization, i.e., in absence of any chemical agent that could eventually develop additional porosity (activation) on the samples. Selected textural and chemical properties of the biochars were determined using different analytical techniques with the purpose of elucidating the adsorption mechanism of the metallic species from aqueous solution.

2. Materials and methods

2.1 Preparation of biochar following the Taguchi method

The biochar was prepared using pecan nut shells (*Carya illinoensis*), an agro-food by-product whose worldwide production exceeds 422,800 ton per year [16]. The nut shell was milled to obtain a particle size of ~1 mm, then washed with deionized water, dried and stored in plastic containers for posterior usage.

The samples of biochar were obtained using radiant heating supplied by a Carbolite MRF 16/22 furnace under the vapors released. To estimate the significance of the preparation conditions of the biochar in the adsorption of metallic species, an L_{16} orthogonal array of the Taguchi method was used. The studied factors were the mass of precursor (factor A), drying temperature (factor B), heating rate (factor C), maximum temperature of thermal treatment (factor D) and holding time (factor E) (See Table 1). The response variable (Y_{ij}) was the removal of the metallic species such as Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} and Al^{3+} in single aqueous solutions. The orthogonal array was analyzed by means of the response variable for each run in the inner array as well as the variation using an appropriately chosen signal-to-noise ratio (S/N), which is derived from a quadratic loss function and it can be calculated by the following equation:

$$\frac{S}{N} = -10 \log \frac{\sum_{i=1}^{16} 1/Y_{ij}^2}{n} \quad (1)$$

Where n is the replication number of the experiment. The parameter A_{ij} is defined as the sum of the experimental indexes of all levels of factor i ($i=A, B, C, D, E$) and the largest value of A_{ij} represents the optimal level of each factor.

The analysis of variance (ANOVA) was applied to the data obtained in order to perform a systematic analysis of the relative importance of each factor on the metallic removal, according to the follow equations:

$$SS_T = \sum_{j=1}^N Y_{ij}^2 - \frac{\left(\sum_{j=1}^N Y_{ij}^2\right)^2}{N} \quad (2)$$

$$SS_i = \frac{1}{n_{Ai}} \sum_{j=1}^{k_A} A_{ij}^2 - \frac{\left(\sum_{j=1}^N Y_{ij}^2\right)^2}{N} \quad (3)$$

$$\sigma_A = SS_A / v_A \quad (4)$$

Where N is the total of number of observations, A_i is the sum of observations under the level i , n_{Ai} is the number of observation under the i level, k_A is the number of levels of the factor A, SS_T is the total sum of squares, SS_A is the sum of squares for factor A, σ_A is the variance of factor A, and v_A are the degrees of freedom of factor A (i.e., k_A-1) [17].

2.2 Characterization of the biochars

Textural parameters of the biochars were calculated from nitrogen adsorption isotherms at -196°C , measured in a Micromeritics ASAP 2420 analyzer. Samples of

biochar were previously outgassed at 200 °C during 8 h and the experimental points of the nitrogen isotherms were analyzed using suitable models for microporous and mesoporous materials.

The functional groups of biochar samples were determined at room temperature using a Nicolet-8700 FT-IR spectrometer (Thermo Electron Co.) equipped with a Smart Orbit accessory, which is a horizontal single-reflection attenuated total reflectance (ATR) accessory (HATR) with a Type IIA diamond crystal. A deuterated triglycine sulfate (DTGS) detector was used to collect the IR spectra in the 4000–500 cm⁻¹ spectral range.

Elemental analysis (C, N, H, S and O) of the samples was carried out in appropriate LECO instruments. Proximate analysis was performed in a TGA Q5000 apparatus (TA Instruments). In a typical proximate analysis experiment, ca. 35 mg of sample was placed in a Pt crucible and heated up to 850 °C at 10 °C/min under 50 ml/min of N₂. Once the maximum temperature was reached, the inlet gas was switched to air (50 ml/min) and kept for 30 min at 850 °C. Moisture, volatile and ash contents were determined from the mass losses ascribed to the different thermal events as follows: moisture, up to 180 °C in N₂, volatile, up to 850 °C in N₂, ash, at 850 °C in air. Additionally, the morphology and surface composition of biochar was studied by SEM/EDX analyses using a FE-SEM system Quanta FEG 650, FEI. Solid particles were dispersed on a graphite adhesive tab placed on an aluminum stub and no further coating was required.

2.3 Adsorption of metallic species and simulation of adsorption mechanism

The adsorption of Pb²⁺, Cd²⁺, Cu²⁺, Zn²⁺ and Al³⁺ in aqueous solutions was studied using as adsorbents the samples of biochar prepared according to the L₁₆ orthogonal array of the Taguchi method. The metal solutions with an initial concentration of 500 mg/L were

prepared by dissolving metallic salts ($\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) in deionized water (Milli-Q). The reagents were analytical grade from J.T Baker and Sigma-Aldrich. The pH of the metallic solutions was adjusted initially with HNO_3 (0.1 M) at pH 5 for Pb^{2+} , Cd^{2+} and Zn^{2+} ; at pH 4 for Cu^{2+} and pH 3 for Al^{3+} . The values were selected according to the speciation diagram of each metal in solution to prevent the metal precipitation in the adsorption experiments [18].

Adsorption experiments were carried out in batch systems under constant stirring (200 rpm). Specifically, 10 ml of the metal solution was added to 0.02 g of biochar and the suspension was stirred at 30 °C until equilibrium was reached (74 h). Finally, the solution was separated and the metal concentration (Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+}) was analyzed by atomic absorption spectroscopy employing a Perkin Elmer Analyst 100 spectrometer. The Al^{3+} concentration was determined by Uv-Vis Spectroscopy using a standardized method of HACH techniques (No 8012) in a Hach DR-5000 spectrophotometer. The metal concentration at the equilibrium was calculated from the respective calibration curve.

The adsorbed amount of metal, q , (mg/g) was calculated using a mass balance using the relationship given in Eq. (5)

$$q = \left(\frac{C_0 - C_e}{w} \right) V \quad (5)$$

Where C_0 and C_e are the initial and equilibrium metal concentration, respectively (mg/L), V is the volume of the solution (L) and w is the mass of the biochar used (g).

Finally, the adsorption mechanism of heavy metals (Pb^{2+} , Cu^{2+} , Cd^{2+} , Al^{3+} and Zn^{2+} respectively) on functionalized graphene with hydroxyl and carboxyl groups (model structure of biochar) was studied by molecular simulation employing the PM3

semiempirical method modeling employing 100 cycles for obtaining Gibbs free energy (ΔG), dipole moment and QSAR properties of the molecules considered in this work. Specifically, the Hyperchem 8v software was employed in the simulation with a DELL computer with i7 processor.

3. Results and discussion

3.1 Yield of Biochar

In the present work, 16 different samples of biochar were prepared according to the L_{16} orthogonal array of the Taguchi method. Table 1 shows the experimental conditions used in the preparation of each sample of biochar and the yield obtained. It is important to remark that the samples of biochar were obtained without physical or chemical activation, at low temperatures of thermal treatment and using relatively short processing times (Factor D and E in Table 1, respectively) in comparison with data reported in the literature. Typically, temperatures between 300 and 900 °C are used for the preparation of biochar by conventional pyrolysis, whereas flash carbonization requires temperatures ranging between 300-600 °C and gasification temperatures are higher than 500 °C [15].

Results shown in Table 1 and Fig. 1 indicate that the yield of the samples of biochar decreases linearly with temperature from 79.5% until 27% (in average), independently of the other conditions of synthesis. The coefficient of linear regression (R^2) of yield vs temperature was 0.9202 with the following linear equation:

$$Y = -0.3415T + 141.73 \quad (6)$$

Where Y is the yield of biochar (%), T is the maximum temperature of thermal treatment (°C) (See Fig. 1). The correlation between yield of biochar and temperature of thermal treatment observed in this study is congruent with other data reported in the literature. For example, in the preparation of biochar from conocarpus waste at different temperatures the yield of biochar decreased from 51.33 to 23.19% when the temperature increased from 200 to 800 °C [19]. Also, for biochars obtained from straw and lignosulfonate, a similar behavior was observed with a diminution in the yield from 84.95 to 30.89 %, when using temperatures of 200 and 600 °C [20].

3.2 Adsorption of metallic species using samples of biochar

The adsorption of some metallic species (Al^{3+} , Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+}) was studied on the 16 samples of biochar. Fig. 2 shows the adsorption results for all samples. In general, the adsorption follows the following trend $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Al}^{3+} > \text{Zn}^{2+}$. Specifically, samples B-4 and B-6 were the most efficient materials for the adsorption of Pb^{2+} , Cu^{2+} and Cd^{2+} with adsorbed amounts between 100 and 130 mg/g for Pb^{2+} ; 39-51 mg/g for Cu^{2+} and 17-21 mg/g for Cd^{2+} . These samples were obtained using the highest temperature of thermal treatment considered in this work (350 °C), which is low compared with data cited in literature (See Table 1) [15]. In this case, with the purpose of determining which factor affects more the removal of metals by the biochars, a variance analysis (ANOVA) was obtained for each metal. It is important to mention that due to the low adsorption of Zn^{2+} on all biochars, results corresponding to this metal were excluded from the statistical analysis (Table 2). In general, for all metallic species, the maximum temperature of the thermal treatment shows the higher variance, thus indicating that this factor has a higher influence in the final properties of biochar for the efficient removal of

heavy metals. Specifically, the variance of Factor D for Pb^{2+} , Cu^{2+} , Cd^{2+} and Al^{3+} was 465.5, 45.4, 71.0 and 37.2, respectively (See Table 2).

In general, the adsorbed amounts of heavy metals on the biochars prepared in this work are higher than or similar to those obtained with other samples of biochar prepared from different type of lignocellulosic wastes. This behavior is possibly due to the principal components of lignocellulosic material (cellulose, hemicellulose and lignin) used as precursor which can be generate biochars with a relatively similar surface chemistry. For example, the biochar obtained by carbonization at 550 °C of a swine manure digestate reaches an adsorbed amount of 5.33 mg Zn^{2+}/g and 1.33 mg Cu^{2+}/g [21]. The biochars prepared from banana peels and cauliflower leaves by pyrolysis at 600 °C were efficient in the removal of Cu^{2+} , Cd^{2+} and Pb^{2+} . Specifically, the biochar prepared from banana peels had adsorption capacities of 75.99 mg Cu^{2+}/g , 121.3 mg Cd^{2+}/g and 247.1 mg Pb^{2+}/g . Additionally, for the biochar derived from cauliflower leaves the results were the following: 53.96 mg Cu^{2+}/g , 73.8 mg Cd^{2+}/g and 177.8 mg Pb^{2+}/g [22]. Also, a magnetic biochar prepared by pyrolysis of waste marine macro-algae doped with iron oxide particles showed adsorbed amounts of Cd^{2+} , Cu^{2+} and Zn^{2+} of 23.16, 55.86 and 22.22 mg/g, respectively [23]. However, the materials prepared in this work have the advantage that they were thermally treated at relatively low temperatures without any additional physical or chemical activation and using relatively short times of synthesis.

3.3 Statistical analysis and determination of optimum conditions of preparation of biochar

The adsorption results of Pb^{2+} , Cd^{2+} , Cu^{2+} and Al^{3+} were analyzed in terms of signal-to-noise ratio (S/N) to maximize the adsorbed amount (See section 2.1). Table 2 shows the

mean of S/N ratio for each factor and metallic species, and with this information, the effect graphs were built (See Fig. 3). The interpretation of the effect graphs allows us to identify the highest values of the S/N ratio for each factor (see arrows in Fig. 3). These maximum values define the optimum conditions to prepare the best biochars for the adsorption of each metallic species. For example, for the removal of Pb^{+2} the optimum carbon must be prepared under the following conditions: Mass of precursor (5 g), drying temperature ($40^{\circ}C$), heating rate ($5^{\circ}C/min$), maximum temperature of thermal treatment ($350^{\circ}C$) and holding time (50 min). These conditions correspond to the following factors and levels (A_1 , B_1 , C_1 , D_4 , E_4). Also, the best conditions to prepare efficient carbons for the removal of Cd^{2+} , Cu^{2+} and Al^{3+} were obtained following a similar procedure. The conditions for Cd^{2+} were A_2 , B_4 , C_2 , D_4 , E_2 ; for Cu^{2+} are A_2 , B_4 , C_4 , D_4 , E_4 and finally, for Al^{3+} are A_4 , B_2 , C_2 , D_4 , E_2 . For all metals, the optimum factor D (maximum temperature of thermal treatment) is always at level 4 ($350^{\circ}C$). This behavior is congruent with the ANOVA analysis because the maximum temperature of the thermal treatment was the factor having a higher influence in the final properties of the biochars for the removal of all heavy metals studied in this work.

Samples of biochar obtained using the optimum conditions for the removal of Pb^{2+} , Cd^{2+} , Cu^{2+} and Al^{+3} were finally prepared and denoted as O-Pb, O-Cd, O-Cu and O-Al. The adsorption results on these optimum carbons are shown in Fig. 2. As expected, the adsorbed amount of all metallic species on the optimum material was higher than the 16 samples of biochar prepared according to the L_{16} orthogonal array of the Taguchi method. Specifically, the adsorbed amounts on the optimum carbons for Pb^{2+} , Cd^{2+} , Cu^{2+} and Al^{3+} were 129.86 mg/g, 21.69 mg/g, 57.83 mg/g and 21 mg/g, respectively.

3.4 Characterization of optimum biochars

The samples of biochar obtained using the optimum conditions for each metallic species were characterized using different analytical techniques with the purpose to determine the principal textural and chemical properties. Table 3 contains the results of the ultimate and proximate analyses of O-Pb, O-Cd, O-Cu and O-Al. In general, the four samples of biochar had higher amounts of carbon (63.66-69.07 %) and oxygen (25.99-33.21 %), whereas sulfur was not detected. This information is congruent with the data obtained by EDX analysis (See Fig. 4), where the principal elements identified were C (62.84-66.55 %), O (28.35-31.97 %) and Ca (2.67 %). Additionally, the biochar denoted as O-Cu was the material with a higher percentage of moisture (10.28 %), volatile matter (37.92 %) and ashes (4.97 %). These values are congruent with the preparation conditions because the heating rate for this sample was the highest (20 °C/min) in comparison with the other optimum biochars (5 and 10 °C/min).

The high heating value (HHV) defined as the complete combustion of a unit quantity of fuel was calculated for the optimum biochar following the equation of Channiwala [24].

$$\text{HHV}(\text{MJ kg}^{-1}) = 0.3491\text{C} + 1.1783\text{H} - 0.1034\text{O} - 0.0211\text{A} + 0.1005\text{S} - 0.0151\text{N} \quad (7)$$

where C is the weight percentage of carbon, H of hydrogen, O of oxygen, A of ash, S of sulfur and N of nitrogen. Specifically, HHVs of the optimum carbons are included in Table 3. The four samples have a high HHV (O-Pb:23.08 MJ/kg, O-Cd: 22.33 MJ/kg, O-Cu: 20.68 MJ/kg and O-Al: 24 MJ/kg). These values are comparable with the data reported in the literature for different type of biochar obtained from oil palm biomass (23 MJ/kg), olive mill waste (31 MJ/kg) and corn Stover (27.5 MJ/kg) [25-27].

On the other hand, Fig. 5 shows the FT-IR spectra of O-Pb, O-Cd, O-Cu and O-Al. The four spectra were quite similar. Particularly, the principal peaks identified in the FT-IR spectra of samples of biochar were the following: At 3400 cm^{-1} and $\sim 2923\text{ cm}^{-1}$ the peaks correspond to O-H and C-H stretching vibrations of phenolic and methyl groups, respectively. The peak at 1620 cm^{-1} is assigned to the C=O stretching vibration of carboxylic groups and the wide peak at $\sim 1101\text{ cm}^{-1}$ is characteristic of the C-O stretching vibration of ether groups [27]. This information is congruent with the functional groups identified in other type of biochar obtained from pine sawdust and from an aerobically composted mixture of sawdust of swine manure [28-29].

Additionally, the N_2 adsorption isotherms at $-196\text{ }^\circ\text{C}$ are shown in Fig. 6 and according with the IUPAC classification the four isotherms are type I, which are characteristics of microporous solids. Selected textural parameters of the optimum biochars were obtained from these experimental data by using BET and Dubinin-Radushkevich models and values of these parameters are collected in Table 4. The four optimum carbons have a relatively low specific surface area, with O-Cu showing the highest S_{BET} ($332\text{ m}^2/\text{g}$). This sample was prepared using the highest maximum temperature of thermal treatment ($350\text{ }^\circ\text{C}$), heating rate ($20\text{ }^\circ\text{C}/\text{min}$) and holding time (50 min). This information is congruent with the morphology of the samples because they are irregular particles with scarce pores (See Fig. 4).

3.5 Adsorption mechanism of metallic species using molecular simulation

The adsorption mechanism of metals (Pb^{2+} , Cu^{2+} , Cd^{2+} , Al^{3+} , Zn^{2+}) on the samples of biochar was analyzed by molecular simulation considering graphene as model structure of

biochar because it has a rigid structure and the interaction with metallic species can be analyzed in terms of the properties of metals. Fig. 7a shows the model structure of graphene containing the main oxygen functional groups identified by FT-IR spectroscopy (carboxylic and phenolic groups). The optimization geometry was calculated using the PM3 semi-empirical method where Table 5 shows that the process of adsorption of heavy metals is carried out spontaneously. Additionally, Fig. 7 include the interaction of the molecule of graphene with the metallic species: Pb^{2+} (b), Cu^{2+} (c), Cd^{2+} (d), Al^{3+} (e) and Zn^{2+} (f). In general, a clear trend was observed with Pb^{2+} ions interacting strongly with the molecule of graphene. Both oxygen functional groups and the aromatic rings of graphene participate in this interaction. In terms of electronegativity, Pb^{2+} has the highest (2.33) in comparison with the rest of metals under study (Cu^{2+} :1.9, Cd^{2+} :1.69, Al^{3+} :1.61 and Zn^{2+} :1.65) and consequently, the dipole moment generated between the Pb^{2+} ions and the graphene is the highest (16.50 Debyes) due to an increase in the polarity of bonds [30]. The dipole moment of the interaction of the metallic species with graphene is shown in Table 5. A clear trend is observed ($\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Al}^{3+} > \text{Zn}^{2+}$), which matches the adsorption results (See Table 5 and Fig. 2).

On the other hand, in Table 6 are showing the bond lengths ($\text{\AA}$) of the principal groups in the model biochar structure (C=O, O-H, C-O and C-C bonds); which were obtained applying the PM3 semi-empirical method. In this case is evident that the hexagons of the graphene do not show deformation due to rigid structure of the molecule and the results of bond lengths are congruent with the data reported in the literature (See Table 6) [31].

The carboxylic acid groups of biochar influence the adsorption of metals by a complexation mechanism [32-33], which is represented by equation (8):

Where M is the metallic ion with charge n^+ . This mechanism predicts an increase of protons in the aqueous solution after the adsorption process and this prediction was corroborated with the measure of the final pH in all adsorption experiments. In general, for all metals a decrease in the solution pH was observed after adsorption on the optimum samples of biochar. For example, the pH of the initial solution of Pb^{2+} was 5 and the equilibrium solution after the adsorption experiments on O-Pb had a pH of 3.53. Similarly, for the solution of Cd^{2+} , the initial pH decreased from 5 to 3.66 (O-Cd), for Cu^{2+} from 4 to 3.09 (O-Cu) and for Al^{3+} from 3 to 2.9 (O-Al).

Additionally, the mechanism depicted by equation 8 was confirmed by FT-IR spectroscopy. Fig. 5 shows the FT-IR spectra of the optimum samples of biochar before (O-Pb, O-Cd, O-Cu and O-Al) and after the adsorption experiments (O-Pb-S, O-Cd-S, O-Cu-S and O-Al-S). Only the peaks assigned to hydroxyl and carboxylic groups were shifting. Specifically, the peak assigned to C-O stretching vibrations at 1101 cm^{-1} shifted after adsorption of heavy metals. This behavior could be related with the possible mechanism of complexation of the carboxylic acid groups with heavy metals. Similar adsorption mechanisms have been reported for adsorbents containing oxygen groups, such as graphene oxide and graphene oxide [34-36]

4. Conclusions

A sustainable process route has been established to obtain biochars from *Carya illinoensis* shells by using short times and relatively low temperatures of carbonization, i.e., with low energy requirements. Also, it is possible to optimize the conditions of preparation of biochars using an orthogonal experimental design. It was found that the Pb^{2+} ,

Cu²⁺, Cd²⁺ and Al³⁺ uptake was higher on the optimum biochars, which were obtained at temperatures as low as 350 °C. Particularly, the mechanisms proposed on the metal removal are governed both by the presence of surface oxygen groups on biochar. Specifically, the adsorption seems related directly with the dipole moment observed in the interaction of biochar with metals, which was higher for the more electronegative metal (Pb²⁺). This metal was absorbed in greater quantity (129.86 mg/g) on biochar, whereas Zn²⁺ was poorly adsorbed (maximum 3 mg/g).

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Graphical Abstract

Highlights

- ▶ Best synthesis conditions of biochar derived from *Carya illinoensis* were studied
- ▶ Low temperatures (200-350 °C) and processing times were used to obtain biochar
- ▶ Biochar with phenolic and carboxylic groups are efficient in the removal of metals
- ▶ Complexation and ionic exchange are the adsorption mechanisms of metals on biochar.

Captions

- Fig. 1 Correlation between the maximum temperature of thermal treatment used in the preparation of biochar and the average yield of biochar.
- Fig. 2 Adsorption results of Pb^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} and Al^{3+} using the samples of biochar prepared by L_{16} orthogonal array of Taguchi method and the optimum carbons
- Fig. 3 Plot of the effect of each factor on the adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} , and Al^{3+} Sem/edx
- Fig. 4 SEM imagen and EDX results of the optimum samples of biochar: O-Pb (a,e), O-Cu (b, f), O-Cd (c, g) and O-Al (d, h)
- Fig. 5 FT-IR spectra of the optimum samples of biochar before (O-Pb, O-Cu, O-Cd and O-Al) and after adsorption of heavy metals (O-Pb-S, O-Cu-S, O-Cd-S and O-Al-S)
- Fig. 6 Nitrogen adsorption isotherms at 77 K of the optimum carbons prepared for the removal of Pb^{2+} , Cd^{2+} , Cu^{2+} and Al^{3+}
- Fig. 7 Geometry optimization determined by PM3 semi-empirical method at 303.15K of graphene-COOH-OH (a), graphene-COOH-OH/ Pb^{+2} (b), graphene-COOH-OH/ Cu^{+2} (c), graphene-COOH-OH/ Cd^{+2} (d), graphene-COOH-OH/ Al^{+3} (e), and graphene-COOH-OH/ Zn^{+2} (f)

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Table 1. Factors and levels studied in the orthogonal design used in the preparation of biochar

Sample	Factor					Yield of Biochar, %
	A	B	C	D	E	
	Mass, g	Drying temperature, °C	Heating rate, °C/min	Maximum temperature of thermal treatment, °C	Holding time, min	
B-1	5	40	5	200	20	81
B-2	5	60	10	250	30	53
B-3	5	80	15	300	40	35
B-4	5	100	20	350	50	21
B-5	10	40	10	300	50	33
B-6	10	60	5	350	40	27
B-7	10	80	20	200	30	79
B-8	10	100	15	250	20	51
B-9	15	40	15	350	30	29
B-10	15	60	20	300	20	38
B-11	15	80	5	250	50	45
B-12	15	100	10	200	40	79
B-13	20	40	20	250	40	47
B-14	20	60	15	200	50	79
B-15	20	80	10	350	20	31
B-16	20	100	5	300	30	37

Table 2. Response for the orthogonal experiments and analysis of variance of the Pb^{2+} , Cd^{2+} , Cu^{2+} and Al^{3+} removal data.

Metal	Factor	Mean $(S/N)_{\text{HB}}$				Analysis of variance		
		Level 1	Level 2	Level 3	Level 4	Degrees of freedom	Sum of Squares	Variance
Pb^{2+}	A	31.6	18.4	30.9	28.4	3.0	444.5	148.2
	B	31.1	30.2	24.7	23.3	3.0	182.0	60.7
	C	32.6	30.3	23.3	23.1	3.0	280.3	93.4
	D	15.8	20.8	34.4	38.4	3.0	1396.4	465.5
	E	20.3	24.1	31.9	33.0	3.0	448.5	149.5
	Error							
	Total					15.0	2751.7	
Cd^{2+}	A	20.7	20.8	16.1	15.5	3.0	97.9	32.6
	B	17.1	15.9	19.2	20.9	3.0	58.5	19.5
	C	19.5	20.0	17.6	16.0	3.0	40.2	13.4
	D	13.4	16.4	20.5	22.8	3.0	213.0	71.0
	E	16.0	19.4	18.8	19.0	3.0	29.4	9.8
	Error							
	Total					15.0	438.9	
Cu^{2+}	A	24.3	27.3	25.0	25.3	3.0	20.6	6.9
	B	24.7	23.6	25.7	27.9	3.0	40.3	13.4
	C	26.4	24.1	24.7	26.8	3.0	19.8	6.6
	D	21.8	24.1	26.3	29.7	3.0	136.1	45.4
	E	22.9	24.8	26.8	27.4	3.0	49.9	16.6
	Error							
	Total					15.0	266.7	
Al^{3+}	A	20.5	19.4	18.6	22.9	3.0	40.9	13.6
	B	19.6	21.3	19.7	20.9	3.0	8.2	2.7
	C	18.4	21.4	20.8	20.8	3.0	21.1	7.0
	D	18.1	21.6	17.6	24.1	3.0	111.7	37.2
	E	19.9	21.6	20.3	19.6	3.0	9.4	3.1
	Error							
	Total					15.0	191.3	

Table 3. Results of ultimate and proximate analysis of the samples obtained by the optimum conditions

Sample	Ultimate analysis (dry basis)					Proximate analysis				
	C, %	H, %	N, %	S, %	O, %	Moisture, %	Volatile matter, %	Ashes, %	Fixed carbon, %	HHV ^a , MJ/kg
O-Pb	68.07	1.99	0.67	<0.01	28.41	4.65	36.96	3.65	54.74	23.08
O-Cd	66.50	2.02	0.62	<0.01	30.69	8.02	37.14	3.91	50.93	22.33
O-Cu	63.66	1.71	0.70	<0.01	33.21	10.28	37.92	4.97	46.83	20.68
O-Al	69.07	2.26	0.57	<0.01	25.99	6.29	33.80	3.67	56.24	24.00

^aHHV: High heating value calculated by Channiwala equation

Table 4. Textural parameters of O-Pb, O-Cd, O-Cu and O-Al

Sample	S_{BET} , m ² /g	V_t , cm ³ /g	V_{mic} , cm ³ /g
O-Pb	217	0.119	0.111
O-Cd	244	0.134	0.116
O-Cu	332	0.188	0.170
O-Al	127	0.067	0.065

^a S_{BET} : BET surface area.

^b V_t : Total pore volume.

^c V_{mic} : Dubinin-Radushkevich micropore volume.

Table 5. Gibbs free energy, dipole moment and QSAR properties of the molecules considered in this work

Properties	Biochar	Biochar -Pb ⁺²	Biochar-Cu ⁺²	Biochar-Cd ⁺²	Biochar-Al ⁺³	Biochar-Zn ⁺²
ΔG (kcal/mol)	- 121,277	- 127,808	- 124,864	- 122,573	- 122, 283	- 116,793
Dipole moment (Debyes)	7.512	16.50	15.32	14.38	13.24	12.19
Mass (amu)	494.42	908.82	621.51	719.22	548.38	625.16
Surface area ($\text{\AA}^2$)	585.03	679.56	877.53	719.64	835.67	637.27
Volume ($\text{\AA}^3$)	1,092.77	1,267.66	1,570.36	1,221.60	1,538.18	1,155.87

Table 6. Bond lengths of the main bonds in the heavy metal adsorption using the PM3 semi-empirical method.

Bonds	Biochar	Biochar	Biochar	Biochar	Biochar	Biochar	Data reported
	-COOH-OH	-COOH-OH	-COOH-OH	-COOH-OH	-COOH-OH	-COOH-OH	in the
		Pb ⁺²	Cu ⁺²	Cd ⁺²	Al ⁺³	Zn ⁺²	Literature
C=O (COOH)	1.2288	1.2191	1.2206	1.2187	1.2277	1.2274	1.22 [31]
C-O (COOH)	1.3271	1.3288	1.3269	1.3211	1.3296	1.3213	1.32 [31]
O-H (COOH)	0.9694	0.9691	0.9657	0.9688	0.9688	0.9691	0.969 [31]
C-O (C-OH)	1.3209	1.3261	1.3274	1.3208	1.3287	1.3221	1.32 [31]
O-H (C-OH)	0.9608	0.9553	0.9592	0.9605	0.9606	0.9605	0.969 [31]
C-C (Graphene)	1.4235	1.4246	1.4254	1.4255	1.4257	1.4258	1.42 [37]