Mercury removal from wastewater using agroindustrial waste adsorbents

Stephanie Giraldo¹ · Irma Robles² · Anyi Ramirez¹ · Elizabeth Flórez¹ · Nancy Acelas¹

Received: 8 December 2019 / Accepted: 9 April 2020 / Published online: 6 May 2020
© Springer Nature Switzerland AG 2020

Abstract

In this study, adsorbent materials were prepared from sugarcane bagasse and modified with thermal treatment and chemical activation through activating agents (ZnCl_2 and H_3PO_4). The modified adsorbents were then used to remove mercury (Hg(II)) from aqueous solutions. Batch adsorption experiments were performed to explore the influence of the kinetics, isotherm, and pH, on Hg(II) adsorption. The results demonstrated their high potential for Hg(II) adsorption (more than 90%) owing to the various functional groups generated via the thermochemical treatment. The adsorption process was best described by the pseudo-second-order kinetics model, the adsorption phenomenon is contemplated as a mechanism mixture due to the complex surface of the studied adsorbents, and the maximum adsorption capabilities in this study exceeded 11.47 mg g^{-1} . Hg(II) removal is related to the existence of functional groups, such as $-\text{COO}^-$, $-\text{O}^-$, $\text{C}=\text{C}$, and $\text{C}=\text{O}$, on the material surface that selectively bind the Hg(II) through complexation, electrostatic interaction, and complexation with electrons π . Based on these results, the adsorbent materials are determined to be effective for eliminating Hg(II) and a valuable alternative for treating water contaminated with mercury.

✉ Nancy Acelas, nyacelas@udem.edu.co | ¹Grupo de investigación Materiales Con Impacto (Mat&mpac), Facultad de Ciencias Básicas, Universidad de Medellín, Carrera 87 No. 30-65, Medellín, Colombia. ²Centro de Investigación y Desarrollo Tecnológico en Electroquímica S. C., Parque Tecnológico Querétaro, 76703 Sanfandila, Pedro Escobedo, Querétaro, México.

Graphic abstract

Keywords Adsorption · Mercury · Agroindustrial waste · Sugarcane bagasse · Kinetics · Isotherms

1 Introduction

Mercury (Hg(II)) is one of the most toxic heavy metals [33]; it causes adverse health effects in organisms upon chronic exposure [9] owing to its characteristics of bioaccumulation and high persistence. Anthropogenic activities, such as fuel consumption and artisanal gold mining, release high concentrations of mercury in air, soil, and water [17, 88]. Therefore, The World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) have declared the maximum acceptable concentrations of Hg(II) to be 0.002 mg L⁻¹ and 0.001 mg L⁻¹ in drinking water, respectively [87, 98]. Because of its toxicity, Hg(II) must be removed from water.

Several efficient techniques exist for Hg(II) removal from wastewater to meet the permissible limits required by law, among which chemical precipitation, reverse osmosis, and ion exchange are the most common ones [81]. Although these methods perform well, they are expensive, with high sludge production and by-product formation [60]. One of the most promising techniques is adsorption, because of its affordability, high efficiency, and easy operability in wastewater treatment plants. For these purposes, selective

and economical materials with high adsorption capabilities need to be developed [9].

Carbonaceous materials [30], such as activated carbon, carbon nanofibers, biochar, carbon nanotubes, and graphene oxides [35, 71, 79, 95], are effective in Hg(II) removal from aqueous solutions. Biochar is a carbon-rich material that contains various functional and is derived by the pyrolysis of waste biomass [15].

In Colombia, approximately 72 million tons of agroindustrial wastes are generated every year [27], which is not only an environmental issue but also an economic problem owing to its high final disposal costs. In the specific case of sugarcane bagasse (SB), 7 million tons are generated per year, of which only a small amount is used for manufacturing paper, energy generation activities [12], animal feeding, fertilizers among others [11]. Hence, the production of adsorbent materials from thermal treatments of agroindustrial residues denotes a very interesting utilization for all these wastes.

Many researchers have modified biochar to improve its metal adsorption performance [94]. For instance, in chemical processes, the transformation is generated through activating agents, of which the most commonly used, due

to their availability and cost, are ZnCl_2 and H_3PO_4 . ZnCl_2 is an efficient dehydration reagent that promotes the decomposition of carbonaceous materials, induces carbon aromatization, and restricts the formation of tars [5, 7, 29, 67, 73, 96], while H_3PO_4 is an oxidizing agent suitable for generating various functional groups on the surface [52, 61, 75, 89].

This activation aims to generate surface area, porosity, and diversity of functional groups, which are highly influenced by the preparation conditions of the adsorbent material, such as biomass nature, activation temperature, activation time, and the impregnation ratio (chemical agent: biomass). Therefore, the challenge in the production of adsorbents is to produce very specific carbonaceous materials that are suitable for certain applications [8, 13]. For example, using the same activating agent (H_3PO_4), surface areas ranging from 9 to $1274 \text{ m}^2 \text{ g}^{-1}$ may be obtained by just modifying some of these variables [4, 38, 49, 57, 58].

Hg(II) adsorption mechanisms are mainly caused by complexation, electrostatic interaction, $\text{Hg}-\pi$ bonds or ion exchange in the presence of superficial functional groups [16, 34, 37, 47, 78, 79, 93]. Therefore, biochar needs to be further improved with novel structures and well-surface properties, such as functional groups create via thermal treatment processes and chemical activations [25]. Because Hg(II) is mainly attracted by the oxygenated groups found in adsorbent materials [3, 79], and the carbonization at high temperatures releases surface groups that contain oxygen, temperatures below 600°C are ideal for adsorbent materials treatments. In addition, several studies have argued that one of the most important effects during Hg adsorption is the pH level of the solution, where greater removal is obtained at high pH values of 5–8 [53, 62, 78, 93]. At low pH values, repulsive forces occur because of the competition for adsorption sites between hydrogen and Hg(II) ions. When the pH level increases, the repulsion among the cations, surface sites of the material, and competitive effect of the hydrogen ions decreases. Therefore, the uptake of the metal increases [40], because the biochar surface contains oxygenated functional groups, such as lactonic, carboxylic, and phenolic groups, which are negatively charged at pH values greater than 5, thereby causing mercury adsorption [3].

In the present study, a novel, sustainable, economical, and ecofriendly adsorbent material to remove Hg was developed. SB waste was modified through thermal treatment and chemical activation using H_3PO_4 and ZnCl_2 , and the effect of the activation method on Hg(II) removal was evaluated. All the experiments were carried out under air calcination conditions, which is a more economical method for obtaining adsorbent materials. These adsorbents showed higher adsorption capacities

at low times compared to organic precursors reported in the literature for the removal of mercury. The materials obtained were characterized; the influence of the pH and the capabilities of the material for removing Hg(II) from aqueous solutions were assessed through adsorption tests using different kinetic and isothermal models that also help to describe the adsorption process of Hg(II) onto the modified SB waste. With this work, a value-added product from the valorization of sugarcane residues was achieved. From the physicochemical characterization as kinetic analysis, isotherms, FTIR, and Raman, it was concluded that mercury adsorption on adsorbent materials is carried out by a combination of adsorption processes, diffusion within pores, and interactions with surface functional groups.

2 Methodology

2.1 Materials and preparation

The stem of SB, of the Tahiti or “Otahití” variety, was obtained from a local beverage sales shop in the city of Medellín. This study used dried SB cut into small pieces of $\sim 5 \text{ mm}$ diameter and washed with abundant distilled water to remove impurities and other compounds. Finally, the biomass was oven-dried at 105°C for 12 h and stored until use.

2.2 Activation methods

The SB was subjected to a heat treatment in a muffle furnace at 550°C for 30 min, in order to produce calcined sugarcane bagasse (CSB); this sample was then chemically activated using H_3PO_4 and ZnCl_2 . For this purpose, 30 g of SB was submerged in a 20% H_3PO_4 solution for 5 h. Then, the activated sample was placed in an oven at 110°C for 12 h, followed by 1 h in a muffle furnace at 300°C ; once the sample reached the room temperature, it was washed with hot water distilled at 80°C , until the pH stabilized between 6 and 7, to obtain the SBH material [28]. On the other hand, 30 g of SB was impregnated with ZnCl_2 and stirred at 200 rpm for 24 h. Then, the activated sample was placed in a muffle furnace at 550°C for 30 min and submerged in HCl, with continuous stirring at 150 rpm for 3 h. After that, the sample was washed with distilled water until its pH level stabilized between 6 and 7, to obtain the SBZ material [64]. Finally, the activated materials with H_3PO_4 (SBH) and ZnCl_2 (SBZ) were vacuum-filtered, oven-dried at 105°C for 12 h, and macerated until being passed through a sieve of particle size $< 0.149 \text{ mm}$.

2.3 Physicochemical characterization

2.3.1 Chemical composition and morphological properties

To determine the biomass composition of SB, a proximate analysis was performed using TGA Q500 from TA Instruments. Additionally, an elemental analysis was conducted using the ASTM D-5373-08 method using the CHNSO TrueSpec® Micro from LECO. The surface area and pore volume of the adsorbent materials were predetermined using the BET method, and the morphology of the materials was determined using SEM (Oxford Instruments).

2.3.2 Superficial chemical characterization

To determine the acidic and basic groups in the materials, Boehm titrations were performed following a standardized method [26], which involved weighing 1 g of the different adsorbent materials and adding them to 50 mL of a 0.05 M NaOH solution and a 0.05 M HCl solution to determine the acidic and basic groups, respectively. The samples were constantly agitated at 200 rpm at 25 °C for 24 h and 5 days, respectively. At the end of the agitation time, a 10 mL aliquot was taken from each sample and titrated, and two drops of the indicator were added, using 0.1% methyl red for the base and 0.1% phenolphthalein for the acid. Finally, NaOH was titrated with 0.05 M HCl, while HCl was titrated with 0.05 M NaOH. The PZC was also determined by solid addition [10]. Finally, to identify the nature of all functional groups present in the modified materials, we used FTIR spectroscopy (Spectrum two-PerkinElmer) and a Raman Microscope DXR spectrophotometer (Thermo Scientific).

2.4 Adsorption tests

Material performance was assessed by conducting batch-type adsorption experiments, with agitation at a rate of 150 rpm using 0.0100 g of the adsorbent materials in 50 mL of 1 mg L⁻¹ synthetic solutions of Hg(II) prepared from HgCl₂ and a pH of 6. This pH was selected because it has been reported that wastewater has a pH level between 6 and 9 [9, 46, 51, 69], and this is the application focus matrix of the material developed. The Hg(II) concentration in the samples after reaching equilibrium was determined by atomic absorption using a cold hydride-steam generator (Thermo Scientific iCE 3000 Series).

The removal percentage (%R) and adsorption capacity (q_t) of Hg(II) were estimated using Eqs. 1 and 2, respectively.

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{C_0 - C_t}{w} \times V \quad (2)$$

where C_0 (mg L⁻¹) is the initial concentration of Hg(II) in the solution, C_t (mg L⁻¹) is the concentration of Hg(II) at time t , q_t (mg g⁻¹) is the amount of Hg(II) adsorbed at time t , V (L) is the volume of the solution, and w (g) is the mass of the adsorbent material.

2.5 Studies of adsorption isotherms

The adsorption experiments were performed at 25 °C using 0.0060–0.0140 g of the adsorbent material, 50 mL of a Hg(II) solution at a concentration of 1 mg L⁻¹, a pH level of 6, agitation at 150 rpm, and equilibrium times of 120, 240, and 300 min for CSB, SBH, and SBZ, respectively.

The Langmuir [44], Freundlich [24], Temkin [82], and Dubinin–Radushkevich [23] isothermal models were evaluated according to Eqs. 3, 4, 6, and 7 (Table 1), respectively.

2.6 Kinetic studies

Kinetics experiments were performed at 25 °C using 0.0100 g of the adsorbent materials, 50 mL of a Hg(II) solution at a concentration of 1 mg L⁻¹, pH level of 6, different contact times from 5 to 480 min, and agitation at 150 rpm.

Table 1 Isotherms of equation models

Langmuir	$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}$	(3)
Freundlich	$\text{Log} Q_e = \text{Log} K_F + \frac{1}{n} \text{Log} C_e$	(4)
Non-dimensional separation factor	$R_L = \frac{1}{1 + K_L C_i}$	(5)
Temkin	$q_e = \frac{RT}{b} \text{Ln} K_T + \frac{RT}{b} \text{Ln} C_e$	(6)
Dubinin–Radushkevich	$\text{Ln}(q_e) = \text{Ln}(q_s) - K_{ad} \epsilon^2$	(7)
Dubinin–Radushkevich constant	$\epsilon = RT \text{Ln} \left(1 + \frac{1}{C_e} \right)$	(8)
Free energy	$E = \frac{1}{\sqrt{2K_{ad}}}$	(9)

C_e : Hg(II) concentration in equilibrium (mg L⁻¹); q_e : amount of Hg(II) adsorbed at equilibrium (mg g⁻¹); Q_m : maximum capacity of adsorbate (mg g⁻¹); K_L : constant of Langmuir (L g⁻¹); K_F : Freundlich dissociation constant (mg g⁻¹); n : constant related to reaction intensity; R_L : non-dimensional separation factor; C_i : initial concentration of Hg(II) (mg L⁻¹); b : constant associated with the heat of adsorption (kJ mol⁻¹); K_T : Temkin constant (L g⁻¹); T : temperature (K); R : gas constant (0.008314 kJ mol⁻¹ K⁻¹); q_s : theoretical capacity of isothermal saturation (mg g⁻¹); K_{ad} : isothermal constant of Dubinin–Radushkevich (mol² kJ⁻²); ϵ : Dubinin–Radushkevich constant; E free energy (KJ mol⁻¹)

Table 2 Equation kinetic models

Pseudo-first order	$\text{Log}(q_e - q_t) = \text{Log}q_e - \frac{k_1}{2.303} t$	(10)
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	(11)
Intraparticle diffusion	$q_t = k_{di} \sqrt{t} + C_i$	(12)
Elovich	$q_t = \frac{1}{\beta} \ln(t) + \frac{t}{\beta} \ln(\alpha\beta)$	(13)

q_t : amount of Hg(II) adsorbed in time t (mg g^{-1}); q_e : amount of Hg(II) adsorbed at equilibrium (mg g^{-1}); t : time (min); k_1 : pseudo-first-order adsorption rate constant (min^{-1}); k_2 : constant rate of pseudo-second order ($\text{g mg}^{-1} \text{min}^{-1}$); k_{di} : intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$); C_i : constant (mg g^{-1}); α : initial rate constant ($\text{mg g}^{-1} \text{min}^{-1}$); β : desorption constant (g mg^{-1})

We assessed the pseudo-first-order [43], second-order [32], intraparticle diffusion [92], and Elovich [45] kinetic models using Eqs. 10–13 (Table 2), respectively.

3 Results and discussion

3.1 Physicochemical characterization

3.1.1 Chemical composition and morphological properties

In Table 3, the proximate analysis of the SB biomass can be observed. This biomass has a high content of volatile material and a fixed carbon content average at $\sim 12\%$, which is the amount of carbon available for transformation through a thermochemical transformation process. The high content of elemental carbon (46.5%) indicates that SB is a waste that can be considered as a precursor while producing adsorbent materials. These results are in the range of values reported in the literature for this agroindustrial waste [6, 78, 93].

In terms of morphology, the SEM micrographs presented in Fig. 1 indicate changes in SB before and after the transformation processes. The SB micrograph (Fig. 1a) shows irregular spaces with rough and uneven appearance, while the materials obtained from the thermal treatment (Fig. 1b) and chemically activated using ZnCl_2 (Fig. 1c) show proper porosity development and a relatively uniform structure. In the surface of the SBH material (Fig. 1d), no porosity development can be observed.

It can be related to the activating method to produce an adsorbent since it has been reported that in most of the biomass activated with H_3PO_4 , the materials with greater surface areas are those in which the activation temperature is greater than 600°C [52, 57, 58]. Therefore, activating method used for material transformations defines the chemical nature of the surface.

The micrographs are related to the values obtained from the surface area (Table 4). Herein, for the case of CSB and SBZ, values of 182.69 and $182.92 \text{ m}^2 \text{g}^{-1}$ are obtained, respectively, whereas for SB and SBH, values of 5.21 and $7.44 \text{ m}^2 \text{g}^{-1}$ are obtained. Consequently, both the chemical activation process using ZnCl_2 and thermal treatment are very efficient in improving the surface area of this agroindustrial waste. Similar studies have reported comparative results [47, 84].

3.1.2 Chemical characterization of the surface

Table 5 presents the quantification of acidic and basic functional groups found on the surface of the materials. Here, the materials without any chemical treatment (SB and CSB) indicate a higher concentration of basic groups, while the chemically activated materials (SBZ and SBH) display a greater number of acidic groups. For SB, the ratio between the acidic groups ($0.553 \text{ mmol g}^{-1}$) and basic groups ($0.621 \text{ mmol g}^{-1}$) is 1.1 , which indicates almost neutral biomass. For CSB, the ratio is 2 , which indicates that the basic groups predominate, whereas acidic groups predominate for SBZ and SBH. Knowledge of the type of functional groups helps to predict the pH level at which these materials can actively remove Hg(II). Notably, the Boehm titration method used herein only considers acidity in phenols, lactones, and carboxylic acids. Hence, the number of acidic groups present may even be higher than that reported for each material. Therefore, species such as quinones and other alcohols, which generate acidity in the materials, are not considered in Boehm titration [85, 93]. Another important parameter to be considered in the surface of adsorbent materials is the pH of PZC (pH_{PZC}) (see Fig. 2), which refers to the pH at which its net surface charge is zero.

Table 3 Biomass properties

Biomass	Moisture content (%)	Proximate analysis (Wt%) ^a			Elemental analysis (Wt%) ^a			
		MV	CF	Ashes	N	C	H	O ^b
SB	5.43	87.54	12.46	0	0.40	46.50	4.90	48.20

MV volatile material, CF fixed carbon, N nitrogen, C carbon, H hydrogen, O oxygen, SB sugarcane bagasse

^aOn dry basis

^bBy difference ($\text{O}\% = 100\% - \text{C}\% - \text{N}\% - \text{H}\%$)

Fig. 1 SEM micrograph of biomass and activated materials. **a** Sugarcane bagasse (SB) biomass; **b** calcined sugarcane bagasse (CSB); **c** sugarcane bagasse activated using ZnCl_2 (SBZ); **d** sugarcane bagasse activated using H_3PO_4 (SBH)

Table 4 Texture properties of the adsorbent materials

Material	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
SB	5.21	0.002
CSB	182.69	0.081
SBZ	182.92	0.079
SBH	7.44	0.013

Table 5 Surface chemical properties of the adsorbent materials

Material	Basic groups (mmol g^{-1})	Acidic groups (mmol g^{-1})	$\text{pH}_{(\text{PZC})}$
SB	0.621 ± 0.019	0.553 ± 0.039	6.650 ± 0.212
CSB	2.220 ± 0.000	1.166 ± 0.079	6.500 ± 0.283
SBZ	0.957 ± 0.019	1.394 ± 0.013	6.450 ± 0.071
SBH	1.288 ± 0.020	1.483 ± 0.059	7.000 ± 0.141

Therefore, when the pH of the system is greater than $\text{pH}_{(\text{PZC})}$, the materials are negatively charged and appropriate conditions are generated for electrostatic interactions with metal cations ($\text{Hg}(\text{II})$), which favors the adsorption process. Some functional groups responsible for this process are $-\text{COO}^-$ and $-\text{O}^-$, which are deprotonated under these pH conditions. In contrast, when the pH of the system is less than $\text{pH}_{(\text{PZC})}$, the material surface is positively charged and metal cations are repulsed. Thus, for the system studied herein, pH values greater than 5 can possibly favor the adsorption process, which agrees with the results of previous reports [9, 69].

To have a broader view of all functional groups present in the adsorbent materials, FTIR analysis are conducted on both the biomass and adsorbent materials. Figure 3 denotes the FTIR spectra of these materials. Generally, for all materials, the same types of signals can be observed; signals of the biomass are more intense than those of the modified materials. An exception to this is the signal at $\sim 3346 \text{ cm}^{-1}$, which is easily observed in SB, a material that has not undergone chemical alterations, whereas for

Fig. 2 $\text{pH}_{(\text{PZC})}$ of biomass and activated materials. **a** Sugarcane bagasse (SB) biomass; **b** calcined sugarcane bagasse (CSB); **c** sugarcane bagasse activated using ZnCl_2 (SBZ); **d** sugarcane bagasse activated using H_3PO_4 (SBH)

the activated materials CSB, SBZ, and SBH, this signal disappears. This signal is attributed to the stretching vibrations of $-\text{OH}$, indicating the presence of water along with hemicellulose for the specific case of the biomass [21]. The decrease in peak intensity for the modified materials is associated with the denaturation of the fibers when subjected to thermal treatments, which generate ruptures in the compounds bonds and species disintegration [63, 78].

Various FTIR signals indicate the richness of the materials in terms of functional groups, among which carboxylic acids, aromatic groups, aliphatic chains, alcohols, ethers, and esters can be highlighted. For example, the signal at $\sim 2975 \text{ cm}^{-1}$ demonstrates the presence of methyl, methylenes, and methoxy groups and is related to the stretching vibration of aliphatic C-H bonds [56]. Aromatics are evidenced by bands located

at $\sim 1635 \text{ cm}^{-1}$ ($\text{C}=\text{C}$) [31] and at $\sim 592 \text{ cm}^{-1}$ (C-H) [22]. Signals at $\sim 1736 \text{ cm}^{-1}$ ($\text{C}=\text{O}$), $\sim 1025 \text{ cm}^{-1}$ (C-O-R), and $\sim 1380 \text{ cm}^{-1}$ (C-O) indicate the presence of carboxylic acids and esters [56, 63, 14]. Similarly, the band located at $\sim 1025 \text{ cm}^{-1}$ corresponds to the C-O-H alcohols [14]. The band at $\sim 1466 \text{ cm}^{-1}$ represents aliphatic chains ($-\text{CH}_2$ and $-\text{CH}_3$) and methoxy groups (O-CH_3) present in lignocellulosic materials even after chemical activation [14]. Notably, the results obtained for SBZ and SBH materials present poorly defined signals, showing a decrease in the intensity of the bands attributed to the oxygenated functional groups, and these results are similar to those reported in the literature for adsorbent materials obtained using agroindustry waste [1, 2, 8, 41, 84, 86].

Fig. 3 FTIR spectra of biomass and adsorbent materials. SB: sugarcane bagasse; CSB: calcined sugarcane bagasse; SBZ: sugarcane bagasse activated by ZnCl_2 ; SBH: sugarcane bagasse activated by H_3PO_4

Raman spectroscopy, which is very sensitive to structural changes that disturb the symmetric transitions generated in different allotropic forms of carbon, is a complementary analysis to FTIR. Generally, a wide band between 1500 and 1550 cm^{-1} in carbonaceous materials is associated with bonds between amorphous structures, particularly with carbons exhibiting interstitial defects [36].

The analyzed samples possess two characteristic bands of carbonaceous structures (at $\sim 1350 \text{ cm}^{-1}$ and at $\sim 1605 \text{ cm}^{-1}$) (Fig. 4). The signal at 1350 cm^{-1} , known as the D band, is related to structural defects (structure disorder), while that at 1605 cm^{-1} , known as the G band, is related to graphite structures. If the modified materials (CSB, SBZ, and SBH) are compared before and after the adsorption process, changes in the intensity can be observed in these two bands, thereby indicating variation in the carbonaceous structure. The degree of graphitization or defects in a carbonaceous material can be estimated by the (I_D/I_G) relation between the D and G bands [97]. Therefore, $I_D/I_G < 1$ values account for a more ordered carbonaceous material. Herein, the values obtained from the I_D/I_G ratio are 1.41, 0.59, and 0.71 for CSB, SBZ, and SBH, respectively. Consequently, the chemically modified

materials exhibit a higher order because the activating agents improve the distribution of the structures in the activation process. Equally, the I_D/I_G ratios for the materials after being used to adsorb Hg(II) are 1.45, 1.42, and 0.64 for CSB, SBZ, and SBH, respectively, indicating that the mercury adsorption for the SBZ material directly affects the order level in the structure.

A lower I_D/I_G value indicates more aromatic ring structures and less carbon-containing defects, which leads to the formation of oxygen-containing functional groups on the carbon materials surface. The I_D/I_G ratio for the H_3PO_4 -activated carbon results in a slightly higher value than ZnCl_2 -activated carbon. This indicates that the use of H_3PO_4 as an activating agent produces more disordered sp^2 carbon atoms. On the other hand, the precursor possesses fewer aromatic ring structures and more carbon-containing defects in the presence of oxygen functional groups on the CSB surface. After the sorption of mercury, the I_D/I_G ratio is modified. Since the I_D/I_G ratio of H_3PO_4 decreases compared to ZnCl_2 and the precursor, a reduction in I_D/I_G ratio may represent the formation of a high-ordered surface, compared to the precursor and the ZnCl_2 -activated carbon, which shows an increase in

Fig. 4 Raman spectroscopy of adsorbent materials before and after adsorption. **a** Calcined sugarcane bagasse (CSB); **b** sugarcane bagasse activated by ZnCl_2 (SBZ); **c** sugarcane bagasse activated using H_3PO_4 (SBH)

Fig. 5 Comparison of Hg(II) removal in the adsorbent materials (adsorbent amount: 0.0100 g, Hg(II) concentration: 1 mg L⁻¹, amount of Hg(II) solution: 50 mL, pH: 6, time: 2 h)

Fig. 6 pH effect on Hg(II) removal using the CSB adsorbent material (adsorbent amount: 0.0100 g, Hg(II) concentration: 1 mg L⁻¹, amount of Hg(II) solution: 50 mL, time: 2 h)

I_D/I_G ratio. This behavior is attributed mainly to the surface modification, and surface defects can promote a higher sorption capacity on the cavities of the porous materials [39, 54, 59].

3.2 Adsorption tests

Figure 5 shows the mercury removal performance of SB, CSB, SBZ, and SBH under the adsorption conditions described in the experimental section. The removal performance for the precursor material SB is 21%, and those for the modified materials, CSB, SBZ, and SBH, are 95%, 85%, and 88%, respectively.

Table 6 Parameters of Hg(II) adsorption isotherms with different adsorbent materials

Material	CSB	SBZ
<i>Langmuir</i>		
Q_m (mg g ⁻¹)	13.55	11.47
K_L (L g ⁻¹)	6.96	10.38
R_L	0.11	0.08
R^2	0.97	1.00
<i>Freundlich</i>		
K_F (mg g ⁻¹)	16.34	13.13
N	2.13	2.77
R^2	0.96	0.96
<i>Temkin</i>		
K_T (L g ⁻¹)	57.81	106.48
b (kJ mol ⁻¹)	0.77	1.01
R^2	0.97	0.99
<i>Dubinin–Radushkevich</i>		
K_{ad} (mol ² kJ ⁻²)	0.02	0.02
q_s (mg g ⁻¹)	12.15	10.98
E (KJ mol ⁻¹)	4.78	5.29
R^2	0.97	1.00

and 88%, respectively. This indicates that the activating methods to modify the biomass are very efficient and can considerably improve Hg(II) adsorption. Additionally, from the experimental data of this study, it can be seen that the removal performance of Hg(II) is related to the nature of the functional groups, rather than to the development of porosity and surface area. For instance, the surface area for SBZ is 24.5 times greater than the SBH area and both have a removal performance of Hg greater than 85%. This trend is consistent with that observed in previous reports [50, 93]. Additional explanations can be also evidenced by the results obtained with the FTIR.

3.3 pH effect

The pH effect is a very important factor in adsorption process, particularly in the adsorption of metals. The pH of the medium controls the magnitude of the electrostatic charges distributed by the metal ion. Therefore, adsorption capacities can change depending on the pH level of the aqueous medium. The variation in the solution pH level affects the complexation behavior of the functional groups. For example, an increase in pH level ($pH > pH_{(PZC)}$) generates the deprotonation of most of the active functional groups in the adsorption making them effective to form complexes with the metallic cation (Hg(II)).

Figure 6 denotes the pH effect on Hg(II) removal percentages for the CSB adsorbent material. It can be observed that as the pH increases, the removal percentage

Fig. 7 Time effect on Hg(II) adsorption on adsorbent materials CSB, SBZ, and SBH

increases from 48 to 71% at pH levels of 4 and 10, respectively. This indicates that at pH around 6, which is closer to $pH_{(PZC)}$, high removal percentages may be obtained. Therefore, this pH level has been selected for all studies. Although a pH level of 4 is not an optimum value for adsorption, a 48% removal is evidenced, which may be related to ion-exchange mechanisms between H^+ and Hg(II), previously reported in the literature [47]. It is well known that the positive surface charge decreases as the pH level of the solution increases, which generates an electrostatic repulsion reduction between the metal and adsorbent material surface, thereby allowing for a greater removal percentage [46].

3.4 Adsorption isotherm analysis

Through isothermal models, the interaction between the metal ion and the adsorbent material, together with the adsorption capacity of the materials, can be determined. Table 6 provides the CSB and SBZ parameters obtained from the four models studied. Herein, R^2 is close to 1, which denotes that the model fits the data well. R_L is a Langmuir factor that specifies whether the adsorption is favorable. In this case, values are within the $0 < R_L < 1$ range, which indicates that the adsorption process is favorable, with maximum adsorption capabilities (Q_m) of 13.55 and 11.47 $mg\ g^{-1}$ for CSB and SBZ, respectively. According to Langmuir, the Hg(II) adsorption process for both CSB and SBZ occurs in homogeneous surface sites. Furthermore, values greater than 1 for the Freundlich constant n indicate that adsorption is a physical process. This synergy between Langmuir and Freundlich indicates that Hg(II) is adsorbed by the adsorbent materials through

Table 7 Kinetic model parameters in Hg(II) adsorption with different adsorbent materials

Material	CSB	SBZ	SBH
$q_{e\ exp}\ (mg\ g^{-1})$	4.82	4.01	4.49
<i>Pseudo-first order</i>			
$k_1\ (min^{-1}) \times 10^{-2}$	2.81	2.92	2.10
$q_e\ (mg\ g^{-1})$	3.21	3.07	1.75
R^2	0.97	0.97	0.92
<i>Pseudo-second order</i>			
$k_2\ (g\ mg^{-1}\ min^{-1}) \times 10^{-2}$	1.67	2.49	3.24
$q_e\ (mg\ g^{-1})$	5.12	4.05	4.61
R^2	1.00	1.00	1.00
<i>Intraparticle diffusion</i>			
$K_{d1}\ (mg\ g^{-1}\ min^{1/2})$	0.69	0.20	0.81
$C_1\ (mg\ g^{-1})$	0.01	1.16	0.05
R^2	0.95	1.00	0.98
$K_{d2}\ (mg\ g^{-1}\ min^{1/2})$	0.18	0.17	0.05
$C_2\ (mg\ g^{-1})$	2.87	2.18	3.71
R^2	1.00	1.00	1.00
<i>Elovich</i>			
$\beta\ (g\ mg^{-1})$	1.09	1.77	1.99
$\alpha\ (mg\ g^{-1}\ min^{-1})$	1.22	2.17	12.97
R^2	0.95	0.87	0.70

different interaction energies, as determined by (1) different functional groups and (2) diffusion within the pores. Both parameters b (Temkin) [99] and E (Dubinin–Radushkevich) [55] exhibit values less than $8\ kJ\ mol^{-1}$, suggesting the existence of weak physical Van der Waals interactions. All these results confirm a mixture mechanism for Hg(II) adsorption using the adsorbent materials.

3.5 Kinetic analysis of the adsorption process

The kinetic parameters are essential to predict the rate through which Hg(II) is removed from the aqueous solutions, understand the adsorption mechanism, and identify the step that determines the adsorption rate. Figure 7 shows the three materials that exhibit fast Hg(II) adsorption in the first 50 min, i.e., 80% for CSB and SBH and 60% for SBZ, followed by a slow process until reach the equilibrium. This can be related to the existence of a high number of active sites (porosity and functional groups) available for the adsorption process. In the case of SBH, where the surface area is much smaller than those of SBZ and CSB, the high removal of Hg(II) is due to the interaction of the metal cation with different functional groups present on the material surface. This result is consistent with those reported by [93], who demonstrated the effect of different functional groups in the adsorption process of Hg(II), where biochar with less surface area exhibits

Table 8 Comparison of maximum adsorption capabilities

Precursor material	Treatment	pH	Q_m (mg g ⁻¹)	Reference
CSB	Thermal treatment	6	13.6	In this study
SBZ	Chemical activation using ZnCl ₂	6	11.5	In this study
Ceiba pentandra hulls	Carbonization, steam activation	6	25.9	[35]
Wood chip	Pyrolysis	6	57.8	[62]
Hickory chips biochar	Pyrolysis	6	5.0	[93]
Bagasse biochar	Pyrolysis	6	13.0	[93]
Sugarcane bagasse	Washed with deionized water	4	35.7	[40]
Coconut activated carbon	Oxidized using H ₂ O ₂	7	5.2	[50]
Soybean stalk	Pyrolysis	7	0.67	[42]
Phragmites karka	Chemical treatment using ethanol, NaOH, CaCl ₂	7	2.3	[66]
Brazilian pepper	Pyrolysis	6	15.1	[18]
Corn straw	Pyrolysis chemical activation using Na ₂ S	6	5.1	[77]
C. arietinum waste	Pyrolysis	7	22.9	[65]
Garlic (<i>Allium sativum</i> L.)	Dried in a vacuum oven	–	0.6	[20]
S-MWCNT4060	Nitric acid oxidation	7	0.7	[19]
Multi-walled carbon nanotubes	–	6.5	13.5	[80]
Cobalt ferrite nanoparticles	Síntesis de nanocompuestos de sílice magnética	–	11.9	[76]
PEI-AC composite	Síntesis de carbón activado con polietilenimina	5	16.4	[72]
Polipirrol-CTS	Chemical polymerization of Py in the presence of a chitosan	–	40.0	[70]
POSS-SH	–	6	46.7	[91]
Guar gum	Cross-linked with epichlorohydrin and then oxidized to the polydialdehyde	5	41.1	[83]

greater effectiveness for Hg(II) adsorption with respect to activated carbon with a high surface area. Similar results for materials with low surface area and high percentages of mercury removal have been reported [47, 84, 90]. After 120, 300, and 240 min, CSB, SBZ, and SBH have correspondingly removed almost 100% of Hg(II) with a final concentration < 0.002 mg Hg(II) L⁻¹, which complies with most of the worldwide environmental agencies [98].

To understand the adsorption process, the pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich kinetic models were used to assess the experimental data. Table 7 presents the kinetic parameters obtained by each model, where the pseudo-second-order model best represents the adsorption process, with values of $R^2 = 1$, estimated values of q_e close to the experimental value, and Δq_e values of 5.78%, 1.04%, and 2.67% for CSB, SBZ, and SBH, respectively. These results suggest that chemisorption is a stage that determines the adsorption process, which confirms a strong interaction due to complexation through coordinated bonds.

In addition, the intraparticle diffusion model identifies the reaction pathways and adsorption mechanisms and predicts the stage that controls the adsorption rate. This model fits the data well for the three adsorbent materials. The values of k_{d1} are greater than those of k_{d2} (Table 7) for CSB, SBZ, and SBH, indicating that surface adsorption is

faster than the adsorption within the pores. Furthermore, the C_1 and C_2 values reveal the boundary layer effects, wherein for greater values of C_1 , there is a greater contribution from surface adsorption to the limiting step of the reaction rate. Finally, for all materials studied, the C_2 values are greater than the C_1 values. Therefore, multiple steps are involved in the Hg(II) adsorption process, external surface adsorption (chemisorption processes), and diffusion within the adsorbent pores. In the literature, similar results have been reported for Hg(II) removal using different biochars [69, 74].

3.6 Comparison with other adsorbents

When comparing the maximum adsorption capacity (Q_m) obtained for the materials transformed herein (Table 8) against others recently reported in the literature, it can be concluded that SB is a promising source for the production of adsorbents with high potential for Hg(II) removal from aqueous solutions.

3.7 Adsorption process

Previous studies have proven the existence of various mechanisms that govern the adsorption of metals on different types of biochar from water [47]. These mechanisms

Fig. 8 FTIR spectra of adsorbent materials before and after adsorption. **a** Calcined sugarcane bagasse (CSB); **b** sugarcane bagasse activated using ZnCl₂ (SBZ); **c** sugarcane bagasse activated using H₃PO₄ (SBH)

Fig. 9 Predominant processes of mercury adsorption in materials from SB

depend on biomass nature, thermochemical transformations, and the conditions during the adsorption process.

Figure 8 shows the spectra and the detailed peak assignments of CSB, SBZ, and SBH materials after being used in the mercury adsorption process. CSB with the thermal treatment shows an increase in the signals at 2975, 1736, and 1635 cm^{-1} because of the addition of mercury, while intensity decreases in the signal at 1025 cm^{-1} after adsorption. For chemically activated materials, the differences in the signals cannot be easily identified because of the absence or addition of mercury. However, SBZ evidences an increase in signals at 2975, 1380, and 1025 cm^{-1} , whereas SBH evidences an increase in signals at 1736 and 1025 cm^{-1} .

Overall, there is a clear interaction between Hg(II) and the oxygenated functional groups because of the interactions with free pairs of oxygen electrons and the aromatic structures (π -type bonds) present in the materials. Previous studies have reported that mercury compounds exhibit typical FTIR signals at 3500, 1750, and 600 cm^{-1} [68]. For the CSB and SBH materials, the band is observed at 1750 cm^{-1} , corresponding to the $\text{C}=\text{O}-\text{Hg}$ interaction, which is a typical signal reported in the literature for this type of process [53, 93]. Using the FTIR analysis, the active functional groups in different materials can be identified for Hg(II) adsorption.

The above mentioned results suggest the following predominant Hg(II) adsorption processes on the CSB, SBZ, and SBH adsorbent materials (Fig. 9): (1) electrostatic interaction between the Hg(II) metal cation and the negatively charged density at the biochar surface, (2) formation of $(-\text{COO})_2\text{Hg}$ and $(-\text{O})_2\text{Hg}$ complexes because of the interaction between Hg(II) and conjugate bases of the carboxylic and phenolic groups ($-\text{COO}^-$ and $-\text{O}^-$), and (3) interactions among Hg(II) and π , $\text{Hg}-\text{C}\pi$ electrons from the graphene structure ($\text{C}=\text{C}$), and $\text{C}=\text{O}$ present in the materials. These results are in agreement with previously reported studies [18, 47, 48, 93] and confirm that oxygenated functional

groups and aromatic structures ($\text{C}=\text{C}$, π electrons) are indispensable in the Hg(II) adsorption process.

4 Conclusions

The results of this study demonstrate that SB waste transformed thermochemically is effective for Hg(II) removal. A pH level of 6, which is closer to $\text{pH}_{(\text{PZC})}$, was deemed appropriate for the adsorption process with a Hg(II) removal rate of more than 90%. This study demonstrated that adsorbent materials (biochar) with low surface area and rich in oxygenated functional groups are effective in removing Hg(II). Hg(II) removal is related to the existence of functional groups, such as $-\text{COO}^-$, $-\text{O}^-$, $\text{C}=\text{C}$, and $\text{C}=\text{O}$, on the material surfaces that selectively bind the Hg(II) present in the aqueous solution through complexation, electrostatic interaction, and complexation with electrons π . These results agree with the kinetic and isothermal parameters, indicating that the adsorption process involves multiple steps and a mixture of physical and chemical interactions generated by the complex surface of the adsorbents studied herein. We thus conclude that adsorbent materials produced from sugarcane residues through simple and easily implemented methodologies can be a cost-effective alternative to using activated carbon to adsorb Hg(II) from wastewater.

Acknowledgements The authors are grateful to Colciencias for financing the project 120677757983, CT-648-2018. S. Giraldo thanks to the Center of Research and Technologic Development in Electrochemistry for allowing the research internship.

Funding This study was funded by Colciencias: Project 120677757983, CT-648-2018.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Ahmad M, Lee SS, Dou X et al (2012) Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. *Bioresour Technol* 118:536–544. <https://doi.org/10.1016/j.biortech.2012.05.042>
- Ahmad M, Lee SS, Rajapaksha AU et al (2013) Trichloroethylene adsorption by pine needle biochars produced at various pyrolysis temperatures. *Bioresour Technol* 143:615–622. <https://doi.org/10.1016/j.biortech.2013.06.033>
- Ahmadpour A, Zabihi M, Bastami TR et al (2016) Rapid removal of mercury ion (II) from aqueous solution by chemically activated eggplant hull adsorbent. *J Appl Res Water Wastewater* 6:236–240

4. Ahmaruzzaman M, Gayatri SL (2010) Activated tea waste as a potential low-cost adsorbent for the removal of p-nitrophenol from wastewater. *J Chem Eng Data* 55:4614–4623. <https://doi.org/10.1021/je100117s>
5. Ahmed MJ, Dhedan SK (2012) Equilibrium isotherms and kinetics modeling of methylene blue adsorption on agricultural wastes-based activated carbons. *Fluid Phase Equilib* 317:9–14. <https://doi.org/10.1016/j.fluid.2011.12.026>
6. Almazán O, Olmo D, Hernández Gutiérrez A et al (2010) Parte V El bagazo de la caña de azúcar. Propiedades, constitución y potencial
7. Angin D (2014) Utilization of activated carbon produced from fruit juice industry solid waste for the adsorption of Yellow 18 from aqueous solutions. *Bioresour Technol* 168:259–266. <https://doi.org/10.1016/j.biortech.2014.02.100>
8. Angin D (2014) Production and characterization of activated carbon from sour cherry stones by zinc chloride. *Fuel* 115:804–811. <https://doi.org/10.1016/j.fuel.2013.04.060>
9. Awad FS, AbouZied KM, Abou El-Maaty WM et al (2018) Effective removal of mercury(II) from aqueous solutions by chemically modified graphene oxide nanosheets. *Arab J Chem.* <https://doi.org/10.1016/j.arabjc.2018.06.018>
10. Banerjee M, Basu RK, Das SK (2018) Cr(VI) adsorption by a green adsorbent walnut shell: adsorption studies, regeneration studies, scale-up design and economic feasibility. *Process Saf Environ Prot* 116:693–702. <https://doi.org/10.1016/j.psep.2018.03.037>
11. Basanta R, García Delgado MA, Cervantes Martínez JE et al (2007) Sostenibilidad del reciclaje de residuos de la agroindustria azucarera : una revisión. *Cienc y Tecnol Aliment* 5(4):293–305. <https://doi.org/10.1080/11358120709487704>
12. Becerra AP, Buitrago AL, Pinto P (2016) Sostenibilidad del aprovechamiento del bagazo de caña de azúcar en el valle del cauca, Colombia. *Ing Solidar* 12(20):133–149. <https://doi.org/10.16925/in.v12i20.1548>
13. Bello OS, Adegoke KA, Oyewole RO (2014) Insights into the adsorption of heavy metals from wastewater using diatomaceous. *Sep Sci Technol* 49:1787–1806. <https://doi.org/10.1080/01496395.2014.910223>
14. Boumediene M, Benaïssa H, George B et al (2015) Characterization of two cellulosic waste materials (Orange and Almond Peels) and their use for the removal of Methylene Blue from aqueous solutions. *Maderas Cienc y Tecnol* 17:69–84. <https://doi.org/10.4067/S0718-221X2015005000008>
15. Chen Z, Jing Y, Wang Y et al (2020) Applied Surface Science Enhanced removal of aqueous Cd(II) by a biochar derived from salt-sealing pyrolysis coupled with NaOH treatment. *Appl Surf Sci.* <https://doi.org/10.1016/j.apsusc.2020.145619>
16. Deng R, Huang D, Wan J et al (2020) Recent advances of biochar materials for typical potentially toxic elements management in aquatic environments: a review. *J Clean Prod* 255:119523. <https://doi.org/10.1016/j.jclepro.2019.119523>
17. Díaz-Arriaga FA (2014) Mercurio en la minería del oro: impacto en las fuentes hídricas destinadas para consumo humano. *Rev Salud Pública* 16:947–957
18. Dong X, Zhu Y, Li Y, Gu B (2013) Mechanistic investigation of mercury sorption by Brazilian pepper biochars of different pyrolytic temperatures based on x-ray photoelectron spectroscopy and flow calorimetry. *Environ Sci Technol* 47:12156–12164. <https://doi.org/10.1021/es4017816>
19. El-sheikh AH, Al-degs YS, Al-as RM, Sweileh JA (2011) Effect of oxidation and geometrical dimensions of carbon nanotubes on Hg(II) sorption and preconcentration from real waters. *Desalination* 270:214–220. <https://doi.org/10.1016/j.desal.2010.11.048>
20. Eom Y, Won JH, Ryu J, Lee TG (2011) Biosorption of mercury (II) ions from aqueous solution by garlic (*Allium sativum* L.) powder. *J Chem Eng* 28(6):1439–1443. <https://doi.org/10.1007/s11814-010-0514-y>
21. Feng NC, Guo XY, Liang S (2010) Enhanced Cu(II) adsorption by orange peel modified with sodium hydroxide. *Trans Nonferrous Met Soc China* 20:s146–s152. [https://doi.org/10.1016/S1003-6326\(10\)60030-1](https://doi.org/10.1016/S1003-6326(10)60030-1)
22. Fernandez ME, Nunell GV, Bonelli PR, Cukierman AL (2014) Activated carbon developed from orange peels: batch and dynamic competitive adsorption of basic dyes. *Ind Crops Prod* 62:437–445. <https://doi.org/10.1016/j.indcrop.2014.09.015>
23. Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. *Chem Eng J* 156:2–10. <https://doi.org/10.1016/j.cej.2009.09.013>
24. Freundlich H (1907) Über die adsorption in lösungen. *Zeitschrift für Phys Chemie* 57:385–470
25. Gao R, Fu Q, Hu H et al (2019) Highly-effective removal of Pb by co-pyrolysis biochar derived from rape straw and orthophosphate. *J Hazard Mater* 371:191–197. <https://doi.org/10.1016/j.jhazmat.2019.02.079>
26. Goertzen SL, Thériault KD, Oickle AM et al (2010) Standardization of the Boehm titration. Part I. CO₂ expulsion and endpoint determination. *Carbon N Y* 48:1252–1261. <https://doi.org/10.1016/j.carbon.2009.11.050>
27. Gonzalez LVP, Gómez SPM, Abad PAG (2017) Aprovechamiento de residuos agroindustriales en Colombia. *Rev Investig Agrar y Ambient* 8:141–150. <https://doi.org/10.22490/21456453.2040>
28. Grisales Motato AL, Rojas Arrieta W (2016) Obtención de carbon activado a partir de activación química de pulpa de café y su aplicación en la remoción de colorantes en aguas residuales industriales. Universidad tecnología de Pereira, Pereira
29. Gundogdu A, Duran C, Senturk HB et al (2012) Adsorption of phenol from aqueous solution on a low-cost activated carbon produced from tea industry waste: equilibrium, kinetic, and thermodynamic study. *J Chem Eng Data* 57:2733–2743. <https://doi.org/10.1021/je300597u>
30. Hadi P, To MH, Hui CW et al (2015) Aqueous mercury adsorption by activated carbons. *Water Res* 73:37–55. <https://doi.org/10.1016/j.watres.2015.01.018>
31. Hashemian S, Salari K, Yazdi ZA (2014) Preparation of activated carbon from agricultural wastes (almond shell and orange peel) for adsorption of 2-pic from aqueous solution. *J Ind Eng Chem* 20:1892–1900. <https://doi.org/10.1016/j.jiec.2013.09.009>
32. Ho Y-S, McKay G (1999) Pseudo-second order model for sorption processes. *Process Biochem* 34:451–465. [https://doi.org/10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5)
33. Hsu C, Chiou H, Chen Y et al (2019) Mercury adsorption and re-emission inhibition from actual WFGD wastewater using sulfur-containing activated carbon. *Environ Res* 168:319–328. <https://doi.org/10.1016/j.envres.2018.10.017>
34. Huang Y, Xia S, Lyu J, Tang J (2019) Highly efficient removal of aqueous Hg²⁺ and CH₃Hg⁺ by selective modification of biochar with 3-mercaptopropyltrimethoxysilane. *Chem Eng J* 360:1646–1655. <https://doi.org/10.1016/j.cej.2018.10.231>
35. Ihsanullah AA, Al-amer AM et al (2016) Heavy metal removal from aqueous solution by advanced carbon nanotubes : critical review of adsorption applications. *Sep Purif Technol* 157:141–161. <https://doi.org/10.1016/j.seppur.2015.11.039>
36. Jawhari T, Roid A, Casado J (1995) Raman spectroscopic characterization of some commercially available carbon black materials. *Carbon N Y* 33:1561–1565. [https://doi.org/10.1016/0008-6223\(95\)00117-V](https://doi.org/10.1016/0008-6223(95)00117-V)
37. Joseph L, Jun B, Flora JRV et al (2019) Removal of heavy metals from water sources in the developing world using low-cost

- materials: a review. *Chemosphere* 229:142–159. <https://doi.org/10.1016/j.chemosphere.2019.04.198>
38. Kalderis D, Bethanis S, Paraskeva P, Diamadopoulos E (2008) Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times. *Bioresour Technol* 99:6809–6816. <https://doi.org/10.1016/j.biortech.2008.01.041>
 39. Khadiran T, Hussein MZ, Zainal Z, Rusli R (2015) Textural and chemical properties of activated carbon prepared from tropical peat soil by chemical activation method. *BioResources* 10(1):986–1007. <https://doi.org/10.15376/biores.10.1.986-1007>
 40. Khoramzadeh E, Nasernejad B, Halladj R (2013) Mercury biosorption from aqueous solutions by sugarcane bagasse. *J Taiwan Inst Chem Eng* 44:266–269. <https://doi.org/10.1016/j.jtice.2012.09.004>
 41. Kim WK, Shim T, Kim YS et al (2013) Characterization of cadmium removal from aqueous solution by biochar produced from a giant *Miscanthus* at different pyrolytic temperatures. *Bioresour Technol* 138:266–270. <https://doi.org/10.1016/j.biortech.2013.03.186>
 42. Kong H, He J, Gao Y et al (2011) Cosorption of phenanthrene and mercury(II) from aqueous solution by soybean stalk-based biochar. *J Agric Food Chem* 59:12116–12123. <https://doi.org/10.1021/jf202924a>
 43. Lagergren S (1898) Zur theorie der sogenannten adsorption geloster stoffe. *K Sven vetenskapsakademiens Handl* 24:1–39
 44. Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc* 40:1361–1403
 45. Largitte L, Pasquier R (2016) A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. *Chem Eng Res Des* 109:495–504. <https://doi.org/10.1016/j.cherd.2016.02.006>
 46. Li B, Li M, Zhang J et al (2019) Adsorption of Hg(II) ions from aqueous solution by diethylenetriaminepentaacetic acid-modified cellulose. *Int J Biol Macromol* 122:149–156. <https://doi.org/10.1016/j.ijbiomac.2018.10.162>
 47. Li H, Dong X, da Silva EB et al (2017) Mechanisms of metal sorption by biochars: biochar characteristics and modifications. *Chemosphere* 178:466–478. <https://doi.org/10.1016/j.chemosphere.2017.03.072>
 48. Li X, Shen Q, Zhang D et al (2013) Functional groups determine biochar properties (pH and EC) as studied by two-dimensional ¹³C NMR correlation spectroscopy. *PLoS ONE*. <https://doi.org/10.1371/journal.pone.0065949>
 49. Liou T (2010) Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation. *Chem Eng J* 158:129–142. <https://doi.org/10.1016/j.cej.2009.12.016>
 50. Lu X, Jiang J, Sun K et al (2014) Influence of the pore structure and surface chemical properties of activated carbon on the adsorption of mercury from aqueous solutions. *Mar Pollut Bull* 78:69–76. <https://doi.org/10.1016/j.marpolbul.2013.11.007>
 51. Ministerio de ambiente y desarrollo sostenible (2015) Resolución 631 De 2015. In: D. Of. No. 49.486 18 abril 2015
 52. Momčilović M, Purenović M, Bojić A et al (2011) Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon. *Desalination* 276:53–59. <https://doi.org/10.1016/j.desal.2011.03.013>
 53. Mora Alvarez NM, Pastrana JM, Lagos Y, Lozada JJ (2018) Evaluation of mercury (Hg²⁺) adsorption capacity using exhausted coffee waste. *Sustain Chem Pharm* 10:60–70. <https://doi.org/10.1016/j.scp.2018.09.004>
 54. Nahata M (2018) Facile synthesis of activated carbon from cellulose in the presence of air for ammonia recovery in resource-constrained settings. University of Michigan, Ann Arbor
 55. Nguyen H, You S, Hosseini-bandegharaei A (2017) Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. *Water Res* 120:88–116. <https://doi.org/10.1016/j.watres.2017.04.014>
 56. Ning-chuan F, Xue-yi G (2012) Characterization of adsorptive capacity and mechanisms on adsorption of copper, lead and zinc by modified orange peel. *Trans Nonferrous Met Soc China* 22:1224–1231. [https://doi.org/10.1016/S1003-6326\(11\)61309-5](https://doi.org/10.1016/S1003-6326(11)61309-5)
 57. Njoku VO, Hameed BH (2011) Preparation and characterization of activated carbon from corn cob by chemical activation with H₃PO₄ for 2,4-dichlorophenoxyacetic acid adsorption. *Chem Eng J* 173:391–399. <https://doi.org/10.1016/j.cej.2011.07.075>
 58. Njoku VO, Islam MA, Asif M, Hameed BH (2014) Utilization of sky fruit husk agricultural waste to produce high quality activated carbon for the herbicide bentazon adsorption. *Chem Eng J* 251:183–191. <https://doi.org/10.1016/j.cej.2014.04.015>
 59. Oginni OJ (2018) Characteristics of activated carbons produced from herbaceous biomass feedstock. West Virginia University, Morgantown
 60. Ojedokun AT, Solomon O (2016) Sequestering heavy metals from wastewater using cow dung. *Water Resour Ind* 13:7–13. <https://doi.org/10.1016/j.wri.2016.02.002>
 61. Palanisamy PN, Sivakumar P (2009) Kinetic and isotherm studies of the adsorption of Acid Blue 92 using a low-cost non-conventional activated carbon. *Desalination* 249:388–397. <https://doi.org/10.1016/j.desal.2009.09.006>
 62. Park J, Wang J, Zhou B et al (2019) Removing mercury from aqueous solution using sulfurized biochar and associated mechanisms, vol 244. Elsevier, Amsterdam, pp 627–635. <https://doi.org/10.1016/j.envpol.2018.10.069>
 63. Peña HKJ, Giraldo L, Moreno JC (2012) Preparación de Carbón Activado a partir de Cáscara de Naranja por Activación Química. Caracterización Física y Química. *Rev Colomb Química* 41:310–323
 64. Ramírez Muñoz AP, Giraldo S, Flórez Yepes E, Acelas Soto NY (2017) Preparación de carbón activado a partir de residuos de palma de aceite y su aplicación para la remoción de colorantes. *Rev Colomb Química* 46(1):33–41. <https://doi.org/10.15446/rev.colomb.quim.v46n1.62851>
 65. Rao MM, Reddy DHKK, Venkateswarlu P, Sessaiah K (2009) Removal of mercury from aqueous solutions using activated carbon prepared from agricultural by-product/waste. *J Environ Manag* 90:634–643. <https://doi.org/10.1016/j.jenvman.2007.12.019>
 66. Raza MH, Sadiq A, Farooq U et al (2015) Phragmites karka as a biosorbent for the removal of mercury metal ions from aqueous solution: effect of modification. *J Chem* 2015:1–12. <https://doi.org/10.1155/2015/293054>
 67. Reza RA, Ahmaruzzaman M, Sil AK, Gupta VK (2014) Comparative adsorption behavior of ibuprofen and clofibrate acid onto microwave assisted activated bamboo waste. *Ind Eng Chem Res* 53:9331–9339. <https://doi.org/10.1021/ie404162p>
 68. Robles-Gutiérrez I (2015) Evaluación de los cambios en los parámetros fisicoquímicos del suelo procedente de San Joaquín. Querétaro; Después del tratamiento electrocinético para la remoción de mercurio, Centro de Investigación y Desarrollo Tecnológico en Electroquímica, S.C.
 69. Sajjadi SA, Mohammadzadeh A, Tran HN et al (2018) Efficient mercury removal from wastewater by pistachio wood waste-derived activated carbon prepared by chemical activation using a novel activating agent. *J Environ Manag* 223:1001–1009. <https://doi.org/10.1016/j.jenvman.2018.06.077>
 70. Salahi S, Parvini M, Ghorbani M (2014) Equilibrium studies in adsorption of Hg(II) from aqueous solutions using biocompatible polymeric polypyrrole-chitosan nanocomposite. *Polycycl*

- Aromat Compd 34:225–236. <https://doi.org/10.1080/10406638.2014.886077>
71. Saleh TA (2015) Isotherm, kinetic, and thermodynamic studies on Hg(II) adsorption from aqueous solution by silica-multiwall carbon nanotubes. *Environ Sci Pollut Res* 22:16721–16731. <https://doi.org/10.1007/s11356-015-4866-z>
 72. Saleh TA, Sari A, Tuzen M (2017) Optimization of parameters with experimental design for the adsorption of mercury using poly-ethylenimine modified-activated carbon. *J Environ Chem Eng* 5:1079–1088. <https://doi.org/10.1016/j.jece.2017.01.032>
 73. Sharma YC (2011) Adsorption characteristics of a low-cost activated carbon for the reclamation of colored effluents containing malachite green. *J Chem Eng Data* 56:478–484. <https://doi.org/10.1021/je1008922>
 74. Solisio C, Al AS, Conventi A (2019) Adsorption of inorganic mercury from aqueous solutions onto dry biomass of *Chlorella vulgaris*: kinetic and isotherm study. *Environ Technol* 40:664–672. <https://doi.org/10.1080/09593330.2017.1400114>
 75. Solomon O, Adesina K, Oluwapamilerin O, Seun O (2019) Heliyon Functionalized locust bean pod (*Parkia biglobosa*) activated carbon for rhodamine B dye removal. *Heliyon* 5:e02323. <https://doi.org/10.1016/j.heliyon.2019.e02323>
 76. Song BY, Eom Y, Lee TG (2011) Removal and recovery of mercury from aqueous solution using magnetic silica nanocomposites. *Appl Surf Sci* 257:4754–4759. <https://doi.org/10.1016/j.apsusc.2010.12.156>
 77. Tan G, Sun W, Xu Y et al (2016) Bioresource technology sorption of mercury (II) and atrazine by biochar, modified biochars and biochar based activated carbon in aqueous solution. *Bioresour Technol* 211:727–735. <https://doi.org/10.1016/j.biortech.2016.03.147>
 78. Tan X, Liu Y, Zeng G et al (2015) Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* 125:70–85. <https://doi.org/10.1016/j.chemosphere.2014.12.058>
 79. Tareq R, Akter N, Azam S (2019) Chapter 10 - Biochars and biochar composites: low-cost adsorbents for environmental remediation. In: Ok YS, Tsang DCW, Bolan N, Novak JM (eds) *Biochar from biomass and waste*, pp 169–210. <https://doi.org/10.1016/B978-0-12-811729-3.00010-8>
 80. Tawabini B, Atieh M, Khaled M (2010) Removal of mercury from water by multi-walled carbon nanotubes. *Water Sci Technol* 61:591–598. <https://doi.org/10.2166/wst.2010.897>
 81. Tejada Tovar C, Villabona Ortiz Á, Ruiz Rangel V (2012) Biomasa residual para remoción de mercurio y cadmio: una revisión. *Ingenium* 6:11–21. <https://doi.org/10.21774/ing.v6i14.189>
 82. Temkin MJ, Pyzhev V (1940) Recent modifications to Langmuir isotherms. *Acta Physicochim URSS* 12:217–222
 83. Thakur S, Kumari S, Dogra P, Chauhan GS (2014) A new guar gum-based adsorbent for the removal of Hg(II) from its aqueous solutions. *Carbohydr Polym* 106:276–282. <https://doi.org/10.1016/j.carbpol.2014.02.041>
 84. Tovar AK, Godínez LA, Espejel F et al (2019) Optimization of the integral valorization process for orange peel waste using a design of experiments approach: production of high-quality pectin and activated carbon. *Waste Manag* 85:202–213. <https://doi.org/10.1016/j.wasman.2018.12.029>
 85. Tschansky L, Graber ER (2014) Methodological limitations to determining acidic groups at biochar surfaces via the Boehm titration. *Carbon N Y* 66:730–733. <https://doi.org/10.1016/j.carbon.2013.09.044>
 86. Uchimiya M, Orlov A, Ramakrishnan G, Sistani K (2013) In situ and ex situ spectroscopic monitoring of biochar's surface functional groups. *J Anal Appl Pyrolysis* 102:53–59. <https://doi.org/10.1016/j.jaap.2013.03.014>
 87. USEPA (2001) National primary drinking water standards. Report EPA 816-F-01-007. Washington, DC
 88. Vanegas DC, Mclamore ES, Hurtado D (2018) Mercury pollution and artisanal gold mining in Alto Cauca, Colombia: woman's perception of health and environmental impacts. *J Environ Dev*. <https://doi.org/10.1177/1070496518794796>
 89. Wang LG, Yan GB (2011) Adsorptive removal of direct yellow 161 dye from aqueous solution using bamboo charcoals activated with different chemicals. *Desalination* 274:81–90. <https://doi.org/10.1016/j.desal.2011.01.082>
 90. Wang T, Wu J, Zhang Y et al (2018) Increasing the chlorine active sites in the micropores of biochar for improved mercury adsorption carbon trap. *Fuel* 229:60–67. <https://doi.org/10.1016/j.fuel.2018.05.028>
 91. Wang W, Chen M, Chen X, Wang J (2014) Thiol-rich polyhedral oligomeric silsesquioxane as a novel adsorbent for mercury adsorption and speciation. *Chem Eng J* 242:62–68. <https://doi.org/10.1016/j.cej.2013.12.063>
 92. Weber WJ, Morris JC (1963) Kinetics of adsorption on carbon from solution. *J Sanit Eng Div* 89:31–60
 93. Xu X, Schierz A, Xu N, Cao X (2016) Comparison of the characteristics and mechanisms of Hg(II) sorption by biochars and activated carbon. *J Colloid Interface Sci* 463:55–60. <https://doi.org/10.1016/j.jcis.2015.10.003>
 94. Yang J, Zhao Y, Ma S et al (2016) Mercury removal by magnetic biochar derived from simultaneous activation and magnetization of sawdust. *Environ Sci Technol* 50:12040–12047. <https://doi.org/10.1021/acs.est.6b03743>
 95. Yu J, Yue B, Wu X et al (2016) Removal of mercury by adsorption: a review. *Environ Sci Pollut Res* 23:5056–5076. <https://doi.org/10.1007/s11356-015-5880-x>
 96. Yu L, Luo YM (2014) The adsorption mechanism of anionic and cationic dyes by Jerusalem artichoke stalk-based mesoporous activated carbon. *J Environ Chem Eng* 2:220–229. <https://doi.org/10.1016/j.jece.2013.12.016>
 97. Yue G, Wang L, Zhang X et al (2014) Fabrication of high performance multi-walled carbon nanotubes/polypyrrole counter electrode for dye-sensitized solar cells. *Energy* 67:460–467. <https://doi.org/10.1016/j.energy.2014.01.058>
 98. Zhang F, Nriagu JO, Itoh H (2005) Mercury removal from water using activated carbons derived from organic sewage sludge. *Water Res* 39:389–395. <https://doi.org/10.1016/j.watres.2004.09.027>
 99. Zhang X, Fu W, Yin Y et al (2018) Adsorption–reduction removal of Cr(VI) by tobacco petiole pyrolytic biochar: batch experiment, kinetic and mechanism studies. *Bioresour Technol* 268:149–157. <https://doi.org/10.1016/j.biortech.2018.07.125>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.