The biochars prepared from cinnamon and cannabis as nature-friendly adsorbents for removal of Cd(II) ions from aqueous solutions

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Abstract

Cinnamon and cannabis were utilized to produce biochars, which operate as promising adsorbents by pyrolysis in various temperatures using the N₂ atmosphere. The novel biochars were analyzed via scanning electron microscopy, X-ray powder diffraction, Fourier-transform infrared spectroscopy, the pH point of zero charges, and N₂ adsorption–desorption isotherm styles, followed by testing the adsorption attributes of these materials using Cd(II) ions in a water bath. The Cd(II) adsorption onto biochars was satisfied in the neutral pH of 7.0 and a temperature of 65 °C. The equilibrium data in aqueous solutions were fitted to Langmuir (L), Freundlich (F), Tempkin (T), and Redlich–Peterson (R–P) models. Kinetic adsorption data were analyzed using the pseudo-first-order (PFO), pseudo-second order (PSO), Elovich (E), and intraparticle diffusion (ID) models. In addition, the Cd(II) adsorption performance was proficiently narrated through Langmuir and pseudo-second-order models and electrostatic force and chemical reaction were originally responsible for adsorption mechanism. Further, the results demonstrated that the obtained $q_{\max}$ from biochars at the pyrolysis temperature of 600 °C was higher than that noticed at pyrolysis temperatures of 300 and 400 °C. Finally, the adsorbent dose of 0.1 g and temperature of 65 °C, as well as supplying $q_{\max}$ of 147.05, 153.84, 158.73, 133.33, 144.92, and 175.43 mg g⁻¹ were observed for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600, respectively.

Keywords Adsorption · Biochar · Cadmium · Kinetic · Pyrolysis

1 Introduction

The pollution of water, sediments, and soils by heavy metal release into the natural environment has become a critical and controversial topic for different industrial factories worldwide [1, 2]. Recent national and international legislation for improving the quality of drinking water are getting tougher due to the variety of pollutant sources. Heavy metals have irreversible damages on the growth of plants and they can lead to the inactivation of numerous enzymes, as well as the destruction of some proteins in the animals and human bodies [3]. Among various metals such as lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), and vanadium (V), Cd is

considered as one of the most perilous metals, which can accumulate by food chain and can be a reason for chronic and acute poisoning [4–6]. In addition, the toxicity and non-degradable of this metal cause nausea, diarrhea, bone malformation, kidney damage, and cancer [4–6]. The World Health Organization has set a maximum concentration of 0.05 µg L⁻¹ Cd in drinking water [7]. So far, previous studies have utilized various traditional approaches to eliminate Cd ions from water, including reverse osmosis, chemical precipitation, flocculation, and ion exchange [8]. Although these strategies can be executable and beneficial, they have high operation and substructure costs and produce large amounts of toxic intermediate materials. The adsorption is unique due to

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some marvelous features such as simplicity, effective, and low-energy consumption [9].

Biochars are considered as a group of carbon materials, which are ordinarily fabricated by pyrolysis various biomasses as feedstock (e.g., wood, sawdust, food, and agricultural wastes) under oxygen-limited situations and a high temperature [10, 11]. These materials can be utilized as an adsorbent due to the large surface area, microporosity, functional groups, and hydrophobicity. However, some chemical and physical characteristics of biochars change with pyrolysis temperature and biomass kind. For example, the amount of dissolved organic carbon in biochar obtained from low temperature was higher compared to high temperature [12, 13]. Biochar mainly includes different compounds (e.g., aliphatic and aromatic) and main functional groups (e.g., hydroxyl, carbonyl, and phenolic hydroxyl groups), that lead to their excellent adsorption capacity for adsorption organic and inorganic pollutants as an inexpensive substitute for the activated carbon. Also, the type of biochar depends on the pyrolysis temperature. When the pyrolysis temperature is too high, the microstructure of biochar develops. However, loss of functional group and carbon on the surface is excessive [14, 15].

Different studies focused on the supreme adsorption capacity of biochar toward heavy metals. For instance, [16]. Reported the Cr(VI) removal using biochar produced from Eucalyptus plant bark at 500 °C. The results indicated that biochar has enormous potentials for Cr(VI) ion removal from water samples. Further, [17]. Demonstrated the elimination of heavy metals via modified biochar from different wastewater and concluded that prepared biochar is considered as an effective adsorbent for removing heavy metals from water.

In the present study, a facile, quick, and economic technique was explained for obtaining biochars with great surface area and porous structure from cinnamon and cannabis seed. Also, the biochars obtained from cinnamon and cannabis seeds is one of the most abundant renewable resources that include carbon, nitrogen, potassium, and calcium. Then, the surface of biochars was activated by hydrogen chloride as the oxidation agent and was utilized as the adsorbent to eliminate Cd(II) ions from water. Furthermore, the adsorption equilibrium test information was modeled using isotherm (Langmuir, Freundlich, Temkin, and Redlich-Peterson) and kinetic (pseudo-first-order, pseudo-second-order, Elovich, and the intraparticle diffusion) models. Additionally, the adsorption parameters such as the pH of Cd(II) solution, adsorbent dose, reaction time, and temperature were evaluated in detail, followed by discussing the regeneration potential of biochars.

2 Materials and methods

2.1 Apparatus and reagents

The cinnamon and cannabis seeds were used as raw materials for biochar production taken from markets in Iran. In addition, hydrogen chloride (HCl), sodium hydrate (NaOH), nitric acid (HNO₃), ethanol (C₂H₆O), and cadmium nitrate (Cd(NO₃)₂·4H₂O) were supplied from Merck (Germany). Further, the Cd(II) stock solution was provided with Cd(NO₃)₂·4H₂O and deionized water.

The contents of Cd(II) were examined by inductively coupled plasma-optical emission spectrometry (ICP-OES, JY138 ultrace, France). Furthermore, scanning electron microscopy (SEM-EDX, XL30, and Philips Netherlands), X-ray powder diffraction (38066 Riva, d/G.Via M. Misone, 11/D (TN), Italy), and N₂ adsorption-desorption isotherm tests, along with Fourier-transform infrared spectroscopy (FTIR) spectra (Perkin Elmer, spectrum100) were utilized to explain the significant details about the structure and morphology of biochars.

2.2 Preparation of biochars

Both samples (cinnamon and cannabis seeds) were rinsed with deionized water several times to eliminate impurities and then dried at 25 °C for 72 h and pyrolyzed at various temperatures (i.e., 300, 400, and 600 °C) through a tube furnace for 2 h under N₂ atmosphere. Next, all samples were crushed via a crusher and passed by a 40 mesh sieve to obtain the primary the biochars. Additionally, 5 g of each sample was refluxed with 0.1 M HCl for 12 h, and then cooled, washed with deionized water, and dried in a vacuum oven at 80 °C. Finally, the prepared biochars at different temperatures were marked as cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 and stored in airtight plastic (Scheme 1).

2.3 Adsorption studies

The Cd(II) adsorption tests by various samples of biochar were conducted in a series of 50 mL conical flasks. Typically, 0.1 g of each adsorbent (i.e., cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600) was added to 10 mL Cd(II) of various primary concentrations of (i.e., 60, 130, 180, 250, 350, and 500 mg L⁻¹) and were then shaken in a thermostatic water bath shaker at 150 rpm. After 24 h, the adsorbent samples were filtered with 0.45 µm filter and the content of the remaining Cd(II) ions in the volume of the solution was evaluated

Scheme 1 Schematic diagram for preparation of biochars

by an ICP-OES analysis. The adsorption ability (q_e) of Cd(II) ions was obtained by Eq. (1) as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg L^{-1}) denote the primary and ultimate contents of Cd(II) ions, respectively. In addition, V (L) and W (g) demonstrates the volume of standard solutions Cd(II) and the mass of each biochar in all tests.

2.4 Kinetic studies

The kinetic studies were performed at primary Cd(II) level of 60 mg L^{-1} . Each 10 mL of Cd(II) solution containing 0.1 g of adsorbent (i.e., cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600) were placed in a thermostatic water bath shaker (150 rpm), and at different time intervals, the residual levels of Cd(II), C_t , were determined by an ICP-OES analysis. The amount of Cd(II) ions adsorbed at each time interval per unit mass of the adsorbent q_t (mg g^{-1}) was evaluated by using Eq. (2):

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

In this equation, C_0 and C_t (mg L^{-1}) are the contents of the liquid phase of Cd(II) at primary and any time t , respectively.

2.5 Effect of pH

The effects of pH in the range of 3.0 to 9.0 with a stirring time of 60 min on the removal of Cd(II) were investigated by using 0.1 mol L^{-1} HCl or NaOH solutions for the initial pH adjustment, with the primary Cd(II) content fixed at 60 mg L^{-1} .

2.6 Effect of the amount of adsorbent

The dependency of the adsorption of Cd(II) ions was studied by 0.04 g to 0.3 g amounts of adsorbent in contact with 10 mL solution of 60 mg L^{-1} of Cd(II) with agitation time of 60 min.

3 Results and discussion

3.1 Characterization of adsorbents

To assess the influence of temperature on prepared biochars, the temperature values at 300–600 °C were synthesized and their structures were characterized by various styles. The X-ray powder diffraction (XRD) patterns of cinnamon 300, cinnamon 400, and cinnamon 600 displayed the peaks at 15°, 25°, 29°, and 38° correspond to the planes of (012), (102), (024), and (125) exhibiting the $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. For cinnamon 600, three new peaks at around 14°, 25°, and 29° possibly connected with the pattern of the CaCO_3 by

comparison with Joint Committee on Powder Diffraction Standards (JCPDS Card, File No. 79-0418). Further, the XRD patterns of cannabis 300, cannabis 400, and cannabis 600 illustrate the amorphous-crystalline of biochar. As shown, the peaks on the structure of biochars increase due to biochars crystallization by enhancing the temperature (Fig. 1).

The Fourier-transform infrared spectroscopy spectra of various biochars are displayed in Fig. 2. Based on the data, the fabricated biochars offer the broad bands at 1300, 1900, and 3400 cm^{-1} , corresponding to the O–H stretching vibration and the adsorption peak at 2900 cm^{-1} , which is related to the aliphatic $-\text{CH}_2$ stretching variation. The peaks occurring at 575, 570, and 567 cm^{-1} indicated the presence of C–Br. Furthermore, the peak at 850 cm^{-1} was assigned to the C–H bond. Additionally, two bands at 1618

and 1179 cm^{-1} were related to the N–H and C=O groups, respectively. The Fourier-transform infrared spectroscopy results represented that all biochars encompassed different functional groups such as O–H, $-\text{CH}_2$, C–H, N–H, and C=O on their surface, which could supply great active positions for eliminating the Cd(II) ions. Finally, the peaks reduced in high pyrolysis temperature due to the breaking bonds of the aliphatic [18, 19].

Figure 3 depicts the scanning electron microscopy images of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600. As shown, the biochars derived from cinnamon and cannabis demonstrate a porous structure and various cavities were detected on their surface when cinnamon and cannabis pyrolyzed at 600 °C.

Fig. 1 XRD patterns of cinnamon 300, cinnamon 400, cinnamon 600 (a) and cannabis 300, cannabis 400, and cannabis 600 (b)

Fig. 2 FT-IR spectrum of cinnamon 300, cinnamon 400, cinnamon 600 (a) and cannabis 300, cannabis 400, and cannabis 600 (b)

Fig. 3 SEM images of cinnamon 300 (a), cinnamon 400 (b), cinnamon 600 (c), cannabis 300 (d), cannabis 400 (e), and cannabis 600 (f)

The porosity and surface area of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 were tested by N_2 adsorption–desorption isotherms (Fig. 4). Based on the results, cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 have a specific surface area of 0.64745, 0.66238 m, 0.67918, 1.1516, 1.2330, and 2.8903 $m^2 g^{-1}$, as well as an average pore size diameter of 34.039, 21.501, 22.816, 0.3523, 108.27, and 29.350 nm, respectively. It was also found out that the nitrogen isotherms for all of the adsorbents are belonged to type IV according to the classification of I.U.P.A.C. In the present study, the S_{BET} of prepared adsorbents by the pyrolysis method increased by increasing the temperature from 300 to 600 °C, which supplied different adsorption positions for Cd ions. Eventually, the results revealed that hydrochloric acid cannot destruct the porous structure of the adsorbents.

3.2 Influence of pH

The pH of the wastewater solution influences both the presence of Cd(II) ions and the charge attributes of the biochars. The primary pH of Cd(II) solution was selected in the range of 3.0–9.0 in order to evaluate the influence by the pH. Figure 5 indicates that the adsorption percentage of Cd(II) ions gradually enhances as the pH of the primary solution of Cd(II) increases from 3.0 to 7.0. Based

on the results, the maximum adsorption efficiency of 95, 96.5, 98.8, 95, 95.5, and 97.3% was obtained for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600, respectively, when the pH level was equal to 7.0. Under acidic pH ($pH < 7.0$), various groups in the biochars are simply protonated, leading to electrostatic repulsion of Cd(II) ions. On the other hand, adsorption efficiency increases due to the deprotonation of the surface groups of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 under alkaline pH ($pH > 7.0$). At the pH of 8.0 and 9.0, the Cd(II) adsorption represented no remarkable change due to electrostatic reaction. In addition, the effect of solution pH on Cd(II) adsorption by each biochar can be well described in terms of the pH point of zero charges (pH_{pZC}) of the adsorbents [20]. The pH_{pZC} of the cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 were found 5.0 and were the same for all these adsorbents. In general, the surface charge of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 is positive when $pH < 5.0$ while that of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 is negative when $pH > 5.0$, making the situation desirable for Cd(II) ion adsorption.

Further, the pH variation was associated with Cd(II) species that were present in several forms in solutions

Fig. 4 Nitrogen adsorption–desorption isotherm for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600

Fig. 5 Influence of solution pH on the removal percentage of Cd(II) ions by cinnamon 300, cinnamon 400, cinnamon 600 (a) and cannabis 300, cannabis 400, and cannabis 600 (b) ($C_0 = 60 \text{ mg L}^{-1}$, adsorbent dose = 0.1 g, contact time = 60 min, and temperature = 65 °C)

such as $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})_2$, $\text{Cd}(\text{OH})_4^{2-}$, and $\text{Cd}(\text{OH})_3^-$ Cd^{2+} . Therefore, Cd(II) ions were adsorbed in pH = 7.0 due to electrostatic attractions between Cd^{2+} and the negative charge of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600. In the pH of above 9.0, the elimination of Cd(II) ions occurred due to the precipitation of $\text{Cd}(\text{OH})_2$ and $\text{Cd}(\text{OH})^+$. A similar behavior has been reported for Cd(II) ion adsorption on

SDS-coated magnetite nanoparticles modified with 2,4-DNPH [9].

3.3 Influence of adsorbent dose

Figure 6 depicts the effect of different amounts (0.04–0.3 g) of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 on the

Fig. 6 Influence of adsorbent dose on the removal percentage of Cd(II) ions by cinnamon 300, cinnamon 400, cinnamon 600 (a) and cannabis 300, cannabis 400, and cannabis 600 (b) (pH=7.0, $C_0=60 \text{ mg L}^{-1}$, contact time=60 min, and temperature=65 °C)

adsorption of Cd(II) ions for primary Cd(II) concentration of 60 mg L^{-1} . As expected, the Cd(II) ions were gradually eliminated by adding the amount of biochars from 0.04 to 0.1 g and remained constant in 0.1 g with the maximum percent of 95.7, 97.0, 98.9, 95.26, 95.9, and 97.8% for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600, respectively. In the first step, a fast increase was observed in elimination percentage, denoting that this observation can be explained via increase in the surface area and availability of more active sites for adsorption. Afterward (from 0.1 g), it becomes fairly constant for any further increase in the adsorbent dose because of the limitation Cd(II) ions as compared with the biochars sites available for the reaction. These results are in agreement with those reported in the literature [21].

3.4 Influence of temperature

The impact of solution temperature on the adsorption process of Cd(II) ions by the obtained biochars from cinnamon and cannabis was analyzed through altering the reaction temperature in the range of 25–65 °C in the similar testable situation (Fig. 7). Based on the results, the elimination percentage of Cd(II) ions increased from 35 to 95, 37.5 to 96, 45.5 to 97.5, 48.2 to 90.9, 46.4 to 93%, and 52 to 96.8% for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600, respectively, when the process temperature increased from 25 to 65 °C. This demonstrated that the Cd(II) ion adsorption was the endothermic operation and expanding temperature encouraged adsorption procedure and temperature 65 °C was appropriate to the spontaneous reaction. Similar results

Fig. 7 Influence of temperature with Standard deviation(s) on the removal percentage of Cd(II) ions by cinnamon 300, cinnamon 400, cinnamon 600 (a) and cannabis 300, cannabis 400, and cannabis 600 (b) (pH=7.0, $C_0=60 \text{ mg L}^{-1}$, adsorbent dose=0.1 g, contact time=60 min)

for the metal ions adsorption at various temperature on $\text{Fe}_2\text{O}_3/\text{SiO}_2$ thin films have also been reported [8].

3.5 Influence of ionic strength

The effect of ionic strength on Cd(II) ions adsorption onto cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 was studied using changing concentrations between 0.0 and 0.5 M. Fig. 7 shows the effect of ionic strength (K^+ and Na^+) on the adsorption of Cd(II) ions. As shown in Fig. 8, the adsorption percentage of Cd(II) ions decreased with increase of ionic strength at all concentrations. This decrease in the Cd(II) elimination may be due to the competition between Cd(II) ions and K^+ and Na^+ for adsorption sites.

3.6 Influence of primary Cd(II) concentration and equilibrium studies

The primary Cd(II) concentration on the adsorption operation of Cd(II) ions via cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600

was checked for the primary concentrations of 60 to 500 mg L^{-1} as the amount of each biochar was constant. The results explain that the elimination efficiency of Cd(II) ions reduced from 92 to 54, 93 to 55, 98.5 to 60, 87 to 47, 89 to 51, and 95 to 64% for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600, respectively, by an increase in the primary concentration from 60 to 500 mg L^{-1} . However, the adsorption ability (q_e) of Cd(II) ions by cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 regularly increased by adding the primary Cd(II) concentration. These outcomes of adsorption can be interpreted by the surface areas of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600. This is attributed to the presence of great empty positions at the Cd(II) concentration of 60 mg L^{-1} due to a growth in the concentration slope and rate of Cd(II) diffusion to cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600.

By utilizing the adsorption isotherm models, the adsorption ability of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 was studied for Cd(II) ion adsorption in the adsorbent dose of 0.1 g and the pH of 7.0 while the primary Cd(II) ion concentration altered from 60 to 500 mg L^{-1} . Accordingly, the linear shape of Langmuir (L), Freundlich (F), Temkin (T), and Redlich–Peterson (R–P) models was employed and revealed as follows [22–25]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_l} \quad (3)$$

$$nq_e = \frac{1}{n} \ln C_e + \ln k_f \quad (4)$$

$$q_e = \text{Bl}nk_t + \text{Bl}nC_e \quad (5)$$

$$\ln \left(q_{R-P} K_{R-P} \frac{C_e}{q_e} - 1 \right) = \ln K_{R-P} + \beta \ln C_e \quad (6)$$

where q_e and q_m (mg g^{-1}) describe the amount of adsorbed Cd(II) ions onto cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 in an equilibrium situation and a maximum level, respectively, in a single layer form. Both k_f and n are assumed as the unchanging factors of F and heterogeneity of biochar surface, respectively. Furthermore, the K_t (L mg^{-1}) and B are related to the equilibrium binding factor and heat of adsorption, respectively. Finally, the k_{R-P} (L g^{-1}) and β denote the fixed factors of the R–P model.

The parameters of the fitting models such as L, F, T, and R–P, as well as their correlation coefficients (R^2) are

Fig. 8 Influence of ionic strength (Na^+ (a) and K^+ (b)) on the removal percentage of Cd(II) ions by cinnamon 300, cinnamon 400, cinnamon 600 (a) and cannabis 300, cannabis 400, and cannabis 600

shown in Fig. 9 and Table 1. The correlation coefficients (R^2) obtained from the L model for Cd(II) adsorption were 0.9989, 0.9924, 0.9908, 0.9942, 0.9890, and 0.9935 for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600, respectively, which were higher ($R^2 > 0.98$) than those of L, F, and R-P models. Additionally, the values of R_L were computed to be 0.245, 0.301, 0.189, 0.364, 0.395, and 0.255 for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600, respectively, representing that the Cd(II) adsorption onto the above-mentioned adsorbents was appropriate and the dependence between Cd(II) ions and biochars was strong.

These results imply that the adsorption of Cd(II) ions onto all biochars follow the L model and adsorption operation led to the homogeneous surface of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 and the monolayer adsorption of Cd(II) ions accomplished on biochars with a finite number of identical sites, that all sites are energetically equivalent, and that there is no interaction between the adsorbed molecules.

The obtained $q_{\max}$ values for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 were 147.05, 153.84, 158.73, 133.33, 144.92, and 175.43 mg g^{-1} , respectively. In addition, the $q_{\max}$ quantities

Fig. 9 The L model for the adsorption of Cd(II) ions onto cinnamon 300, cinnamon 400, cinnamon 600 (a) and cannabis 300, cannabis 400, cannabis 600 (b)

Table 1 Obtained parameters for adsorption of Cd(II) ions onto cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600

Isotherm	Parameters	Cinnamon 300	Cinnamon 400	Cinnamon 600	Cannabis 300	Cannabis 400	Cannabis 600
L	q_m (mg g^{-1})	147.05	153.84	158.73	133.33	144.92	175.43
	b (L mg^{-1})	0.0513	0.0386	0.0711	0.029	0.0255	0.0485
	R_L	0.2451	0.3015	0.1898	0.3641	0.3957	0.2552
	R^2	0.9989	0.9924	0.9908	0.9942	0.9890	0.9935
F	K_F ($\text{L mg}^{(1-(1/n))} \text{g}^{-1}$)	15.50	18.757	32.505	14.049	13.668	21.977
	n	2.131	2.537	3.312	2.464	2.373	2.468
	R^2	0.9466	0.9533	0.9599	0.9296	0.9721	0.9556
T	B	33.245	28.225	22.446	25.497	27.523	31.952
	K_T (L mg^{-1})	2.189	1.646	2.947	2.399	2.775	1.241
	R^2	0.9875	0.9845	0.9599	0.9867	0.9860	0.9871
R-P	q_{R-P}	254.2	276.1	300.02	192.21	210.52	245.37
	K_{R-P}	0.2151	0.124	0.152	0.224	0.218	0.291
	β	1.021	0.985	0.971	1.152	1.126	1.075
	R^2	0.990	0.9872	0.9889	0.9851	0.9760	0.9912

were in the order of cannabis 600 > cinnamon 600 > cinnamon 400 > cinnamon 300 > cannabis 400 > cannabis 300, indicating that temperature plays an overcoming role on the structure of biochars. In other words, the produced biochars at a higher temperature (i.e., cinnamon 600 and cannabis 600) had more active sites and specific surface area compared to the other biochars. Further, the obtained $q_{\max}$ values from cinnamon 600 and cannabis 600 for Cd(II) ions were significantly larger than those formerly introduced in the literature for the elimination of Cd(II) ions using different adsorbents (Table 2).

3.7 Influence of equilibrium time and kinetic studies

The tests were completed at various times of 0–80 min with 0.1 g from each adsorbent and the primary Cd(II) concentration of 60 mg L⁻¹ in order to observe the influence of adsorption activity time on the removal efficiency and ability of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600. The results revealed that the elimination rate of Cd(II) ions via cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 was extraordinary at the outset, probably given that more adsorption positions were present at the primary phase compared to the following phases. Thus, the Cd(II) ions can connect comfortably with these places. However, Cd(II) elimination by all biochars reduced over time and most active positions on the surface of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 were occupied by these ions and the adsorption rate of Cd(II) diminished as well. In general, the quantity of the adsorbed Cd(II) ions enhanced

by increasing the reaction time and peaked after 60 min. The reaction time of 60 min was adequate for achieving the adsorption equilibrium for all synthesized biochars at various temperatures.

To understand managing adsorption procedure between adsorbents (i.e., cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600) and Cd(II) ions, four kinetic models containing the pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich (E), and the intraparticle diffusion (ID) were utilized to analyze the empirical data. Equations (7)–(10) represent the linear relations of the four models [32, 33].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (9)$$

$$q_t = k_{ID} t^{0.5} + A \quad (10)$$

where q_e and q_t (mg g⁻¹) indicate the ability of each biochar for Cd(II) ion adsorption at equilibrium time and any time t (min), respectively, and k_1 (min⁻¹) and k_2 (mg g⁻¹ min⁻¹) denote PFO and PSO rate fixed factors, respectively. In addition, K_{ID} and A (mg g⁻¹) are considered as the ID unchanging factors and α and β represent the E constant parameters.

The quantities of the kinetic parameters of four linear models (i.e., PFO, PSO, E, and ID) are shown in Table 3

Table 2 Comparison of q_m of different adsorbents for adsorption of Cd(II) ions

Adsorbent	q_m (mg g ⁻¹)	References
Pristine biochar	30.58	[26]
Fe–Mn binary oxide-biochar	95.23	[26]
Corn stalk	40.0	[27]
Iminodiacetic acid-modified magnetic biochar	197.9	[28]
Imprinted polymers	107.0	[29]
Amino modification of rice straw-derived biochar	72.1	[5]
<i>P. semisulcatuse</i> chitin	19.15	[7]
Mercapto-modified coal gangue	110.4	[30]
<i>Callinectes sapidus</i> biomass	29.23	[31]
Cinnamon 300	147.05	In this study
Cinnamon 400	153.84	In this study
Cinnamon 600	158.73	In this study
Cannabis 300	133.33	In this study
Cannabis 400	144.92	In this study
Cannabis 600	175.43	In this study

Table 3 Constant of kinetic models for adsorption of Cd(II) ions onto cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600

Isotherm	Parameters	Cd(II) ions					
		Cinnamon 300	Cinnamon 400	Cinnamon 600	Cannabis 300	Cannabis 400	Cannabis 600
PFO	k_1 (min ⁻¹)	0.0415	0.0497	0.0617	0.0551	0.0372	0.0338
	q_e (mg g ⁻¹)	16.36	18.04	19.321	10.797	11.438	9.369
	R^2	0.9546	0.9227	0.9546	0.9220	0.7896	0.8175
PSO	k_2 (g mg ⁻¹ min)	0.0031	0.0035	0.0042	0.0088	0.0048	0.0067
	q_e (mg g ⁻¹)	32.57	32.15	32.78	29.41	31.54	31.152
	R^2	0.9988	0.9984	0.9987	0.9998	0.9983	0.9994
E	α	10.46	9.643	14.540	71.97	17.823	57.33
	β	0.169	0.162	0.1705	0.250	0.185	0.2311
	R^2	0.9801	0.9788	0.9642	0.9180	0.9507	0.9782
ID	K_{ID} (mg g ⁻¹ min ^{1/2})	2.230	2.276	2.173	1.457	2.009	1.6329
	A	10.27	10.294	12.37	16.37	12.82	16.13
	R^2	0.9803	0.9240	0.8918	0.7947	0.8826	0.9087

Fig. 10 PSO model for the adsorption of Cd(II) ions onto cinnamon 300, cinnamon 400, cinnamon 600 (a) and cannabis 300, cannabis 400, cannabis 600 (b)

and Fig. 10. Based on the data in Table 2, the PSO model revealed higher correlation coefficients ($R^2 > 0.9980$) compared to PFO, E, and ID models for the adsorption action of Cd(II) ions onto cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600. Further, the amount of PSO rate constant (k_2) for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 were 0.0031, 0.0035, 0.0042, 0.0088, 0.0048, and 0.0067, respectively, pointing that the Cd(II) adsorption matched with PSO model. Furthermore, the PSO model expressed that the relation between Cd(II) ions in solution phase and cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis

400, and cannabis 600 was chemisorption and biochars had a heterogeneous surface. The q_e derived from the PSO model was more close to the empirical data. Finally, the adsorption action was in agreement with the PSO model when the primary Cd(II) concentration in the solution phase was small.

3.8 Desorption studies

Further evaluation of the adsorbent reuse is required from the economic and environmental points of view, particularly in industrial fields. Therefore, desorption estimates were performed in two steps in order to check the

Fig. 11 Influence of type of eluting agent) with Standard deviation(s) on recovery (%) for Cd(II) ions adsorbed onto cinnamon 300, cinnamon 400, cinnamon 600 (a) and cannabis 300, cannabis 400, and cannabis 600 (b)

reusability of the cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600. Cd(II) adsorption analyses were accomplished by 10.0 mL Cd(II) solution 60 mg L⁻¹ and 0.1 g of each biochar with a pH of 7.0 and the equilibrium time of 60 min at 25 °C. Then, the Cd(II) ion loaded biochars were isolated and conveyed to 5.0 mL desorbing solvent (0.1 mol L⁻¹ HCl and 0.1 mol L⁻¹ NaOH), followed by determining the Cd(II) ion concentration by the ICP-OES after the desorption process. The desorption tests demonstrated that Cd(II) ions were recovered by using the solution of 0.1 mol L⁻¹ HCl from each of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 with the values of 98, 97, 99, 96, 98.8, and 99.5%, respectively (Fig. 11). Also, Cd(II) ions were recovered by using the solution of 0.1 mol L⁻¹ NaOH from each of cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 with the values of 91, 93, 95.5, 92, 93, and 93%, respectively. This confirmed the excellent capacity of the prepared biochars for eliminating the Cd(II) ions from water.

4 Conclusions

In the present study, cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 were fabricated to evaluate the influence of pyrolysis temperature on adsorption ability and surface properties of biochars derived from cinnamon and cannabis for the Cd(II) ion removal. The ideal condition for Cd(II) adsorption onto the biochars included a pH of 7.0, the adsorbent dose of 0.1 g, and the temperature of 65 °C, supplying the $q_{\max}$ of 147.05, 153.84, 158.73, 133.33, 144.92, and 175.43 mg g⁻¹ for cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600, respectively. The cinnamon 600 and cannabis 600 revealed the highest

adsorption of Cd(II) ions due to an increase in the pyrolysis temperature increased surface area of the adsorbents. The data were well modeled by the Langmuir model compared to Freundlich, Temkin, and Redlich-Peterson models while the kinetic fitted with the pseudo-second-order model and the quick adsorption of Cd(II) ions occurred in 60 min. Eventually, the alkaline solution of 0.1 mol L⁻¹ NaOH and 0.1 mol L⁻¹ HCl were efficacious for Cd(II) ion desorption, as well as cinnamon 300, cinnamon 400, cinnamon 600, cannabis 300, cannabis 400, and cannabis 600 recycling.

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Compliance with ethical standards

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

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