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Highly efficient adsorption of cadmium(II) onto durable coconut fiber residue

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ABSTRACT

Removing heavy metals from wastewater is a significant challenge in environmental remediation, and many materials have been studied for their heavy metal adsorption potential. This study investigated the ability of raw coconut fiber residue (CFR), a durable, cost-effective lignocellulose material, to adsorb divalent cadmium (Cd(II)). First, experiments analyzed the influence of pH on CFR adsorption of Cd(II). Cd(II) effectively adsorbed onto CFR; the optimum pH value for adsorption was approximately 5.5. Second, the study examined the adsorption kinetics of Cd(II) by CFR under different initial Cd(II) concentrations and different CFR dosages. Three kinetic models were used to investigate the adsorption mechanism, including pseudo-first-order kinetic, pseudo-second-order kinetic, and intra-particle diffusion models. The adsorption aligned with the second-order kinetic model, with an adsorption isotherm that was well described by the Langmuir model. The data from the Langmuir models were used to determine thermodynamic parameters. The maximum adsorption capacity of CFR for Cd(II) was 62.512 mg/g, significantly higher than other lignocellulosic materials. Finally, the study evaluated adsorption mechanisms, using Fourier transform infrared spectroscopy, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy results, and the Dubinin–Radushkevich (D–R) isotherm model and thermodynamic results. Cd(II)) biosorption occurred by chemisorption, though Cd(II) complexation by the CFR surface groups. This research found that CFR may be a promising biosorbent for removing Cd(II) from aqueous solutions, and therefore, could represent a new potential tool for wastewater treatment.

Keywords: Cd(II); Coconut fiber residue; Lignocellulose material; Biosorbent

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1. Introduction

Cadmium (Cd) is widely used in nickel–cadmium battery manufacturing, electroplating, pigment development, phosphate fertilizer development, mining, refining, and alloy manufacturing. As such, Cd is frequently found in the environment from both natural and man-made sources [1]. Cd is a toxic heavy metal, even at low concentrations [2,3]. The maximum concentration of Cd(II) in drinking water has been set at 0.003 mg/L by the World Health Organization [4]. Moreover, Cd has been classified as a Group B1, probable human carcinogen by the United States Environmental Protection Agency [5]. Due to the widespread existence, persistence, and difficulty in removing Cd(II), Cd(II)-contaminated wastewater treatment options have attracted significant research [6].

There are several ways to removing heavy metals from aqueous solutions, such as filtration, ion exchange, precipitation, electrolysis, and flocculation [7–9]. However, these methods are limited by high costs and secondary pollution. With the development of biomass-based adsorption, or biosorption, studies have turned to the use of low-cost agro-industrial wastes for heavy metal adsorption [10–13].

The coconut is a popular and economically important crop in tropical and subtropical regions of China and is cultivated on approximately 12 million hectares worldwide. A mature coconut contains white meat, surrounded by a hard protective shell and thick husk. Coconut components have many uses: milk is used for cooking, meat serves as a snack, and the husk and shell can be used for building and fuel [14]. Coconut fiber, called "coir," can be extracted from the coconut husk for environmental and economic applications. Coconut fiber is a lignocellulose material, rich in lignin (40–50% of weight), hemicellulose (20–30% of weight), and cellulose (30–40% of weight) [15,16]. Raw coconut fiber residue (CFR), usually generated by extracting coir fiber from coconut husk, is a fluffy, light, and spongy lignocellulose material that resists decomposition [17]. Past research has considered the ability of coconut-related materials to adsorb heavy metals [18]. Further, the coconut shell or husk is often converted into activated carbon for environmental applications [19]. However, little research specifically focuses on the ability of CFR to adsorb heavy metals.

This research investigated CFR adsorption of Cd (II) from aqueous solutions, and evaluated the adsorption kinetics, isotherms, and mechanism of Cd(II) onto CFR.

2. Methods

2.1. Materials and chemicals

For these experiments, CFR was washed using deionized water and then ground into a powder, with particle diameter less than 1.0 mm. It was then dried at 373 K to a constant weight for use. $CdSO_4 \cdot 8H_2O$, H_2SO_4, and NaOH were purchased from Guangzhou Chemical Co. (China). All chemicals were of analytical grade and used as received. The surface area and pore size of the CFR were measured using BET analysis with nitrogen as the adsorbate. The CFR surface area was 1.94 m^2/g and the pore size of blank beads was approximately 27.57 A.

2.2. Characterization and analyses

The Fourier transform infrared spectra (FTIR, Perkin-Elmer 1725X, USA) were recorded as KBr pellet in the range of 4,000–400 cm^{-1}. A scanning electron microscopy with energy dispersive X-ray spectrometer (SEM/EDS, JSM-5910 Microscope and Noran EDS, Japan) was used to investigate CFR surface morphologies and elemental information before and after Cd(II) adsorption.

The Cd(II) concentration in the $CdSO_4 \cdot 8H_2O$ solution was determined using flame atomic absorption spectrophotometry (WFX-130, Rayleigh, Beijing, China). The pH value of the Cd(II) solution was detected using a pH meter (pHS-3, Shanghai, China).

2.3. Adsorption at different pH values

Part of this experiment involved evaluating the influence of pH on the CFR adsorption of Cd(II). To do this, 0.10 g of CFR was added to 100 mL of 50 mg/L Cd(II); the mixture was stirred in a flask at 298 K for 3 h to achieve adsorption equilibrium. The initial pH of the Cd(II) solution was adjusted using 1.0 mol/L H_2SO_4 and 1.0 mol/L NaOH to achieve the target pH for each test [20]. The samples were then centrifuged; the amount of Cd(II) remaining in the supernatant was calculated by measuring the absorbance using flame atomic absorption spectrophotometry. The pH yielding the greatest adsorption rate was subsequently used in the following kinetic and isotherm experiments.

2.4. Adsorption kinetics

To assess adsorption kinetics, 0.10 g of CFR was added into the 100 mL of Cd(II) solution at the selected pH value and at room temperature (298 K), with different initial concentrations of the adsorbate (10–50 mg/L) and different adsorbent doses (0.10–0.25 g/L). CFR adsorption kinetics was analyzed using pseudo-first-order kinetic model (Eq. (1)), the pseudo-second-order kinetic model (Eq. (2)), and the intraparticle diffusion model (Eq. (3)) [21–23].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{2}$$

$$q_t = K_{\mathrm{dif}}t^{1/2} + C \tag{3}$$

In these equations, q_e (mg/g) and q_t (mg/g) are the adsorption capacities at equilibrium and time t, respectively; k_1 (min^{-1}) and k_2 (g/mg min) are the rate constants for the pseudo-first-order and the pseudo-second-order kinetic model, respectively. K_{dif} is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and C (mg/g) is the intercept.

2.5. Adsorption isotherms

To study the adsorption isotherms, 0.02 g of CFR was added to 20 mL of Cd(II) solution. The mixture was shaken in a glass vial sealed with Teflon-lined screw caps at the selected pH value and at different temperature (288, 298, 308, 318, and 328 K) for 24 h to reach the adsorption equilibrium. After the interaction, the samples were centrifuged and the amount of Cd(II) left in the supernatant was calculated. Adsorption isotherms were analyzed using Langmuir isotherm model (Eq. (4)), Freundlich isotherm model (Eq. (5)), and Dubinin–Radushkevich (D–R) isotherm (Eq. (6)) [12,24,25].

$$\frac{1}{q_e} = \frac{1}{C_e q_{\max} K_L} + \frac{1}{q_{\max}} \tag{4}$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{5}$$

$$\log q_e = \log q_{\max} - K_{DR}\varepsilon^2 \tag{6}$$

In these equations, C_e (mg/L) and q_e (mg/g) are the adsorbate concentrations and adsorption capacity at equilibrium, respectively; $q_{\max}$ (mg/g) is the maximum adsorption capacity, and K_L (L/mg) is the Langmuir adsorption equilibrium constant. K_F ((mg/g)(mg/L)^n) is the Freundlich adsorption equilibrium constant; $1/n$ is the heterogeneity factor. K_{DR} (mol^2/kJ^2) is a constant related to the mean adsorption energy and ε is the Polanyi potential, calculated using Eq. (7). T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J/mol/K). The mean biosorption energy (E: kJ/mol) follows (Eq. (8)):

$$\varepsilon = RT\log\left(1 + \frac{1}{C_e}\right) \tag{7}$$

$$E = \frac{1}{\sqrt{-2K_{DR}}} \tag{8}$$

2.6. Desorption studies

Desorption and regeneration studies are important in adsorption studies. The desorption of Cd(II)-loaded CFR was studied using 0.1 M of HCl as the desorbing agent [26]. After determining the Cd(II) concentration, the biosorbent was washed with an acid solution and deionized water, so it could be used for the next experiment. Consecutive sorption–desorption cycles were repeated to determine the biosorbent's reusability potential.

3. Results and discussion

3.1. The influence of pH value

A solution's pH value can influence Cd(II) solubility and complexation with adsorption surface groups [12]. Lignocellulosic materials, such as CFR, have many pH-sensitive surface groups, such as hydroxyl, carboxylic, amino, and phenolic groups [6,15,20,27,28]. In low pH solutions, H^+ may compete with Cd(II) for active CFR adsorption sites. As pH increases, the negatively charged active CFR adsorption sites increase and the pH-sensitive surface groups benefit, to complex the metal cations. Generally, Cd(II) precipitates at pH levels above 7.5 [29], which could result in secondary pollution and treatment difficulty. To avoid precipitation, a weak acidic environment is best for removing Cd(II). Therefore, experiments investigated CFR adsorption of Cd(II) at pH values ranging from 3.5 to 7.5.

Past research notes that the ionization constants of various carboxyl groups are 3.0–4.0 [30]; those of amine and phenolic groups are 9.0–11.0 [31]. There may be a synergic influence of different groups on the CFR adsorption of Cd(II) as pH changes. CFR consists mainly of lignin, cellulose, and hemicellulose. Lignin is a natural complex, three-dimensional, phenolic macromolecule with a common phenylpropane structure. Cellulose is the main polysaccharide, located predominantly in the secondary cell wall. Hemicelluloses are often co-located with cellulose in the cell wall. Large amounts of different functional groups of lignin, cellulose, and hemicellulose enable lignocellulosic materials to remove Cd(II) at pH 5.0–6.0 [20,24,32]. In this study, results show an optimum pH of 5.5 for CFR adsorption of Cd(II) (Fig. 1). As such, subsequent experiments were conducted at a pH of 5.5.

3.2. Adsorption kinetics of Cd(II)

Adsorption kinetics experiments were conducted at a pH of 5.5 and at 298 K; Figs. 2 and 3 show the results. Table 1 shows the CFR adsorption rate constants using the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, and intraparticle diffusion model. The pseudo-second-order kinetic model was better than the other models in describing the CFR adsorption kinetics of Cd(II). This corresponds well with other research about Cd(II) adsorption onto other lignocellulose materials [20,24,32]. As the initial Cd(II) concentration increased from 10 to 50 mg/L, the CFR adsorption capacity of Cd(II) increased from 10.561 to 27.183 mg/g and the adsorption kinetic constants decreased from 0.039 to 0.006 g/mg min. As the adsorbent dosage increased from 1.0 to 2.5 g/L, the CFR adsorption capacity of Cd(II) decreased from 27.183 to 16.013 mg/g and the adsorption kinetic constants increased from 0.006 to 0.051 g/mg min.

The experimental q_e values studied for CFR were close to q_e values calculated from the pseudo-second-order kinetic model. This suggests that the adsorption mechanism is a pseudo-second-order reaction [33,34]. Table 1 lists the diffusion model's correlation coefficients as 0.819–0.926, indicating that the adsorption of Cd(II) on CFR could be followed by an intraparticle diffusion. But these lines did not pass through the origin, suggesting that intraparticle diffusion was not the only rate-limiting mechanism [33].

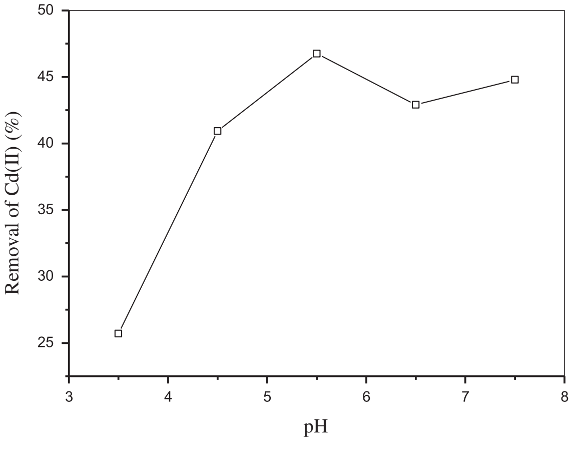

Fig. 1. The influence of pH value on the adsorption of 50 mg/L Cd(II) by CFR of 1 g/L at 298 K.

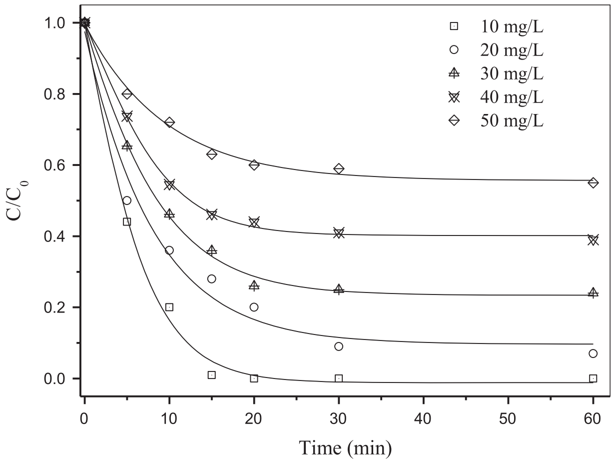

Fig. 2. Adsorption of different initial concentrations of Cd(II) by CFR of 1 g/L at pH 5.5 and 298 K.

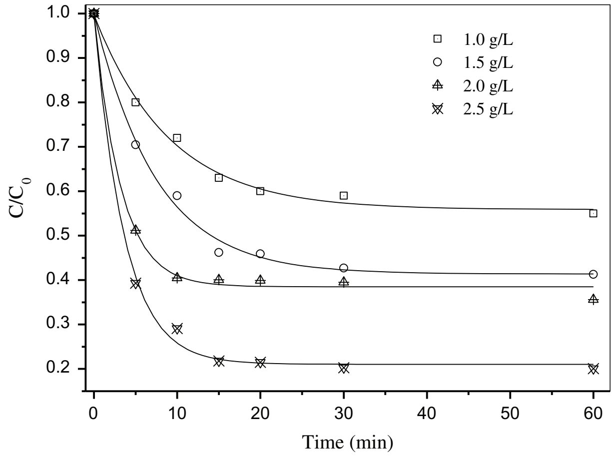

Fig. 3. Adsorption of 50 mg/L Cd(II) onto different dosages of CFR at pH 5.5 and 298 K.

3.3. Adsorption isotherm of Cd(II)

The adsorption isotherm describes the equilibrium of metal cations between solid and liquid phases. To explore this equilibrium, the CFR adsorption isotherm of Cd(II) was studied at different temperatures(288, 298, 308, 318, and 328 K). Compared with the Freundlich isotherm model and Dubinin–Radushkevich (D–R) model, the Langmuir isotherm model was better for describing the CFR adsorption isotherm of Cd(II). As Table 2 shows, when the temperature is 298 K, the

Table 1
Adsorption kinetic parameters of Cd(II) by CFR

		Pseudo-first-order kinetic			Pseudo-second-order kinetic			Intraparticle diffusion		
		q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2	k_p (mg/g min$^{0.5}$)	C (mg/g)	R^2
Cd(II), C_0 (mg/L)	10	15.381	0.290	0.822	10.561	0.039	0.995	0.668	5.919	0.926
	20	19.452	0.119	0.949	20.475	0.009	0.999	1.586	7.806	0.830
	30	25.704	0.155	0.944	25.163	0.008	0.993	2.064	9.598	0.863
	40	27.777	0.133	0.975	26.874	0.007	0.994	2.165	10.373	0.908
	50	31.477	0.089	0.951	27.183	0.006	0.997	2.134	7.989	0.881
CFR, dosage (g/L)	1.0	31.477	0.089	0.951	27.183	0.006	0.997	2.134	7.989	0.881
	1.5	27.829	0.1085	0.835	22.326	0.011	0.996	1.619	9.072	0.819
	2.0	17.502	0.1012	0.681	16.436	0.036	0.999	0.541	12.562	0.916
	2.5	22.646	0.1656	0.842	16.013	0.051	0.999	0.597	12.247	0.845

adsorption equilibrium constant (K_L) for CFR adsorption of Cd(II) was 0.107 L/mg; the maximum adsorption capacity (q_m) was 62.512 mg/g.

The D–R isotherm model did not fit the equilibrium data since the R^2 value was found to 0.532–0.812. The biosorption mean free energy was 8.120–10.235 kJ/mol within a 288–328 K temperature range. An E value between 8 and 16 kJ/mol indicates that the biosorption process occurs chemically [35], and the biosorption of Cd(II) onto CFR may be proceeded by binding surface functional groups. This was confirmed by FT-IR spectroscopy and thermodynamic results.

The adsorption capacity of Cd(II) onto CFR was compared with other adsorbents reported in the literature; Table 3 shows that CFR compared well with other studied adsorbents [20,32,34]. Due to its high capacity and low cost, CFR may be a promising alternative for removing Cd(II) from aqueous solutions.

3.4. Adsorption thermodynamics studies

The decrease in adsorption capacity with rising temperature (Table 2) was attributed to the exothermic nature of the process, and was further explained by

Table 2
Adsorption isotherm parameters of Cd(II) by CFR

		CFR		
Isotherms	Temperature (K)	q_{max} (mg/g)	K_L (L/mg)	R^2
Langmuir model	288	62.361	0.089	0.954
	298	62.512	0.107	0.939
	308	42.214	0.092	0.982
	318	30.121	0.072	0.963
	328	22.214	0.062	0.987
		K_F ((mg/g) (mg/L)^n)	n	
Freundlich model	288	7.912	1.401	0.921
	298	8.398	1.433	0.890
	308	7.321	1.321	0.901
	318	6.231	1.212	0.875
	328	4.321	1.021	0.932
		q_{max} (mg/g)	E (kJ/mol)	
Dubinin–Radushkevich model	288	43.321	8.321	0.812
	298	44.215	10.235	0.784
	308	25.421	9.123	0.532
	318	18.213	8.120	0.654
	328	16.214	6.621	0.734

Table 3
The performance of different types of agro-industrial wastes for Cd removal from aqueous solutions

Adsorbent (modifying agent)	$q_{\max}$ (mg/g)	Mechanism	Refs.
Agave bagasse (raw)	13.27	Ion exchange, complexation	[43]
Agave bagasse (NaOH)	18.23	Ion exchange, complexation	[43]
Rice straw (raw)	13.89	Ion exchange, chelating	[20]
Grapefruit peel (raw)	42.09	Ion exchange	[36]
Corncob (citric acid)	49.20	Ion exchange	[44]
Wheat stem (raw)	11.60	Complexation	[32]
Wheat stem (NaOH)	21.84	Complexation	[32]
Coconut shell (raw)	37.78	–	[34]
CFR	62.51	Complexation	[Present study]

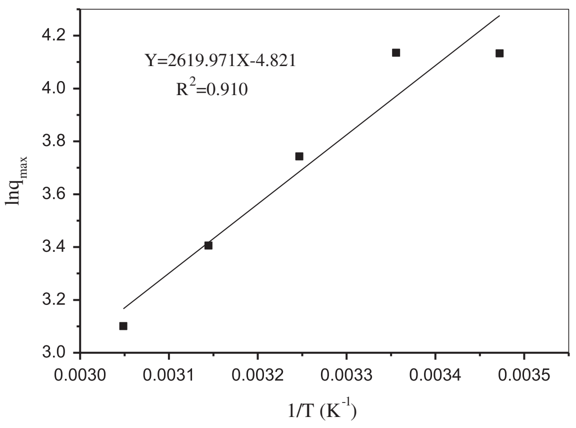

Fig. 4. van’t Hoff plot for estimation of thermodynamic parameters.

evaluating thermodynamic parameters. Thermodynamic properties, such as Gibbs free energy (ΔG°, kJ/mol) and enthalpy (ΔH°, kJ/mol), were assessed using experiments at different temperatures and by applying the following equations (Eqs. (9) and (10)):

$$\Delta G^\circ = -\mathrm{RT} \quad \ln q_{\max} \tag{9}$$

$$\ln q_{\max} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

In these equations, T is the temperature in Kelvin and R is the gas constant. The ΔH° and ΔS° variables were calculated from the slope and intercept of van’t Hoff plots of $\ln q_{\max}$ (from the Langmuir isotherm) vs. $1/T$ (Fig. 4) [36]. Table 4 lists ΔH°, ΔS°, and ΔG° at different temperatures.

The Gibbs free energy changes during the adsorption process were all negative, indicating a spontaneous adsorption process. The negative ΔH° (−21.78 kJ/mol) indicates the exothermic nature of the biosorption; its magnitude provides information about the type of biosorption, which can be either physical or chemical. An enthalpy or heat of biosorption, ranging from 0.5 to 5 kcal/mol (2.1–20.9 kJ/mol) would correspond with physical sorption. Chemical sorption would result in a range of 20.9–418.4 kJ/mol [37].

Here, the ΔH° values indicate that the biosorption process of Cd(II) onto CFR takes place via chemisorption. The energy value obtained from the D–R model also confirms this result. The negative entropy change for the ΔS° (−40.08 J(mol K)) process was caused by the decrease in degree of freedom of the adsorbed species [38,39].

3.5. FTIR and SEM/EDX

FTIR is important in characterizing lignocellulosic materials containing lignin, cellulose, and

Table 4
Thermodynamic parameters for Cd(II) adsorption on CFR

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
288	−9.90	−21.78	−40.08
298	−10.25		
308	−9.58		
318	−9.00		
328	−8.46		

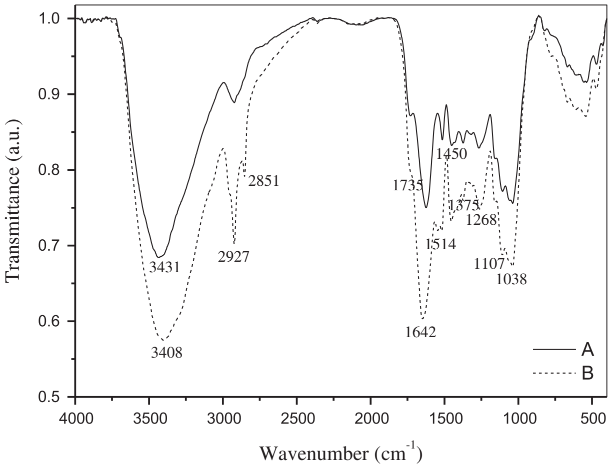

Fig. 5. FTIR spectra of CFR before and after the adsorption of Cd(II): (A) after adsorption and (B) before adsorption.

hemicellulose, such as CFR (Fig. 5) [40,41]. Bands at 3,408 and 3,431 cm^{-1} can be attributed to the stretching of the strong hydroxyl bond (O–H); the band at 2,927 cm^{-1} is due to the stretching of C–H; and the bands around 1,642 cm^{-1} can be attributed to the O–H stretching of adsorbed water and C=O stretching with the aromatic ring [42]. There were bands at 2,851 cm^{-1} associated with C=O stretching in conjugated p-substituted aryl ketones, a band at 1,735 cm^{-1} due to unconjugated C=O stretching of acetyl or carboxylic acid in xylans (hemicellulose), a band at 1,514 cm^{-1} associated with C=C stretching of aromatic ring (lignin), a band at 1,450 cm^{-1} due to C–H deformation of –OCH$_3$ in lignin, a band at 1,375 cm^{-1} due to C–H deformation and vibration of C–O–O in cellulose and hemicellulose, a band at 1,268 cm^{-1} due to C–O stretching in lignin and C–O linkage of guaiacyl aromatic methoxyl groups, a band at 1,107 cm^{-1} due to aromatic skeletal and C–O stretching, and a band at 1,038 cm^{-1} due to C–O stretching in cellulose and hemicellulose [28,40,41]. After Cd(II) adsorption, the relative intensities of all bands decreased, perhaps due to chemisorption with Cd(II) complexation through the CFR surface groups.

Fig. 6 shows the study's SEM/EDS results. CFR has a spongy, layer texture, showing little structural change before and after Cd(II) adsorption. CFR contains C, O, Al, Si, and Ca, the main constituents of lignin, cellulose, and hemicellulose, before Cd(II)

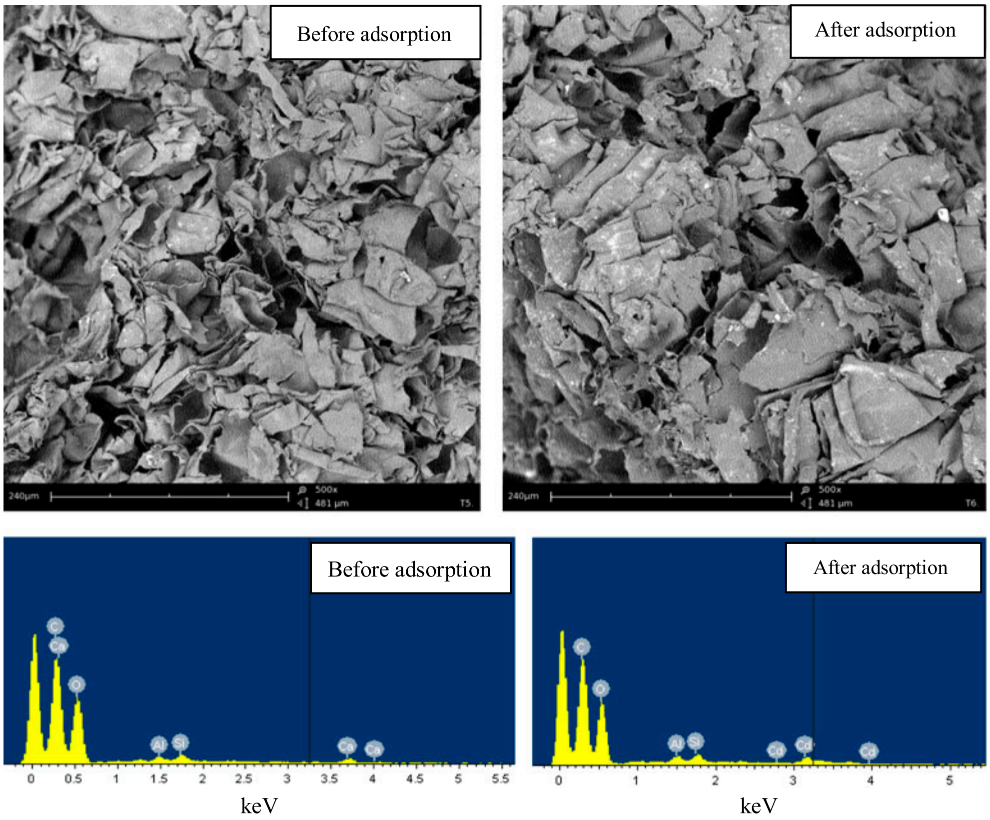

Fig. 6. SEM/EDX of CFR before and after the adsorption of Cd(II).

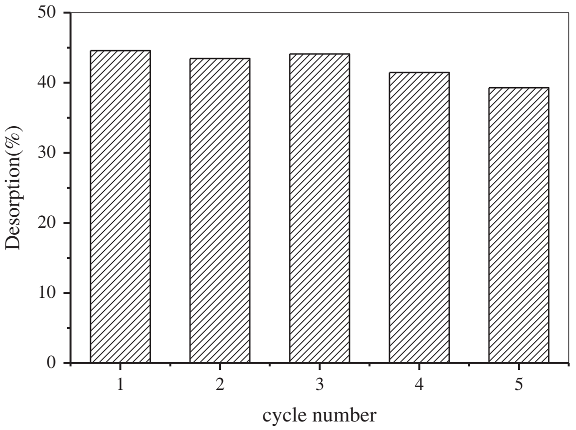

Fig. 7. Reusability of CFR with repeated sorption–desorption cycles (C_o: 50 mg/L; pH 5.5; adsorbent dosage: 1 g/L; time: 60 min).

adsorption. The Ca disappears after Cd(II) adsorption, suggesting that the Cd and Ca exchange might happen on the CFR surface.

3.6. Mechanism

Several possible mechanisms could be involved in lignocellulose material adsorption of heavy metals [27]. Cation exchange, complexation, and chemisorption are the most commonly reported mechanisms. The SEM/EDS results of CFR adsorption of Cd(II) capture the cation exchange of Cd with Ca. CFR contains approximately 0.2% Ca in weight, which may contribute to an adsorption capacity of 5.62 mg/g as Ca is exchanged with Cd. The adsorption isotherm results show that the maximum adsorption capacity (q_m) was 62.512 mg/g. Thus, the cation exchange of Cd with Ca would account for less than 10% of CFR's removal of Cd(II). Besides the cation exchange, the contribution of chemisorptions may be more than 90%. Based on this, it appears that chemisorption through Cd(II) complexation by the CFR surface groups plays an important role in removing Cd(II).

3.7. Desorption efficiency and reusability

Biosorbent regeneration is a key factor in assessing its potential for commercial applications. Njikam and Schiewer [26] suggested that mineral acids, such as HCl, are promising desorbing agents for efficient CFR regeneration, because they are inexpensive and relatively harmless. Therefore, 0.1 M of HCl was used as the desorbing agent for the elution of Cd(II) from Cd-loaded CFR. More than 90% of the desorbed Cd(II) was desorbed from the Cd-loaded biosorbent. CFR reusability was investigated for five consecutive sorption–desorption cycles (Fig. 7). Results indicate that the CFR has the potential for repeated use to remove Cd(II) from aqueous solutions.

4. Conclusions

This study concluded that CFR is an effective adsorbent for removing Cd(II) from the aqueous solution. The solubility of Cd(II) and its complexation with adsorbent surface groups depends partially on the solution's pH value. A weak acidic environment supported Cd(II) adsorption onto the CFR. Compared with the contribution of cation exchange below 10%, chemisorption through the complexation of Cd(II) by CFR surface groups dominated CFR removal of Cd(II). CFR is suitable for removing Cd(II) from aqueous solutions, because it has a relatively high adsorption capacity and low cost. Further study is needed to assess the economic feasibility of adsorbent regeneration and its ability to treat real industrial wastewater.

Acknowledgments

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