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Sorption of Cd (II) ion by lignocellulose biomass from leaves of camphor tree

Chongqing Wang[a], Hui Wang[a,*], Guohua Gu[b], Younian Liu[a]

[a]*School of Chemistry and Chemical Engineering, Central South University, Changsha, 410083 Hunan, China, email: zilangwang@126.com (C. Wang), huiwang1968@163.com (H. Wang), liuyounian@csu.edu.cn (Y. Liu)*

[b]*School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China, email: guguohua@126.com*

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ABSTRACT

Lignocellulose biomass (CLBA) from leaves of camphor tree was used for Cd (II) removal from aqueous solution. X-ray diffraction (XRD), X–ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) studies were conducted to characterize the surface groups and morphology of CLBA. The effects of CLBA dosage, pH, contact time and initial concentration on Cd (II) sorption were evaluated by batch experiments. Sorption kinetics were investigated by pseudo–first order, pseudo–second order and intraparticle diffusion kinetic models. Sorption equilibrium was examined by Langmuir and Freundlich isotherms. The sorption process follows pseudo-second order model and the Langmuir model. The removal rate is up to 99.12%, and the maximum sorption capacity is 10.99 mg g^{-1}. The sorption mechanism may be attributed to surface complexation and ion exchange. Effective desorption of Cd (II) suggests that CLBA can be reused for many times. This work indicates that camphor leaves can be an effective and low-cost biosorbent for Cd (II) removal from wastewater.

Keywords: Sorption; Cadmium; Biomass; Kinetics; Wastewater

1. Introduction

Pollution of wastewater with heavy metals such as copper, lead, cadmium and chromium is an ongoing problem all over the world owing to the great toxicity of these metals. Industries, including electroplating, mining, metallurgy, electronics, and ceramic industry, produce a large amount of wastewaters containing heavy metals, causing serious environmental problems [1,2]. Heavy metals even at low concentration can be detrimental to a variety of living species, including human beings. Specifically, heavy metals can damage nerves, liver and bones, and interfere with the normal functioning of various metallo-enzymes [3,4]. Moreover, heavy metals are of special concern because of their accumulation in the environment.

Enormous efforts have been made for removal of heavy metals from wastewater. Chemical precipitation, lime coagulation, ion exchange, reverse osmosis, adsorption and solvent extraction were developed for this purpose [5,6]. However, most of these methods are limited for real application due to high cost, low efficiency and generation of toxic wastes. Compared with other techniques, adsorption as a promising alternative shows the advantages of low cost, high efficiency and environmental-friendliness. Furthermore, there exists a good potential for metal recovery from loaded adsorbents through elution or incineration.

Lignocellulose, referred to plant dry matter (biomass), is one of the most abundantly available raw materials. It is composed of biomacromolecular components, such as cellulose, hemi-cellulose and lignin. Lignocellulose biomass can be generally classified into virgin biomass, waste biomass and energy crops. Waste biomass is generated as a low value by-product of various industrial or agricultural activities. Abundant waste materials may be potential inexpensive adsorbents for removing heavy metals in wastewater. Previous studies suggest that such materials have

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*Corresponding author.

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good sorption potential for metal ions. Various agricultural by-products, including wood [7], pine bark [8], banana and orange peels [9], rice husk [10], peanut shell [11], and straws [12], have been investigated for treatment of heavy metals.

Cadmium is one of the most toxic metals. Cd (II) ion in waste streams mainly comes from mining and metallurgy of cadmium, battery or accumulator manufacturing, electroplating, pigments and ceramic industries. Activated carbons prepared from some agricultural wastes [13,14] are some examples of low-cost materials used for Cd (II) removal from wastewater. Low-cost biosorbents are still imperative for removal of Cd (II) ions from wastewater.

Camphor tree (*Cinnamomum camphora*) is a native evergreen tree, widely planted in southwestern parts of China, and also distributed in other countries. There are few reports about using camphor leaves as biosorbent. The sorption characteristics of Pb(II), Cu(II) and *Rhodamine B* from aqueous solution onto camphor leaves were reported [15,16]. Camphor leaves show large binding capacity for metal ions. To the best of our knowledge, there is still no study about sorption of Cd (II) onto camphor leaves. In this study, camphor leaves were studied as potential biosorbent of Cd (II) ions. The material was characterized by X-ray diffraction (XRD), X–ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The influence of process parameters, such as sorbent dosage, contact time, pH and initial ion concentration, were investigated. The experimental data were evaluated by sorption equilibrium isotherms and kinetic models.

2. Materials and methods

2.1. Materials

The fresh leaves from camphor tree were obtained from the campus of Central South University, China. The sample was washed repeatedly with tap water and distilled water to remove dust and soluble impurities. The camphor leaves were dried in an oven at 80°C for 24h, ground by a plant crusher (FW-177, Tianjin Taisite Instrument Co., Ltd., China) and screened with China standard sieves. The particle size used in this study is 60–200 mesh. The powders were further washed with distilled water until water were free of color before dried at 80°C for 24 h. The prepared sample of camphor leaves (hereafter called CLBA) was used as biomass biosorbent without any pre–treatment.

All chemicals used were analytical reagent grade. The stock solutions of 1000 mg L^{-1} Cd (II) were prepared by dissolving $3CdSO_4{\cdot}8H_2O$ in a 1 L volumetric flask and diluted to the mark. Experimental solutions of the desired concentrations were obtained by successive dilutions. The pH of solutions was adjusted using 0.1 mol L^{-1} HNO_3.

2.2. Characterizations

The XRD with Cu Kα radiation (SIMENS D500, BRUKER) was used to analyze the crystalline phases of the material. The morphology and chemical composition of CLBA were investigated on a SEM equipped with energy dispersive spectrometer (EDS) (Quanta FEG 250) with an accelerating voltage of 10 kV. Surface elements of CLBA were analyzed with a XPS (ESCALAB 250Xi, Thermo Fisher Scientific) using an Al–α X–ray source operating at 12 keV and 72 W.

The samples (1 mg) were mixed with 100 mg of spectroscopy grade KBr powder, and then pressed into a small pellet. The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer (Nicolet Magua Corporation, USA) in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were analyzed by Origin™ software in order to identify the main characteristic bands of the samples.

2.3. Sorption experiments

Sorption experiments were conducted in 250 mL conical flasks located in an oven oscillator (SHA-B, Changzhou Aohua Instrument Co. Ltd., China) at fixed stirring speed of 150 rpm. Typical experiments were performed under conditions of 1.4g CLBA, 25 mL of 200 mg L^{-1} Cd (II) solution, contact time of 60 min and temperature 30°C. The natural pH of Cd (II) solution was 5.8 ± 0.2, and this pH was maintained throughout for all the experiments except for studies of pH effect. The regions of CLBA dosage, pH, contact time, and initial concentration were 4–72 g L^{-1} CLBA, 1–5.8, 0–120 min, and 60–1000 mg L^{-1}, respectively. After sorption, the sorbent was filtered, and the content of Cd (II) in the solutions was determined by inductively coupled plasma–optical emission spectrometry (ICP-OES; Perkin Elmer Optima 5300 DV). The sorption capacity and removal rate for sorption Cd (II) onto CLBA was calculated by Eqs. (1) and (2). Desorption experiments were performed in 0.05 mol L^{-1} ethylenediaminetetraacetic acid disodium salt $(EDTA(Na)_{2)}$ solution, and the concentration of metal ions after desorption was determined by ICP-OES. The results were obtained from at least three experiments.

$$Q = (C_0 - C_e)V/m \tag{1}$$

$$R = (C_0 - C_e)/C_0 \times 100 \tag{2}$$

where Q is the sorption capacity of CLBA, mg g^{-1}; C_0 and C_e is the initial and sorption equilibrium concentration of Cd (II) ion, respectively, mg L^{-1}; V is the volume of solution, L; m is the mass of CLBA, g; R is the removal rate of metal ions, %.

3. Results and discussion

3.1. Characterizations of CLBA

3.1.1. XRD of CLBA

XRD was conducted to characterize CLBA. As shown in Fig. S1 (in Supplementary Materials), the XRD pattern indicates that CLBA possess low degree of crystallinity, and this may be due to amorphous lignin and hemicelluloses. The peaks at 14.98° and 21.48° is typically attributed to crystalline planes cellulose *I*, while the peaks at 24.38° and 30.15° may be due to water-insoluble low molecular weight crystalline substances [17]. No obvious changes in XRD pattern are observed after binding Cd (II) onto CLBA, implying that no crystalline products form in sorption process.

3.1.2. XPS of CLBA

The elements in CLBA determined by XPS are shown in Fig. 1. The XPS spectrum of CLBA shows that the sorbent is mainly made up of carbon, oxygen and a small amount of nitrogen. This confirms the lignocellulose nature of camphor leaves, which consists mainly of cellulose, hemi-cellulose and lignin.

3.1.3. SEM of CLBA

The morphology of CLBA was characterized by SEM. As shown in Fig. 2a, the morphology of CLBA facilitates sorption of metal ions owing to the highly irregular surface of camphor leaves. Therefore, CLBA presents an adequate morphological profile for sorption metal ions. The main elements of CLBA determined by EDS manifest the major contents of CLBA are carbon and oxygen. This is attributed to the lignocellulose nature of camphor leaves. In addition, there exist a few alkali and alkali-earth metals (Na, Ca, Mg and K), and this is consistent with other plant materials [1,18].

3.1.4. FTIR studies

The FTIR technique is an important tool to identify characteristic groups of carbohydrates. The FTIR spectra for CLBA and Cd (II) loaded CLBA are shown in Fig. 3. The FTIR spectrum of CLBA shows a typical molecular vibrations at 3403 cm^{-1} (stretching vibration of –OH), 2920 cm^{-1} and 2851 cm^{-1} (asymmetric and symmetric –CH$_2$), 1735 cm^{-1} (COOH), 1654 cm^{-1} (C=O), 1517 cm^{-1} (C–C stretching), 1442

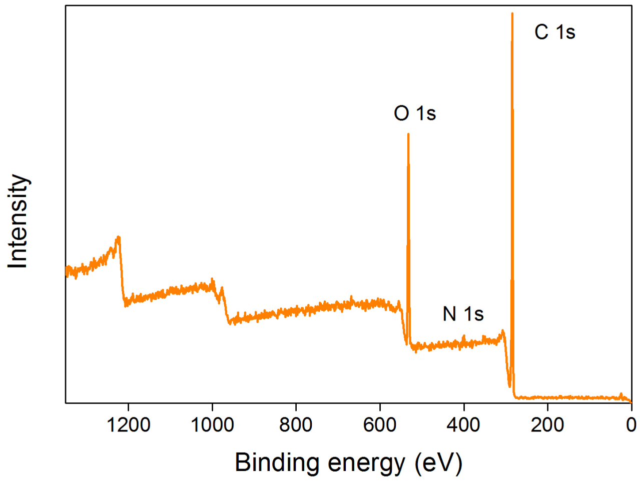


Fig. 1. Survey XPS spectra of CLBA.

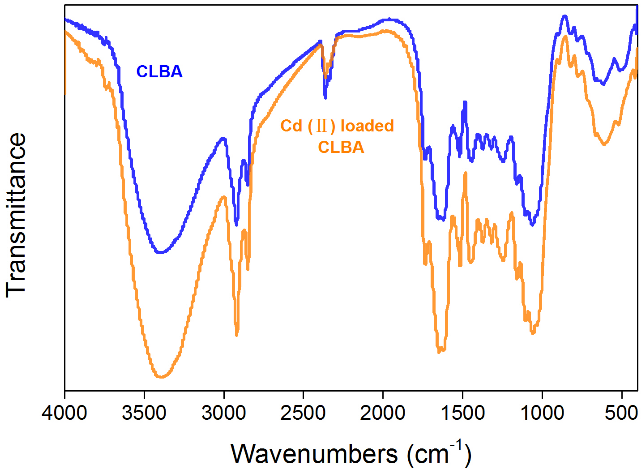
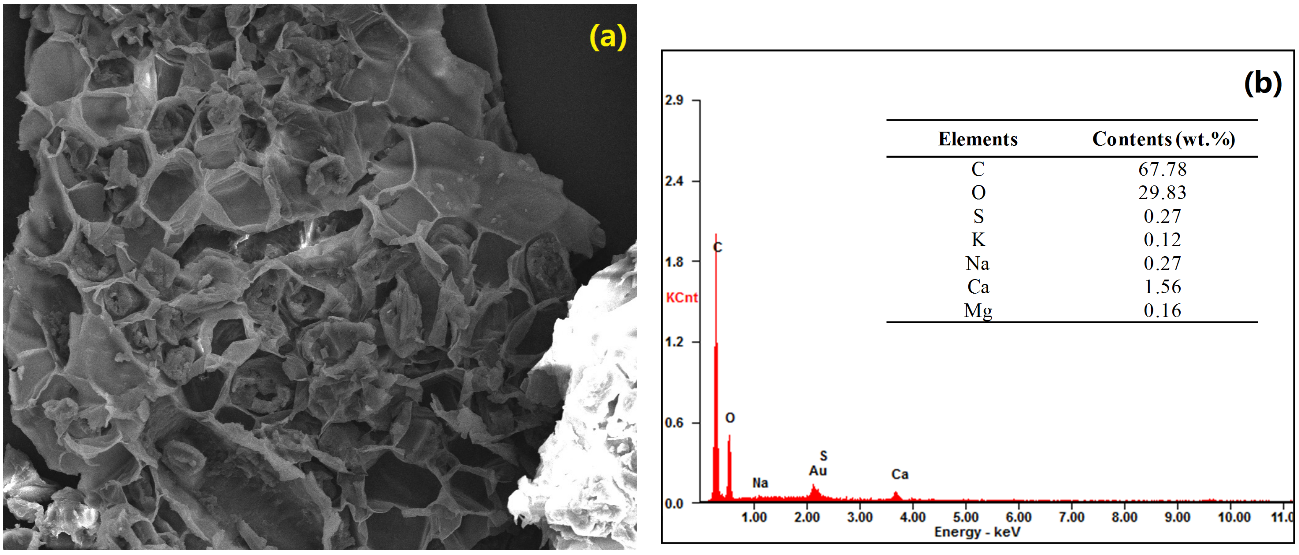


Fig. 3. FTIR spectra of CLBA and Cd (II) loaded CLBA.



Elements	Contents (wt.%)
C	67.78
O	29.83
S	0.27
K	0.12
Na	0.27
Ca	1.56
Mg	0.16

Fig. 2. SEM (a) and EDS (b) spectra of CLBA.

cm^{-1} (C–H and in-plane –OH bending), 1243 cm^{-1} (C–O stretching), 1105 cm^{-1} (C=O bending), and 1062 cm^{-1} (C–OH in-plan bending) [15,19]. The strong peak at 3403 cm^{-1} is due to vibration of the presence of hydroxyl group linked in cellulose and lignin, and water molecules in the sample. The presence of carbonyl, phenolic, carboxyl, and methoxyl groups of carbohydrates in CLBA provides attractive potential for sorption of heavy-metal ions.

The spectrum of Cd (II) loaded CLBA is similar to that of CLBA, but some peaks shifts slightly after Cd (II) sorption. Specifically, the peaks at 3403 cm^{-1} (–OH group), 1654 cm^{-1} (C=O), 1442 cm^{-1} (C–H and in-plane –OH bending) and 1062 cm^{-1} (C–OH in-plan bending), shift to 3489 cm^{-1}, 1652 cm^{-1}, 1449 cm^{-1} and 1060 cm^{-1}, respectively. Therefore, it can be concluded that such functional groups as –OH and –COOH, are active sites for sorption of Cd (II). Cd (II) can bind with functional groups by coordinate-type interaction. Cd (II) forms a coordinate bond with the electron pair of oxygen functional groups such as –OH and –COOH in cellulose, hemi-cellulose and lignin. Therefore, surface complexation can play an important role in sorption process.

3.2. Effect of CLBA dosage

The removal rate and sorption capacity as a function of CLBA dosage is shown in Fig. 4. With an increase of CLBA dosage, the removal rate of Cd (II) increases sharply at low dosages. After the dosage above 56 g L^{-1}, the removal rate becomes flatness. The removal rate of Cd (II) is up to 95.92%, implying that CLBA is effective to remove Cd (II) ions from aqueous solution. However, the sorption capacity reduces with an increase of CLBA dosage. This can be attributed to lack of enough Cd (II) ions in aqueous solution and insufficient utilization of active sites for sorption on CLBA surface. Given the effect of CLBA dosage on the removal rate and sorption capacity, 56 g L^{-1} CLBA was chosen for sorption of Cd (II).

3.3. Effect of pH

The pH of aqueous solution is an important factor in sorption of metal ions using biosorbents. The influence of initial pH of solutions on the sorption of Cd (II) onto CLBA was examined. As shown in Fig. 5, both removal rate and sorption capacity decreases with a reduction of pH value. This implies the characteristic of chelation mechanism, which attributes to the presence of abundant oxygen-containing groups confirmed by FTIR spectrum. The reduction of sorption efficiency might be due to the protonation of functional groups and competitive sorption of hydrogen ions. In addition, less insignificant competitive sorption of hydrogen ions occurs at pH > 3. No sorption experiments were conducted at pH above 5.8 owing to the formation of cadmium hydroxide precipitate. A pH of 5.8 was chosen subsequent experiments.

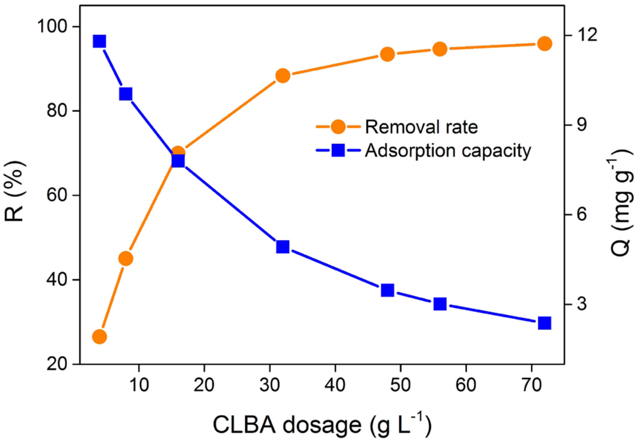


Fig. 4. Effect of CLBA dosage on the removal rate and sorption capacity of Cd (II) onto CLBA.

3.4. Sorption kinetics

As shown in Fig. 6, the removal rate increases with increasing of contact time. It is obvious that during short contact time intervals, sorption is very fast (within 5 min more than 92% Cd ions was loaded) due to the presence of large number of active sites for sorption on CLBA surface. Additionally, the sorption equilibrium is achieved after 60

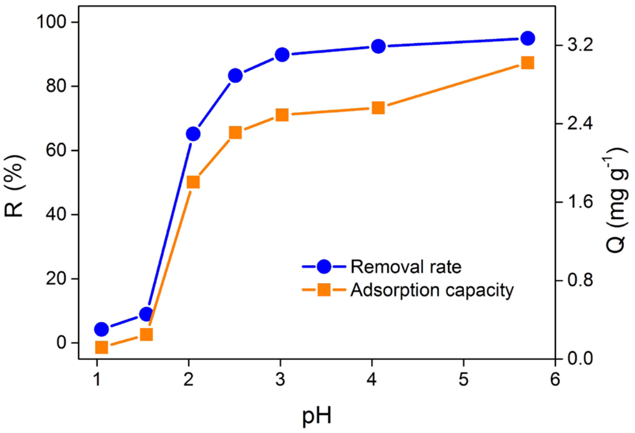


Fig. 5. Effect of pH on the removal rate and sorption capacity of Cd (II) onto CLBA.

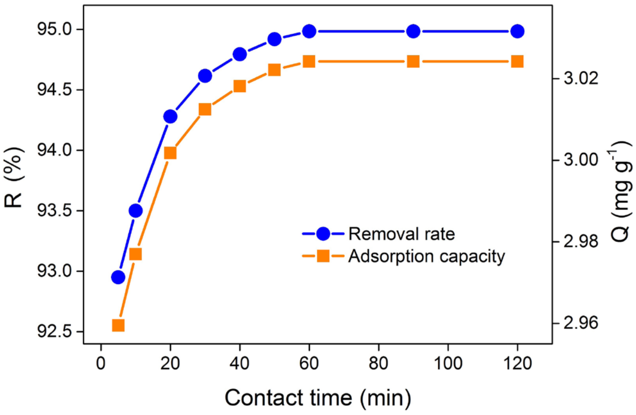


Fig. 6. Effect of contact time on the removal rate and sorption capacity of Cd (II) onto CLBA.

min for Cd (II). Moreover, with an increase of contact time, the sorption capacity rises significantly, indicating that more and more active sites are used for sorption.

In order to investigate the sorption kinetics, experimental data were mostly fitted by pseudo–first order kinetic model [20], pseudo–second order kinetic model [21] and intraparticle diffusion kinetic model [22], which can be expressed as Eqs. (3), (4) and (5), respectively. Q_e and k_1 can be determined from the slope and intercept of the plot of $\ln(Q_e - Q_t)$ vs. t (the figure is not given). The second order rate equation constant k_2 can be determined by plotting t/Q_t vs. t shown in Fig. S2 (in Supplementary Materials). The values k_i and C_i can be calculated from the slope and intercept of the plot of Q_t vs. $t^{0.5}$. The kinetic parameters for different models are summarized in Table 1.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{3}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{4}$$

$$\mathrm{Q_t} = k_i t^{0.5} + C_i \tag{5}$$

where k_1 (min^{-1}), k_2 (g mg^{-1} min^{-1}) and k_i (mg g^{-1} min$^{-0.5}$) are the rate constant of pseudo-first order kinetic, pseudo-second order kinetic and intraparticle diffusion kinetic; t is the contact time; Q_t (mg g^{-1}) and Q_e (mg g^{-1}) is the sorption amount of metal ions at contact time t and equilibrium sorption amount; C_i (mg g^{-1}) is a constant.

Although the plot of pseudo-first order model shows good linearity (regression coefficient is 0.9937), the calculated value of sorption amount at equilibrium is different from the experimental one, indicating that sorption process does not match pseudo-first order model. In the case of pseudo-second order model, the regression coefficient is up to 0.9999 and the calculated value of sorption capacity agrees well with the experimental one. Both facts suggest that the sorption of Cd (II) by CLBA follows the pseudo-second order kinetic model, implying that the rate-limiting step may be a chemical sorption. As to intraparticle diffusion model, the data exhibit multilinear plots, indicating that the sorption process is controlled by two or more steps. The initial steep stage might be due to the fact that the immediate utilization of the most readily available adsorbing sites on the adsorbent surface leads to a rapid external surface sorption. Additionally, a gradual sorption where intraparticle diffusion is the dominant factor is attributed to slow diffusion of Cd (II) ions from the surface sites into the inner pores.

Table 1
Kinetic parameters for sorption of Cd (II) onto CLBA

	$Q_{e,\,exp}$ (mg g^{-1})	3.0243
Pseudo-first order model	Q_e (mg g^{-1})	0.1163
	k_1 (min^{-1})	0.081
	R^2	0.9937
Pseudo-second order model	Q_e (mg g^{-1})	3.0303
	k_2 (g mg^{-1} min^{-1})	2.3674
	R^2	0.9999
Intraparticle diffusion model	k_{i1} (mg g^{-1} min$^{-0.5}$)	0.5245
	C_{i1} (mg g^{-1})	91.8237
	R^2	0.9814
	k_{i2} (mg g^{-1} min$^{-0.5}$)	0.1642
	C_{i2} (mg g^{-1})	93.7357
	R^2	0.9655

3.5. Sorption isotherms

From Fig. 7, it can be seen that with increasing of initial concentration, the removal rate drops dramatically and the sorption capacity increases significantly. At higher concentration, the active sites are made good use for sorption Cd (II), while the sorption capacity is very low due to lack of Cd (II) ions. Additionally, the removal rate of Cd (II) is up to 99.12% when the initial concentration is 60 mg L^{-1}, implying that CLBA is very effective for removal of low-concentration Cd (II).

Sorption isotherms are important to understand the mechanism of the sorption process. Two models are mainly used to describe sorption isotherms, namely Langmuir model and Freundlich model [23,24]. The linear forms of Langmuir and Freundlich isotherm can be shown as Eqs. (6) and (7), respectively.

$$\frac{C_e}{\mathrm{Q}_e} = \frac{\mathrm{b}}{Q_{\max}} + \frac{C_e}{Q_{\max}} \tag{6}$$

$$\log \mathrm{Q}_e = \log \mathrm{K}_F + \frac{1}{n} \log C_e \tag{7}$$

$$\mathrm{R_L} = \frac{1}{1 + bC_0} \tag{8}$$

where C_e is the equilibrium concentration of metal ions in the solution, mg L^{-1}; Q_e is the sorption amount of metal ions onto CLBA at equilibrium, mg g^{-1}; Q_{max} is the maximum

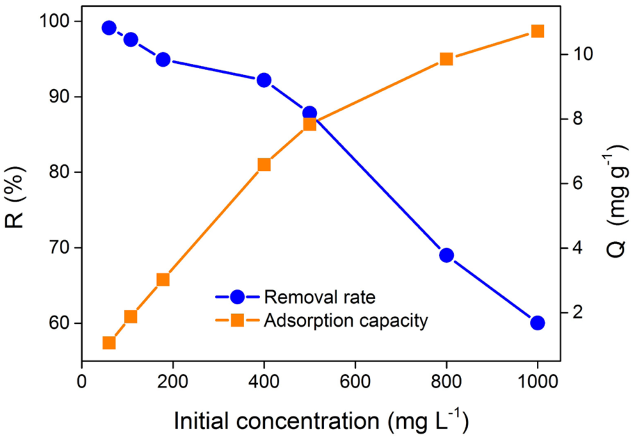


Fig. 7. Effect of initial concentration on the removal rate and sorption capacity of Cd (II) onto CLBA.

sorption amount, mg g^{-1}; b is a constant that relates to the heat of sorption, L mg^{-1}. K_F and n are Freundlich constants indicating sorption capacity and intensity, respectively. R_L is a dimensionless constant, referring to separation factor or equilibrium parameter, and C_0 is the initial concentration of metal ions.

The sorption isotherms are plotted in Fig. S3 (in Supplementary Materials). The parameters and correlation coefficients obtained from the plots of Langmuir and Freundlich isotherms are listed in Table 2. The values of correlation coefficients (R^2) suggest that Langmuir model shows closer fittings than Freundlich model. Isotherm constants can suggest whether a sorption system is favorable or unfavorable. The Langmuir parameter R_L (shown in Eq. 8) is between 0 and 1.0, indicating that the sorption is favorable [25]. Moreover, the n value ($2 < n < 10$) of Freundlich isotherm demonstrates well sorption characteristics of Cd (II) onto CLBA.

The maximum monolayer sorption capacity of CLBA is 10.99 mg g^{-1} for Cd (II) (Table 2). Comparison the sorption capacity obtained from this study with that of other biosorbents can suggest the effectiveness of CLBA as a potential sorbent for treatment of water containing Cd (II). The sorption capacity of different biosorbents is shown in Table 3. It can be seen that the maximum sorption capacity of CLBA for Cd (II) is comparable to other previously reported sorbents. The sorption capacity of fig leaves is much higher than that of camphor leaves, but camphor leaf is an abundant and locally available material and used without chemical pretreatment. Therefore, camphor leaves can be an effective and low-cost potential biosorbent for removal of Cd (II) in aqueous solution.

Table 2
Isotherm parameters for the sorption of Cd (II) onto CLBA

Langmuir				Freundlich		
Q_m (mg g^{-1})	b (L mg^{-1})	R_L	R^2	K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	n	R^2
10.9914	17.9413	0.0011	0.9962	1.4241	2.7248	0.9592

Table 3
Comparison of maximum sorption capacity of CLBA with other biosorbents

Biosorbents	Maximum sorption capacity (mg g^{-1})	References
Camphor leaves	10.99	Present study
Fig leaves	103.09	Benaïssa [26]
Rice husk	8.58	Kumar and Bandyopadhyay [10]
Walnut shell	1.50	Orhana and Büyükgüngör [27]
Sawdust	5.37	Bulut and Tez [28]
Bamboo charcoal	12.08	Wang et al. [19]
Sugarcane bagasse	10.7	Basso et al. [29]
Cassava waste	14.3	Abia et al. [30]
Maize bran	7.43	Singh et al. [31]

3.6. Sorption mechanism

The biomacromolecular components of camphor leaves including cellulose, hemi-cellulose and lignin provide functional groups for sorption, such as carbonyl, phenolic, and carboxyl groups. Sorption of Cd (II) can be achieved by surface complexation. Moreover, the presence of alkali and alkali-earth metals (Na, Ca, K and Mg) in CLBA can provide additional sites for Cd (II) uptake through ion exchange. ICP determination of the prepared Cd (II) solution was conducted before and after sorption by CLBA. As displayed in Table 4, Cd is the main element in the aqueous solution before sorption. After sorption by CLBA, the concentration of Ca, Mg, K and Na increases significantly, implying that these elements might be transferred from CLBA surface to aqueous solution. Therefore, ion exchange also plays an important role in sorption process. And this is consistent with sorption process reported by other study [15]. Furthermore, the content of Ca and Mg in treated solution is higher than that of Cd, implying that the presence of alkali-earth metals has little influence on sorption of Cd (II) by CLBA. The schematic presentation of sorption mechanism is shown in Fig. 8.

Table 4
Concentration of elements in aqueous solution before and after exposition to CLBA for 60 min

Elements	Initial concentration (mg L^{-1})	Final concentration (mg L^{-1})
Cd	180.14	8.94
Ca	0.11	75.86
Mg	0.03	15.53
K	0.13	4.28
Na	0.27	2.01

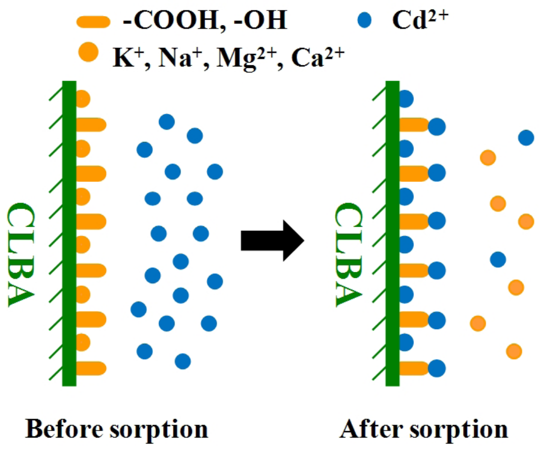


Fig. 8. The schematic mechanism for Cd (II) sorption onto CLBA.

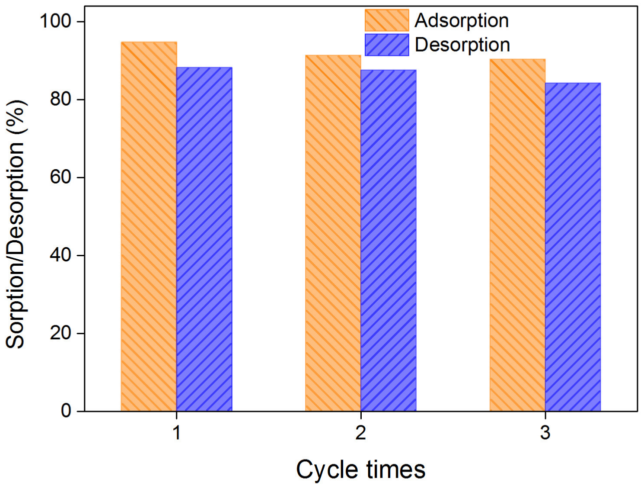


Fig. 9. Sorption-desorption experiments.

3.7. Desorption experiments

After sorption of 200 mg L^{-1} Cd (II) solution using 56 g L^{-1} CLBA, 25 mL 0.05 mol L^{-1} EDTA(Na)$_2$ solution were used to desorb the Cd(II) uptake onto CLBA. Experiments were conducted for three sorption–desorption cycles. As shown in Fig. 9, the desorption efficiency does not significantly decreases as the regeneration cycles progressed, implying that EDTA(Na)$_2$ solution can effectively desorb the Cd(II) ion from CLBA. The good sorption–desorption efficiency confirms that camphor leaves would be a promising biosorbent for fast removal of Cd(II) from water, especially in emergency disposal of heavy metal pollution accidents.

4. Conclusions

Camphor leaves were investigated as biosorbent for removal of Cd (II) ion from aqueous solution. The biosorbent was characterized by XRD, XPS, SEM and FTIR. The biomacromolecular components of camphor leaves, including cellulose, lignin and hemi-cellulose, provide enormous active sites for sorption of heavy metal ions. A detailed study of experimental parameters including dosage, pH, contact time and initial concentration were conducted at bench scale. Sorption process follows the pseudo-second order model and the Langmuir model. The removal rate and maximum sorption capacity of Cd (II) is up to 99.12% and 10.99 mg g^{-1}. The sorption mechanism is surface complexation and ion exchange. Desorption experiments demonstrate CLBA can be regenerated and used for many times. It is anticipated that camphor leaves would find important application for wastewater management in China, due to the advantages of high efficiency, low cost, and wide availability.

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Supplementary materials

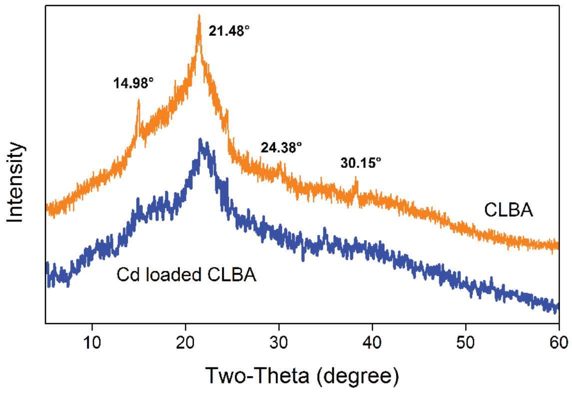

Fig. S1. XRD spectra of CLBA before and after sorption.

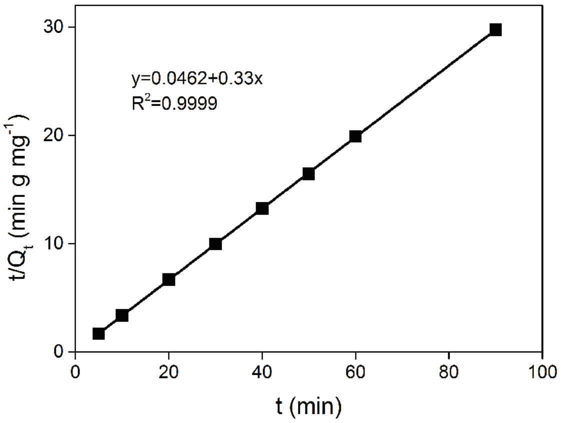

Fig. S2. Pseudo−second order kinetic plot for the sorption of Cd(II) onto CLBA.

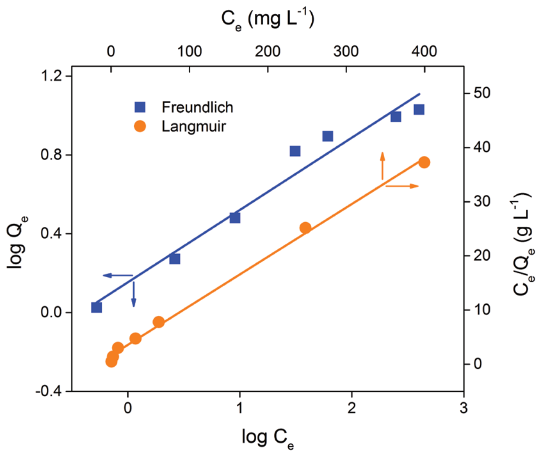

Fig. S3. Langmuir and Freundlich plots for Cd (II) sorption onto CLBA.