Efficient Removal of Cd (II) From Aqueous Solution By Chitosan Modified Kiwi Branch Biochar

Yuehui Tan

Northwest Agriculture and Forestry University College of Resources and Environment

Xirui Wan

Northwest Agriculture and Forestry University College of Resources and Environment

Xue Ni

Northwest Agriculture and Forestry University College of Resources and Environment

Le Wang

Northwest Agriculture and Forestry University College of Resources and Environment

Ting Zhou

Northwest Agriculture and Forestry University College of Resources and Environment

Huimin Sun

Northwest Agriculture and Forestry University College of Resources and Environment

Nong Wang

Agro-Environmental Protection Institute

Xianqiang Yin (✉ xqyin@nwsuaf.edu.cn)

Northwest Agriculture and Forestry University <https://orcid.org/0000-0002-0831-4181>

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Abstract

A novel chitosan-modified kiwi branch biochar (CHKB) was successfully fabricated as cut-price modified biochar to remove Cd (II) from wastewater. Characterization experiments with SEM-EDS, FTIR and XPS suggested that CHKB had more cations and surface functional groups compared with the original kiwi biochar (KB). The adsorption experiment results of Cd (II) on CHKB showed that the adsorption isotherms can be described best by the Langmuir model and that the pseudo-second-order model fits the Cd (II) adsorption kinetics well, indicating that the process was monolayer and controlled by chemisorption. CHKB exhibited the Langmuir maximum adsorption capacity of Cd (II) (126.58 mg g^{-1}), however, that of KB is only 4.26 mg g^{-1} . The adsorption ability of CHKB was improved by the increase of the surface area and abundant surface functional groups (-OH, -NH, C=O and so on). And the cation exchange, electrostatic interaction, surface complexation and precipitation were main mechanisms in the sorption of Cd (II) on CHKB. In addition, CHKB can be regenerated and reused for Cd (II) sorption by the eluent of EDTA-2Na. Excellent adsorption performance, low-cost, and environmental-friendly made CHKB become the fantastic adsorbent to remove Cd (II) in wastewater.

Introduction

With the development of factories, environmental problems are getting serious, including potentially toxic metal pollution, which has been a threat to the ecology, environment and human health due to the characterizations of high toxicity and bioaccumulation. Among them, Cd (II) is a typical pollutant, and its sources from electroplating, paints, electronics and so on (Mohan et al., 2014). It is well known that Cd (II) is environmentally persistent and not degraded in water, and what's more, Cd (II) can be harmful to the human body and life (Kołodzyńska et al., 2017; Zhou et al., 2018). Some common ways, such as ion exchange, sorption and ultrafiltration are used to remove heavy metal from wastewater (Luo et al., 2014; Romero-Dondiz et al., 2016; Salima et al., 2013; Wang et al., 2018b). But these methods still face challenges due to the restrictions including implementation process and expenditure (Ding et al., 2014). Among the different methods, adsorption run costs are lower and its processes studied to remove heavy metal are simpler relatively (Hernández-Montoya et al., 2013; Shaban et al., 2018). And studying a high adsorption capacity and low-cost sorption material to repair the wastewater polluted by Cd (II) was important and meaningful.

Biochar is known as a fantastic sorbent to adsorb heavy metals (Lu et al., 2017; Lu et al., 2015b; Nyamunda et al., 2019; Paranaivithana et al., 2016). Research shows that the pore structure and surface properties of biochar can affect the removal efficiency of heavy metals (Huff & Lee, 2016; Wang et al., 2015; Xiao et al., 2018). With the larger superficial area and further surface function groups, biochar will obtain more interaction sites to remove heavy metals (Ahmad et al., 2018; Beesley & Marmiroli, 2011; Xian et al., 2018). But it is not easy to obtain biochar with both abundant void structures and surface functional groups using common preparation methods (Gronnow et al., 2013). Normally, functional groups decrease and surface area increases with increasing pyrolysis temperature (Jing et al., 2018; Tomczyk et al., 2020). Because these contradictions limit the use of biochar as an effective adsorbent,

biochar needs to be modified to improve its performances (Hu et al., 2015; Jin et al., 2018; Lu et al., 2015a).

Novel biochar modification methods are used to boost biochar adsorption capacity to pollutants from wastewater. The methodologies of surface modification are concerned widely due to its simple modification procedure and sorption effectiveness. Biochar-based materials can be obtained by impregnating or covering biochar surface with compounds (Michalekova-Richveisova et al., 2017), carbonaceous structures such as sulfapyridine, amino, naphthenic acids and so on (Frankel et al., 2016; Inyang et al., 2015; Yang & Jiang, 2014). The adsorption capacity of biochar can be improved by increasing the number of adsorption sites, oxygen-containing functional groups or other specific adsorption structures on the surface of biochar by methods of surface modification, oxidant or chemical synthesis (Bashir et al., 2020; Gu et al., 2020; Yazovskikh et al., 2020; Zhang et al., 2020).

Chitosan is a low-cost material, which is prepared by hydrolysis of chitin with sodium hydroxide, and the amide functional group was converted into amino functional groups. Because amino polysaccharide is renewable and biodegradable worldwide, chitosan is relatively cheap. What's more, chitosan have been used to remove heavy metal ions and have fantastic adsorption ability to heavy metals from soil and water as an adsorbent (Gerente et al., 2007; Pontoni & Fabbicino, 2012). In addition, Chitosan contains a large number of amino functional groups, which have strong binding ability to different heavy metals. Therefore, chitosan can be introduced into the surface of adsorption materials to improve adsorbents' adsorption ability to heavy metals (Bhatnagar & Sillanpaa, 2009; Gerente et al., 2007; Pontoni & Fabbicino, 2012). There is a hypothesis that chitosan accumulates easily, which can become more disperse by combining chitosan with biochar. The combination is very advantageous, both materials are cheap and environmentally friendly. What's more, chitosan modified biochar will combine the larger surface area and porous network structure of biochar as well as the higher adsorption capacity of chitosan, so the chitosan modified biochar obtained will have a stronger adsorption capacity for heavy metals. However, no previous studies explored in detail the adsorption characteristics, influencing factors and potential mechanisms of Cd (II) on kiwi biochar modified with chitosan.

In this research, a novel chitosan-modified kiwi branches biochar (CHKB) was synthesized and used as an adsorbent for the removal of Cd (II). Batch sorption experiments were used to examine the sorption behaviors of Cd (II) on the CHKB under various conditions. The objectives of this study were to: (a) synthesize and characterize an effective CHKB adsorbent that can be used for Cd (II) removal; (b) determine the adsorption mechanisms of the CHKB to Cd (II); (c) investigate the kinetics and equilibrium isotherms of Cd (II) adsorption on CHKB; and (d) identify the effect of solution pH, dosage and regeneration cycles of the Cd (II) adsorption on the CHKB.

Material And Methods

2.1. Materials

Kiwi branches were obtained from a kiwi orchard in Shaanxi Province to make biochar. And the kiwi branch from kiwi fruit was separated, chopped, washed and dried. Then it was pyrolyzed at the temperature of 500 °C in a Vacuum tube furnace (SG-GL1200K, Shanghai, China) under N₂ flow conditions. The biochars prepared were broken and sifted to keep a uniform size of 0.053-1 mm and collected. The CHKB composites could be obtained according to Zhou et al (Zhou et al., 2013). Briefly, putting 5.0 g of chitosan into 250 mL acetic acid (2 %), then 5.0 g of kiwi biochar was added, and the admixture was stirred about 1 h. The above suspension was added dropwise into a 1500 mL NaOH (1 %) solution, then keeping about 24 h. Finally, the CHKB was obtained by washing, drying, milling and sieving (0.053-1 mm) above compound.

2.2. Sorption kinetic experiments

Cd (II) sorption on KB and CHKB were studied through putting 0.01 g of the CHKB into 50 mg L⁻¹ and 200 mg L⁻¹ Cd (II) solutions of 20 mL in 50 mL centrifuge tubes the temperature of 25 °C respectively. The IS and pH of experiments were set to 0.01M and 6.0 ± 0.2. At the temperature of 25 °C, the centrifuge tubes were then vibrated at 190 rpm for 24 h in an oscillator. Moreover, at definite time spacing (5 min–24 h for KB and CHKB), the admixtures were quickly percolated with 0.22 µm pore size nylon membrane filters. The Cd (II) concentration was measured by Atomic Absorption Spectroscopy (Z-2000, Hitachi, Japan). The concentration of Cd (II) adsorbed was known according to the aqueous concentrations of incipient and eventual.

2.3. Sorption isotherm experiments

Cd (II) sorption on KB and CHKB were measured through putting 0.01 g CHKB into 20 mL diverse concentration Cd (II) solutions, which were from 0.5 to 100 mg L⁻¹ and 0.5 to 500 mg L⁻¹ in 50 mL centrifuge tubes respectively. The IS and pH of experiments were set to 0.01M and 6.0 ± 0.2. The centrifuge tubes were vibrated in an oscillator at 190 rpm for 24 h at the temperature of 25 °C. Then the mixtures were quickly filtered to determine Cd (II) concentration according to the same method and procedure of sorption kinetic. The Cd (II) concentrations adsorbed were known through the aqueous concentrations of incipient and eventual. The post-adsorption KB and CHKB materials were gathered, cleaned and dried at 80 °C for characterizations after the experiments.

2.4. Effects of pH and dosage

The influence of incipient solution pH which was from 3 to 7 (3, 4, 5, 6 and 7) on the CHKB adsorption to Cd (II) was tested. In addition, the influence of the dosage was tested by putting a range of 0.01–0.05 g (0.01, 0.02, 0.03, 0.04 and 0.05 g) of CHKB into the 200 mg L⁻¹ Cd (II) solutions of 20 mL in 50 mL centrifuge tubes. At the temperature of 25 °C, the centrifuge tubes were then vibrated at 190 rpm for 24 h in an oscillator. Mixtures were quickly filtered to determine Cd (II) concentration according to the same method and procedure of sorption kinetic. The Cd (II) concentrations adsorbed were known according to the aqueous concentrations of incipient and eventual.

2.5. Sorption-desorption cycles experiments

Sorption-desorption cycle studies were conducted by using Cd (II) saturated CHKB through sorption isotherm experiment. Then putting Cd (II) saturated CHKB (0.01 g) were added in 20 ml of desorption medium (0.2 mol L^{-1} EDTA-2Na) in 50 mL centrifuge tubes. EDTA-2Na was used to elute sorbents which were shaken at 190 rpm for 24 h in a shaker, and then desorbed adsorbents were washed. All of the above tests were repeated.

2.6. Materials characterization

The characterization experiments were tested about KB and pre- and post-sorption CHKB. V-Sorb 2800P surface area and pore size analyzer (GAPP-spectrum, Beijing, China) determined the KB and CHKBs' Brunauer-Emmett-Teller (BET) specific surface area. X-ray diffraction (XRD) analysis was used to study structure using the X-ray diffractometer (D/RAPID II, Rigaku, Japan). Fourier transform infrared spectroscopy (FTIR) (Tensor27, Bruker, Germany) was used to study the functional groups impact in the period of sorption. Scanning electron microscopy (SEM) coupled with Energy dispersive spectrometer (EDS) (S-4800, Hitachi Limited, Japan) confirmed the component elements' morphology and content of biochars. Composition and speciation of surface elements of biochar samples were analyzed by using X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha+, America). The characterizations of KB, pre- and post-sorption CHKB were compared to clarify the mechanisms of adsorption.

Results And Discussion

3.1. Main adsorption mechanism

The KB's BET surface is $1.5 \text{ m}^2 \text{ g}^{-1}$, lower than the CHKB's BET surface of $3.3 \text{ m}^2 \text{ g}^{-1}$. In a way, the specific surface area was a key parameter which is generally desirable for Cd (II) adsorption. The SEM-EDS analyses of the obtained sorbents composites are presented in Fig. 1a-c. The morphology described no regular or amorphous characteristics using SEM (Fig. 1a-c). Compared with the KB's glazed surfaces (Fig. 1a), CHKB composites showed the surface's pimpling (Fig. 1b) through SEM images, which indicated the chitosan was modified on biochar matrix. The KB used as an excellent matrix to disperse chitosan and CHKB sorption sites for Cd (II) increased, so the chitosan modification is a good influence on improving Cd (II) adsorption (Fig. 1b). EDS demonstrated abundant O and Na elements in CHKB rather than KB's, which may be the reason for existing abundant oxygenated functional groups on the CHKB composites' surface and it was further supported that the CHKB was modified with chitosan successfully (Fig. 1a-b). And CHKB can improve the adsorption ability to Cd (II), one of the mechanisms might be the ions substitution of cations (Na^+ , K^+ , Mg^{2+} and so on) with Cd (II) (Wang et al., 2018a).

The CHKB's XRD pattern showed its amorphous properties, and the chitosan is represented by dominant peaks (Fig. 1d). The XRD pattern of CHKB in the range of $10-80^\circ$ is shown in Fig. 1d. Chitosan was found in CHKB pre- and post- Cd (II) sorption, the broad diffraction peaks of CHKB at $2\theta = 19.8^\circ$ matched to chitosan (Gartner et al., 2011). XRD analysis of the pre- and post-CHKB confirmed the hypothesis that the chitosan particles were introduced on the CHKB surface through XRD. In addition, CHKB contains calcium

carbonate, which forms cadmium carbonate precipitate after adsorbing Cd (II) (Fig. 1d). Compared with other sorption mechanisms, the precipitation also plays a key role in Cd (II) removal.

Figure 1e shows the FTIR spectrogram of KB, CHKB pre- and post-sorption of Cd (II). The FT-IR spectra differences in the adsorbents were known by concentrating on 4000 – 400 cm^{-1} wavenumber interval. The FTIR plots of CHKB pre- and post-sorption of Cd (II) have differences, and the functional groups had some changes pre- and post-sorption of Cd (II) on CHKB. The pre- and post-sorption CHKB composites' some peaks emerged or heightened at 3648, 3447, 2876, 1680, 1574, 1374, 1021 and 519 cm^{-1} (Fig. 1e) compared with KB, it might be the reason that chitosan treatment increased the concentrations of functional groups and changed the types of functional groups formed in biochar (Fang et al., 2015). In the FTIR spectroscopy analysis, the broad bands around 3648 and 1574 cm^{-1} corresponds to the -NH stretching vibration, and the band at 3447 cm^{-1} are due to the -OH stretching vibration. There are -CH, C = O, -CH₃ and -CO stretching vibrations around 2876, 1680 cm^{-1} , 1374 cm^{-1} and 1021 cm^{-1} respectively. In addition, the vibrational property of the organic halide bond is observed at around 519 cm^{-1} (Fig. 1e). This result further suggests that the surface of CHKB has been covered by chitosan. These peaks altered after the chitosan particles introduction and the Cd (II) sorption (Fig. 1e), indicating that chitosan particles had a key role in Cd (II) sorption. And these functional groups improve the adsorption ability of CHKB by complexation and electrostatic interaction with Cd (II), such as -NH, -OH, C = O and so on (Jin et al., 2018; Park et al., 2019; Pontoni & Fabbicino, 2012).

The XPS survey spectra of KB, CHKB pre- and post-sorption of Cd (II) are displayed in Fig. 1f. And the C 1 s, N 1 s, O 1 s and Cd3d peaks can be seen from the Fig. 1f. What's more, Fig. 1g show the C 1 s spectra of KB, CHKB pre- and post-sorption of Cd (II), the C 1 s peaks of KB at 284.8, 285.44 and 288.22 eV represents the C–C, C–O and C = O groups respectively (Lyu et al., 2017). And the C-N groups appeared at 286.78 eV after chitosan modified with KB. The proportion of C-N groups in CHKB before and after adsorption decreased obviously from 24.25–3.6%, indicating that C-N groups interacted with Cd (II). Figure 1h show the O 1 s spectra of KB, CHKB pre- and post-sorption of Cd (II), the O 1s peaks of KB at 532.44 and 533.96 eV represents the C = O and C–O groups respectively (Yu et al., 2021). The proportion of C-O groups increased from 26.65–68.51% after chitosan modified with KB, then decreased from 68.51–48.45% after Cd (II) adsorption on CHKB. It suggests that Cd (II) combined with the oxy-containing functional groups in CHKB during adsorption. Figure 1i show the N 1 s spectra of KB, CHKB pre- and post-sorption of Cd (II), the N 1s peaks of KB at 398.64 and 401.63 eV represents the N-H and -NH₂ groups respectively (Palansooriya et al., 2021; Song et al., 2021). The N-H groups disappeared and were replaced by N-C = O at 400 eV after chitosan modified with KB. The proportion of N-C = O groups decreased from 89.39–66.67%, the -NH₂ groups disappeared and the CH₃CO-NH groups appeared after Cd (II) adsorption on CHKB. It indicates that indicating that N atoms interacted with Cd (II) by chemical reaction. After adsorption, peaks of Cd 3d appeared (Fig. 1j), confirming that Cd (II) interacted with CHKB through chemical reactions. The characteristics of the peaks indicated that Cd (II) were presented in the forms of CdO and Cd(OH)₂ in CHKB after adsorption (Yu et al., 2021). And the precipitation and chelation Cd (II) as forms of CdO and Cd(OH)₂ are the main reasons for Cd (II) adsorbed on CHKB.

3.2. Adsorption kinetics

The Cd (II) adsorption kinetics of KB and CHKB were depicted in Fig. 2a and b. The Cd (II) sorption on KB and CHKB composites augmented with the increase in time employing the incipient Cd (II) concentration (50 mg L^{-1} of KB and 200 mg L^{-1} of CHKB), and sorption of Cd (II) by KB and CHKB reached equilibrium within 120 min. The data of adsorption kinetics experiments were simulated by some models. Moreover, the pseudo-first-order (Lagergren, 1898) and pseudo-second-order model (Blanchard et al., 1984), Elovich model (Low & M., 1960) and Constant double model (Peng & Robinson, 1976) were applied to describe the Cd (II) sorption kinetics on KB and CHKB were summarized (Table 1). The Pseudo-second-order was the optimum model in showing the sorption kinetics of Cd (II) on KB and the CHKB with the highest R^2 ($R^2 > 0.99$), with the homologous match of Q_e about 3.52 and 111.11 mg g^{-1} respectively. The sorption of Cd (II) on CHKB suited Pseudo-second-order model perfect, explaining the complexation and precipitation were related with the process of metal ions sorption for the rate limited chemisorption (Kołodzyńska et al., 2012). Results also suited to Elovich kinetic model relatively (Table 1), that ensured the chemisorption contribution with functional groups, such as $-\text{NH}$, $-\text{OH}$ and $-\text{C}=\text{O}$, and exchangeable Na^+ (Jayakumar et al., 2015; Zou et al., 2006).

Table 1 Constants and correlation coefficient of Kinetic models of Cd (II) adsorption on KB and CHKB.

Model	Parameter 1	Parameter 2	R^2
KB			
Pseudo-first order	$k_1 = 0.0006$	$Q_e = 3.4657$	0.2554
Pseudo-second order	$k_2 = 0.0190$	$Q_e = 3.5211$	0.9997
Elovich	$A = 2.0954$	$B = 0.4797$	0.8183
Constant double	$A = -0.2601$	$B = 0.2481$	0.7827
Intra-particle diffusion	$k = 0.1520$		0.7778
CHKB			
Pseudo-first order	$k_1 = 0.0001$	$Q_e = 110.9637$	0.2923
Pseudo-second order	$k_2 = 0.0090$	$Q_e = 111.1111$	1.0000
Elovich	$A = 77.5940$	$B = 5.3952$	0.8230
Constant double	$A = 4.3666$	$B = 0.0558$	0.7948
Intra-particle diffusion	$k = 0.4574$		0.7234

The high removal rate of Cd (II) by CHKB might be the reason for the ions substitution of CHKB initially (Venkata Mohan et al., 2002). The slow process might be related with biochar's pore network and surface,

which promoted the dispersion of CHKB to effectively augment its reaction with Cd (II). The high linear correlation ($R^2 > 0.72$) was known by sorption of pre-equilibrium Cd (II) on the square root of time (Fig. 2c and d). The consequence showed intraparticle surface diffusion was significant in deciding Cd (II) sorption on the CHKB (Moral-Rodríguez et al., 2016).

3.3. Adsorption isotherms

The equilibrium adsorption isotherms of Cd (II) by KB and CHKB are presented in Fig. 3a and b. The Cd (II) sorption capacity of KB and CHKB are 4.24 and 118.43 mg g⁻¹ respectively. Langmuir (Schmid et al., 1999), Freundlich (Yang, 1998) and Temkin (Johnson & Arnold, 1995) models were studied to explain the Cd (II) sorption on biochars. The corresponding parameters were enumerated in Table 2, these data are modeled and these results were shown in Fig. 3. For the CHKB, the Langmuir maximum capacity of CHKB was 126.58 mg g⁻¹ larger than the KB's of 4.25 mg g⁻¹, and CHKB determination coefficients (R^2) around 0.9497. As shown, the Cd (II) sorption on KB is best fitted with the Temkin model, but on CHKB suits the Langmuir model. This result indicates the adsorption mechanism of Cd (II) removal with CHKB by single-layer adsorption onto the chitosan particles on CHKB composites surface. However, determination coefficients (R^2) of Freundlich model about CHKB is also high around 0.9299, and it indicates the single and double-layer adsorption play the key roles on Cd (II) adsorption on CHKB.

Table 2 Constants and correlation coefficient of isotherm models of Cd (II) adsorption on KB and CHKB.

Model	Parameter 1	Parameter 2	R^2
KB			
Langmuir	$K_L=0.0792$	$q_{max}=4.2553$	0.9133
Freundlich	$K_F=0.6383$	$1/n=0.4236$	0.9598
Temkin	$A=-0.6273$	$B=2.4457$	0.9613
CHKB			
Langmuir	$K_L=0.0187$	$q_{max}=126.5823$	0.9497
Freundlich	$K_F=12.0837$	$1/n=0.3973$	0.9299
Temkin	$A=-57.4460$	$B=69.2890$	0.9276

The Table 3 shows a summary of Cd (II) adsorption capacity on modified biochars in other studies and the CHKB in this study. Through comparing different modified biochars reported previously, it could be known that the maximum adsorption capacities (Q_m) of CHKB in this study (126.58 mg g⁻¹) is notably higher than the other modified biochars in literature (0.98–81.1 mg g⁻¹). What's more, it indicates that the kiwi branch is a valuable precursor for the production of engineered biochars and kiwi biochar-based chitosan composites have obvious advantages to Cd (II) removal.

Table 3
The comparison about the adsorption capacity of Cd (II) on various modified BCs.

Material	Surface area (m ² g ⁻¹)	Q _m (mg g ⁻¹)	References
CMSSB	25.60	36.50	(Zuo et al., 2017)
HMB	8730	0.98	(Ding et al., 2016)
MBR	70.91	45.8	(Liang et al., 2017)
BC-1438	7.88	1.61	(Gao et al., 2020)
BC-MnO _x	110.68	81.10	(Li et al., 2017)
MgO–BCR	20.64	18.10	(Xiang et al., 2018)
CHKB	3.30	126.58	The study

3.4. Influence of pH and dosage

The CHKB's sorption ability to Cd (II) from pH 3 to 7 was shown in Fig. 4a. The Cd (II) sorption ability increased with the increase of pH, and the results showed the high pH is beneficial for Cd (II) removal. It can be seen from the Fig. 4a that pH has a great influence on adsorption. With the increase of pH from 3 to 7, the removal efficiency increased. When pH increased from 3 to 5, the removal efficiency of Cd (II) didn't change obviously. This is because of the competition between Cd (II) and H₃O⁺ at pH = 3 (Wang et al., 2015). With the deprotonation of hydroxyl group, the adsorption of Cd (II) increased. When pH increased from 5 to 6, the removal efficiency of Cd (II) on CHKB also didn't change significantly. This might be because the deprotonation of hydroxyl group had reached the maximum. When pH increased to more than 6, the removal rate of Cd (II) increased rapidly, which is the reason for the precipitation formation of Cd (OH)₂ (Liang et al., 2017). There are some different charges hydrolysates of Cd(OH)₂, Cd(OH)⁺ and Cd₂(OH)³⁺. Thus, Cd (II) may be removed through precipitation and electrostatic interaction (Su et al., 2014).

The optimum dosage of CHKB for Cd (II) removal in adsorption process is vital for its efficient use. In order to maximize the interaction between active sites of CHKB and Cd (II), the experiments about the dosage effect of CHKB to the Cd (II) removal rate and sorption ability have been conducted, and the data were shown in Fig. 4b. With the increasing of the CHKB dosage from 0.01 to 0.05 g, the removal ability of Cd (II) increased linearly from 22.89 % to 82.07 % and the sorption ability lessened from 117.88 mg g⁻¹ to 88.89 mg g⁻¹. In general, because of the augment in sorption sites and CHKB's surface area, CHKB dosage augment improved the Cd (II) removal (Chen et al., 2011; Ozturk & Bektas, 2004). Because some sorption sites remained unsaturated at higher CHKB loading during the process of sorption, the sorption ability of the CHKB (Q_e) was lower at higher CHKB loading (Hamoudi et al., 2007).

3.5. Regeneration cycles

The regeneration cycles tests were studied with 0.2 mol L^{-1} EDTA-2Na solution as eluent. Figure 5 showed that the adsorptivity of the CHKB and desorption ability of EDTA-2Na to Cd (II) saturated CHKB had no appreciable decrease after five cycles, and the CHKB could be regenerated and reused for Cd (II) sorption. The consequence described the CHKB's excellent stability, indicating CHKB is a low cost and effective material in the treatment of Cd (II) polluted wastewater.

Conclusions

In this work, a novel chitosan-modified kiwi branches biochar (CHKB) was successfully fabricated and was developed for the removal of Cd (II) from aqueous solutions. The adsorption experiment results of Cd (II) on CHKB showed that the adsorption isotherms can be described best by the Langmuir model and that the pseudo-second-order model fits the Cd (II) adsorption kinetics well, indicating that the process was monolayer and controlled by chemisorption. Compared to KB, Cd sorption ability of CHKB (118.43 mg g^{-1}) to Cd (II) was about 28 times higher than that of KB (4.24 mg g^{-1}). And CHKB showed the maximum sorption ability of Langmuir for Cd (II) (126.58 mg g^{-1}), owing to larger micropore sizes, bigger specific surface areas, more adsorption sites and the great deal of oxygen-containing functional (-OH, -NH, C = O and so on) groups compared with KB. The main mechanisms of CHKB's higher adsorption capacities may be cation exchange, electrostatic interaction, surface complexation and precipitation. The adsorption ability can be changed in various conditions. When CHKB dose increased, the adsorption ability dwindled and the removal efficiency increased. What's more, the high pH is beneficial for Cd (II) sorption on CHKB. By comparing various biochar adsorbents, CHKB has excellent advantages of a simpler preparation method and higher adsorption ability. And CHKB can be regenerated and reused for Cd (II) sorption by the eluent of EDTA-2Na. Therefore, CHKB would be a promising, low-cost, and effective adsorbent for Cd (II) removal from wastewater in practical applications.

Declarations

Authors Contributions Yuehui Tan: Sampling, writing-original draft. Xirui Wan: Data analysis. Xue Ni: Data analysis. Le Wang: Sampling and Review. Ting Zhou: Sampling and Review. Huimin Sun: Editing and project administration, funding acquisition. Nong Wang: Editing. Xianqiang Yin: Conceptualization, writing, review and editing, supervision, project administration, funding acquisition.

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Consent to Participate Not applicable.

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Competing Interests The authors declare no competing interests.

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Figures

Figure 1

SEM-EDS analysis of KB (a), pre-sorption CHKB (b) and post-sorption Cd-impregnated CHKB (c); XRD patterns (d) and FTIR spectra (e) of KB and pre- and post-sorption Cd-impregnated CHKB. A, CaCO₃; C,

Chitosan; D, CdCO₃. XPS spectra of original biochar and the pre- and post-sorption CHKB (f); High resolution XPS spectra of C1s (g), O1s (h), N1s (i) and Cd3d (j) in KB and pre- and post-sorption CHKB.

Figure 2

Adsorption kinetic data and modeling for Cd (II) onto KB (a) and CHKB (b); Internal diffusion for Cd (II) onto KB (c) and CHKB (d); IS=0.01M NaCl; pH= 6.0 ± 0.2; T= 25 ± 2 °C.

Figure 3

Adsorption isotherm of Cd (II) onto KB (a) and CHKB composite (b); IS=0.01M NaCl; pH=6.0 $\pm$ 0.2; T=25 $\pm$ 2 $^{\circ}$ C.

Figure 4

Effect of pH (a) and dosage (b) on Cd (II) adsorption onto CHKB composites; T=25 $\pm$ 2 $^{\circ}$ C.

Figure 5

Sorption-desorption cycles of CHKB for Cd (II) with 0.2 mol l⁻¹ EDTA-2Na