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Removal of cadmium (II) and lead (II) from aqueous systems with pretreated fish bone waste by ethanol

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ABSTRACT

Due to its availability in large quantities, fish bone waste was treated by ethanol and used as adsorbent for Cd (II) and Pb (II) removal from aqueous solutions. The removal efficiency of the heavy metal ions using ethanol-modified fish bone (*EFB*) was investigated as a function of dosage of adsorbent and pH. For Pb (II) and Cd (II) removal, the adsorbent optimum dosages were found to be 1.0 and 0.3 $g \cdot L^{-1}$, respectively. The maximum adsorption capacities of Cd (II) and Pb (II) were achieved at pH 6.0 and were 33.05 and 32.67 $mg \cdot g^{-1}$, respectively. The adsorption behavior could be described well by the pseudo-second-order model and the adsorption process was endothermic, as indicated by the increase of the pseudo-second-order rate constant with the temperature increasing to 40°C. The adsorption of the Cd (II) and Pb (II) on the *EFB* is the boundary layer adsorption with intra-particle diffusion. The adsorption isotherms were well fitted by Freundlich model, suggesting the multilayer adsorption for Cd (II) or Pb (II). The Cd (II) and Pb (II) removal process naturally presents chemical, indicated by the sorption energy, which was determined from Dubinin-Radushkevich isotherm. The adsorption process is spontaneous, favorable, endothermic and random, indicated by the thermodynamic equilibrium. With the use of a Scanning Electron Microscope (SEM), a large amount of Cd (II) and Pb (II) were seen as adsorbed on the surface of *EFB*. The maximum adsorption capacities of *EFB* were compared with other adsorbents reported. The results showed the possibility of utilizing natural wastes as low-cost and effective alternative absorbents to remove Cd (II) or Pb (II) from aqueous solutions.

Keywords: Adsorption; Ethanol; Fish bone; Heavy metal; Wastewater treatment

1. Introduction

The pollution of the aqueous environment by heavy metals, such as Cd, Pb and Cu, has attracted considerable attention from the public due to adverse effects on human health and environment [1–4]. Several techniques have been applied to reduce the concentrations of Cd (II) and Pb (II) the permissible limits (0.03 ppm for Cd (II) and 0.01 ppm for Pb (II)) a parameter set by the World Health Organization (WHO) [5]. Of the traditional methods considered, including chemical precipitation, membrane processes, ion exchange and adsorption, adsorption is the only process that appears to be highly effective and versatile for heavy mental removal from low concentration wastewater

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and this method can solve the problem of sludge disposal [6,7]. Commercially activated carbon, one of the most commonly used adsorbents, is sometimes restricted in the application owing to its high synthesis cost [8]. In recent years, the environment-friendly adsorbents from agricultural, industrial, and household wastes have received considerable attention, not only due to their low cost of raw materials, but also due to their biodegradability in nature [9–11]. For example, Çekim et al. [12] investigated and determined the optimum conditions for biosorption of Cu^{2+} on tobacco leaves. Yargıç et al. [13] used tomato wastes as an low-cost biosorbent to remove aqueous Cu (II). Mafu et al. [14] studied the adsorption properties of eggshell membranes, eggshells, and orange peels for the simultaneous removal of As and Se. Cechinel et al. [15] prepared activated carbon from cow bones and modified it with HNO_3 to remove Pb (II). Naiya et al. [16,17] applied neem bark and sawdust as a low-cost natural adsorbent to remove Pb (II), Cd (II,) and Zn (II) from water. Singha et al. [18] investigated the applicability of hyacinth roots, neem leaves, coconut shell, rice husk, rice bran, and rice straw for the removal of Pb (II) ions from battery industry effluent and aqueous solution. The studies offer a main method of environmental management in "waste control by waste" manner.

More than 30 million tons of fish are consumed every year in China. Fish bone waste in large quantities is significant. Until now, the fish bone wastes have not been extensively used for environmental applications. Fish bones are composed of 70% inorganic and 30% organic phases by weight. Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is the major part of the inorganic phase [19]. Due to ion exchange reaction between calcium ions and heavy medals, HAP is an effective material for removal of heavy metals. Therefore, large quantities of fish bone wastes can be reused as inexpensive adsorbent for heavy metal.

Some biomaterials based on fish bone have been reported as effective in heavy metal removal. However, these concentrations of heavy metals were higher than 50 mg·L^{-1}. There is less literatures reporting the removal of low-concentration (1–10 mg·L^{-1}) heavy metal [20]. In this research, the fish bone waste was treated by ethanol and used as adsorbent for Cd (II) and Pb (II) removal. Batch experiments were carried out to investigate the influence of the adsorbent dosage and pH on the removal efficiency of heavy metals from aqueous systems. The adsorption behavior was analyzed by pseudo-first-order, pseudo-second-order and intra-particle diffusion models. The equilibrium data were fitted by Langmuir and Freundlich models. The SEMs of *EFB*, Cd-loaded *EFB* and Pb-loaded *EFB* were carried out.

2. Materials and methods

2.1. Pretreatment of the fish bone wastes

The fish bone wastes were collected from the local restaurants in Jinan City, Shandong Province, China. Firstly, they were rinsed with fresh tap water and soaked for 24 h, then dried at 50°C for 36 h and treated as follows:

(1) Bone was added to ethanol. The mixture was digested at 0.10 MPa and 120°C for 30 min.
(2) The fish bone was soaked in the solution containing 0.1 M NaOH and 2% degrease cleaner. Then, the solution was oscillated at 120 rpm and 60°C for 3 h.
(3) The solid was washed with deionized water and dried at 50°C for 24 h. The products were sieved to 0.075–0.25 mm fraction and labeled as *EFB*.

2.2. Adsorption experiments

Stock solutions of 1000 mg·L^{-1} of Cd (II) and Pb (II) were prepared by dissolving analytical grade $Cd(NO_3)_2{\cdot}4H_2O$ or $Pb(NO_3)_2$ in distilled water. Working concentrations were obtained by diluting stock solution to desired values.

All the experiments were performed in 250-mL Erlenmeyer flasks at room temperature (25 ± 1°C). *EFB* was added to 100 mL of 10 mg·L^{-1} Cd (II) or Pb (II) solution. The initial solution pH was adjusted by adding 0.1 M HNO_3 and 0.1 M NaOH solutions. The solution was shaken at 120 rpm for 36 h. The samples were taken and filtered through 0.45-μm polytetrafluoroethylene (PTFE) film. The residual concentration of Cd (II) or Pb (II) was determined using an Atomic Absorption Spectrophotometer (ABS-990, Beijing Purkinje General Instrument, China). The equilibrium absorption capacity q_e (mg·g^{-1}) of Cd (II) or Pb (II) can be calculated by Eq. (1):

$$q_e = \frac{(C_0 - C_e)\cdot V}{m} \tag{1}$$

where q_e (mg·g^{-1}) is the adsorption capacity for adsorbate at equilibrium; C_0 (mg·L^{-1}) is the initial concentrations of Pb (II); C_e (mg·L^{-1}) is the equilibrium Pb (II) concentration; V (*L*) is the volume of solution; m (*g*) is the weight of adsorbent.

2.3. Adsorption kinetics

The adsorption kinetic experiments were carried out by adding 0.03 g *EFB* to 100 mL of the Cd (II) or Pb (II) solution (10 mg·L^{-1}) at different temperatures (10, 20, 30, and 40°C). The pH was adjusted to 6.0. The samples were drawn after 5, 10, 15, 20, 30, 45, 60, 90, 120, 240, 360, 540, 720, 960 min and then were filtered to be measured. The absorption capacity q_t (mg·g^{-1}) at time t was calculated by Eq. (2):

$$q_t = \frac{(C_0 - C_t)\cdot V}{m} \tag{2}$$

where C_t (mg·L^{-1}) is the Cd (II) concentration at time t (min).

2.4. Adsorption isotherms

The adsorption equilibrium experiments were conducted at 25°C. *EFB* (0.03 g) was added to 100 mL of Pb (II) solutions containing 0.5 1, 2, 5, and 10 mg·L^{-1} of Cd (II) or Pb (II). The pH was adjusted to 6.0. After 960 min, the suspensions were filtrated by 0.45-μm PTFE film and were analyzed by ABS-990. The equilibrium absorption capacity q_e (mg·g^{-1}) of Cd (II) or Pb (II) was calculated by Eq. (1).

2.5. Characterization of adsorbent

Scanning electron micrographs (SEM) of the three samples (*EFB*, Pb-loaded *EFB* and Cd-loaded *EFB*) were obtained

with a Thermal Field Emission Scanning Electron Microscope (SUPRA55, Carl Zeiss AG, Germany). The functional groups of *EFB*, Cd-loaded *EFB*, and Pb-loaded *EFB* were investigated by using FTIR spectrum, which was scanned from 400 to 4000 cm^{-1}.

3. Results and discussion

3.1. Effect of adsorbent dosage on Cd (II) or Pb (II) removal

In this study, the specific surface area (BET) was improved from 2.673 m^2/g for the original fish bone to 28.412 m^2/g for pretreated fish bone (*EFB*). This makes *EFB* a highly efficient adsorbent for heavy metal removal. The effects of *EFB* dosage on the removal efficiency and the final concentration of Cd (II) or Pb (II) were presented in Fig. 1.

As the adsorbent dosage increased from 0.1 to 1.5 $g{\cdot}L^{-1}$, the removal efficiency of Cd (II) increased from 86.0% to 99.7%. A similar trend is observed for the removal efficiency of Pb (II), which increased from 97.6% to 99.9%. This phenomenon can be interpreted by the increasing surface area and adsorption sites, which remain unsaturated with increasing adsorption sites during the adsorption process [16,21,22]. When the dosage is higher than 1.0 or 0.3 $g{\cdot}L^{-1}$, the final Pb (II) or Cd (II) concentration is within the permissible limits.

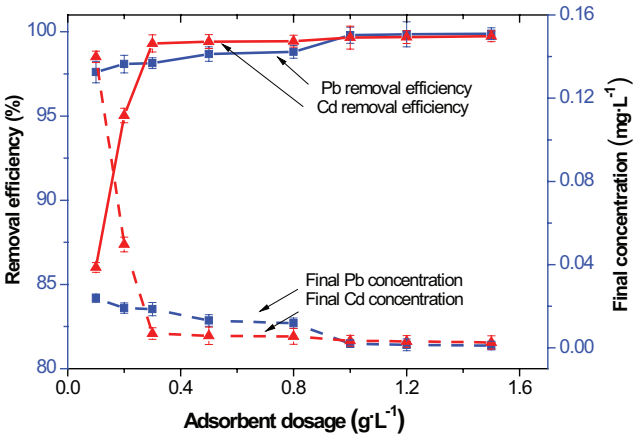

Fig. 1 Effect of EFB dosage on Cd (II) and Pb (II) adsorption by EFB (the initial Cd (II) or Pb (II) concentration = 10 $mg{\cdot}L^{-1}$, pH = 6.0, contact time = 16 h, and the temperature = 25 ± 1°C).

3.2. Effect of pH on Cd (II) or Pb (II) removal

PH value can influence the ionization of heavy metals and the surface properties of the adsorbent. In water, the hydrolysis of Cd (II) and Pb (II) was as follows [23,24]:

$$Cd^{2+} + nH_2O = Cd(H_2O)_n^{2+} \quad (3)$$

$$Cd(H_2O)_n^{2+} \rightarrow Cd(H_2O)^{n-1} + H^+ \quad (4)$$

$$nCd^{2+} + mH_2O = Cd(OH)_m^{2n-m} + mH^+ \quad (5)$$

$$Pb^{2+} + nH_2O = Pb(H_2O)_n^{2+} \quad (6)$$

$$Pb(H_2O)_n^{2+} \rightarrow Pb(H_2O)_{n-1}OH^+ + H^+ \quad (7)$$

$$Pb^{2+} + nH_2O = Pb(H_2O)_{n-1}OH^+ + H^+ \quad (8)$$

As illustrated in Fig. 2, q_e-values of Cd (II) and Pb (II) were low at pH 2 and increased with pH increasing to 6.0. Then, the adsorption capacity decreased when pH was further increased to 8. At low pH (pH < 6), high positive charge existed due to more protons. The competition between protons and Cd (II) or Pb (II) for the fixed number of adsorption sites and the electrostatic repulsion between H_3O^+ and Cd (II) or Pb (II) caused low adsorption capacity [25]. As the pH increased, the positive charge density decreased. The effects of electrostatic repulsion and the proton competition reduced and adsorption capacity improved. At adsorption equilibrium,

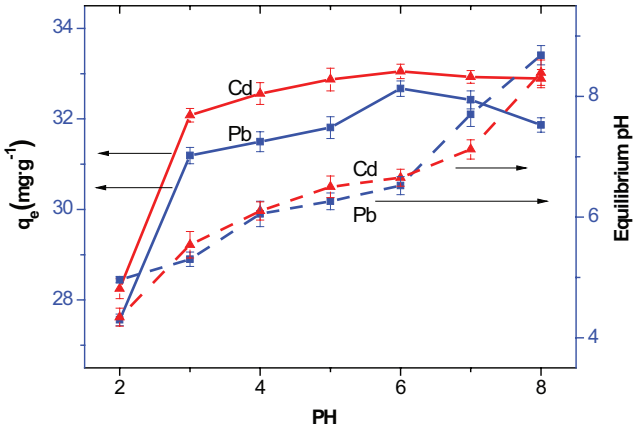

Fig. 2 Effect of initial solution pH on Cd (II) and Pb (II) adsorption by EFB (the initial Cd (II) or Pb (II) concentration = 10 $mg{\cdot}L^{-1}$, adsorbent dosage = 0.3 $g{\cdot}L^{-1}$, contact time = 16 h, and the temperature = 25 ± 1 °C).

the pH values of solutions were higher than the initial values, confirming that proton competition affects the adsorption process. It can be concluded that Cd (II) or Pb (II) adsorption onto *EFB* mainly involves electrostatic interactions between Cd (II) or Pb (II) and the binding sites. For further improvement of pH > 6, the formation of Cd and Pb predicated species resulted in the decrease of adsorption capacity. The highest adsorption capacity (32.672 $mg{\cdot}g^{-1}$ for Pb (II) and 33.051 $mg{\cdot}g^{-1}$ for Cd (II)) was achieved at pH 6.0, indicating that *EFB* presents a great potential for its applications in the treatment of industrial wastewater. The same trend has been reported by other researchers [26,27].

3.3. Adsorption kinetics

To investigate the adsorption kinetics of metal solutions, samples at regular time intervals were taken and monitored. Fig. 3 illustrates the amount of Cd (II) and Pb (II) adsorbed by *EFB* as a function of contact time at pH 6.0.

The adsorption capacity of Cd (II) and Pb (II) increased continuously with increasing time from 5 to 240 min owing to the

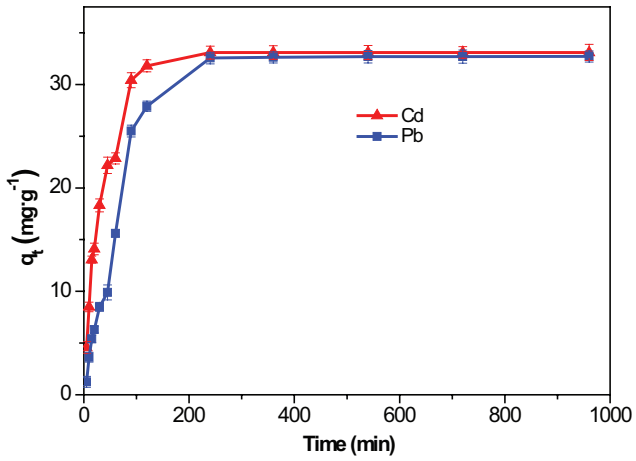

Fig. 3 Adsorption kinetic profile of Cd (II) and Pb (II) by EFB (the initial Cd (II) or Pb (II) concentration = 10 mg·L^{-1}, adsorbent dosage = 0.3 g·L^{-1}, pH = 6.0, and the temperature = 25 ± 1 °C).

abundant vacant sites available for heavy metal loading [28,29]. While contact time further increased to 960 min, no noticeable change of q_e was observed for Cd (II) and Pb (II). Within 90 min, about 90% of equilibrium adsorption capacity was reached. The efficient and fast adsorption equilibrium reaching properties of BFE demonstrated that it can be extensively applied to treat contaminated water, especially in an emergency.

In order to investigate the potential rate controlling steps and elucidate the adsorption mechanism, the kinetics data were fitted by the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models.

The linear pseudo-first-order and the linear pseudo-second-order are given in Eqs. (9) and (10) [29,30]:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{9}$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{10}$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order model; k_2 (g·mg^{-1}·min^{-1}) is the rate constant of the pseudo-second-order model; q_t (mg·g^{-1}) is the adsorption capacity of Cd (II) or Pb (II) at time t (min); q_e (mg·g^{-1}) is the equilibrium time.

The intra-particle diffusion model is expressed in Eq. (11) [31]:

$$q_t = K_w \cdot t^{0.5} + C \tag{11}$$

where K_w (mg·g^{-1}·min$^{1/2}$) is the intra-particle diffusion rate constant; C is the intercept.

The fitted curves of the three models and the corresponding kinetic parameters are shown in Fig. 4 and Table 1, respectively.

At different temperatures, the experimental data fit the pseudo-second-order kinetic model better than the pseudo-first-order kinetic model (shown in Figs. 4(a), (b), (C) and (d)). This is indicated by the higher correlation coefficients (R^2, 0.997–1.000) and the better agreement between the q_e calculated from the fitting plots and experimental data. These results indicated that the absorption rate was mainly controlled by the chemisorption [32]. In addition, pseudo-second-order rate constant (k_2) gradually increased as the temperature increasing, which implied the exothermic nature of the adsorption of Cd (II) and Pb (II) (shown in Figs. 4(c) and (d)).

Besides adsorption at the surface of adsorbent, there is a possibility of the ions migrating into the micropores [33]. As shown in Figs. 4(e) and (f), the intra-particle diffusion kinetic model was used to fit the data in three linear stages. The first stage is transportation of Cd (II) or Pb (II) from solution to the exterior surface of *EFB*. The second stage is diffusion from the external surface into the internal pores of the adsorbent. The final stage is the adsorption phase. The first portion of the plot had a steeper q_t verses $t^{0.5}$ slope, indicating external diffusion was rate limiting. Worthwhile, the second portion of the plot had a gently q_t verses $t^{0.5}$ slope, indicating intra-particle diffusion was rate limiting. The values of C give an indication of the boundary layer thickness [34]. All the C-values were non zero, suggesting that the intra-particle diffusion is not the sole rate-controlling step and that the boundary layer diffusion affected the adsorption process [35]. The results showed that the removal for the Cd (II) and Pb (II) is the boundary layer adsorption with intra-particle diffusion.

3.4. Adsorption isotherms

The Langmuir and Freundlich isotherm models were employed to fit the data at 25°C. The Langmuir isotherm assumed that the solid surface is uniform with a monolayer adsorption, where there are no interactions between adsorbed molecules [36]. The Freundlich isotherm assumes multi-layer on heterogeneous surfaces [37,38]. The Langmuir isotherm and the Freundlich isotherm are given in Eqs. (12) and (13) [39]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{bQ_{\max}} \tag{12}$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{13}$$

where $Q_{\max}$ (mg·g^{-1}) is the maximum ad sorption amount; b (L·mg^{-1}) is the Langmuir constant related to the binding sites affinity; K_F (mg$^{1-1/n}$·L$^{1/n}$·g^{-1}) is the Freundlich constants measuring the adsorption capacity and n is the adsorption intensity.

The fitted curves and corresponding parameters were summarized in Fig. 5 and Table 2.

Higher correlation coefficients R^2 indicated that the equilibrium data fitted the Freundlich isotherm model better than the Langmuir isotherm for the adsorption of Cd (II) and Pb (II) (shown in Figs. 5(a) and (b)). This result suggested that the adsorption process was multilayer and occurred at heterogeneous sites within the adsorbent surface with different distribution of energy levels. As can be seen from Table 2, the n-values are higher than 1, indicating that the adsorption of Cd (II) or Pb (II) on *EFB* is favorable.

To understand the adsorption mechanism, Dubinin–Radushkevich (DR) isotherm was used to test the equilibrium data. The DR isotherm can be expressed as follows:

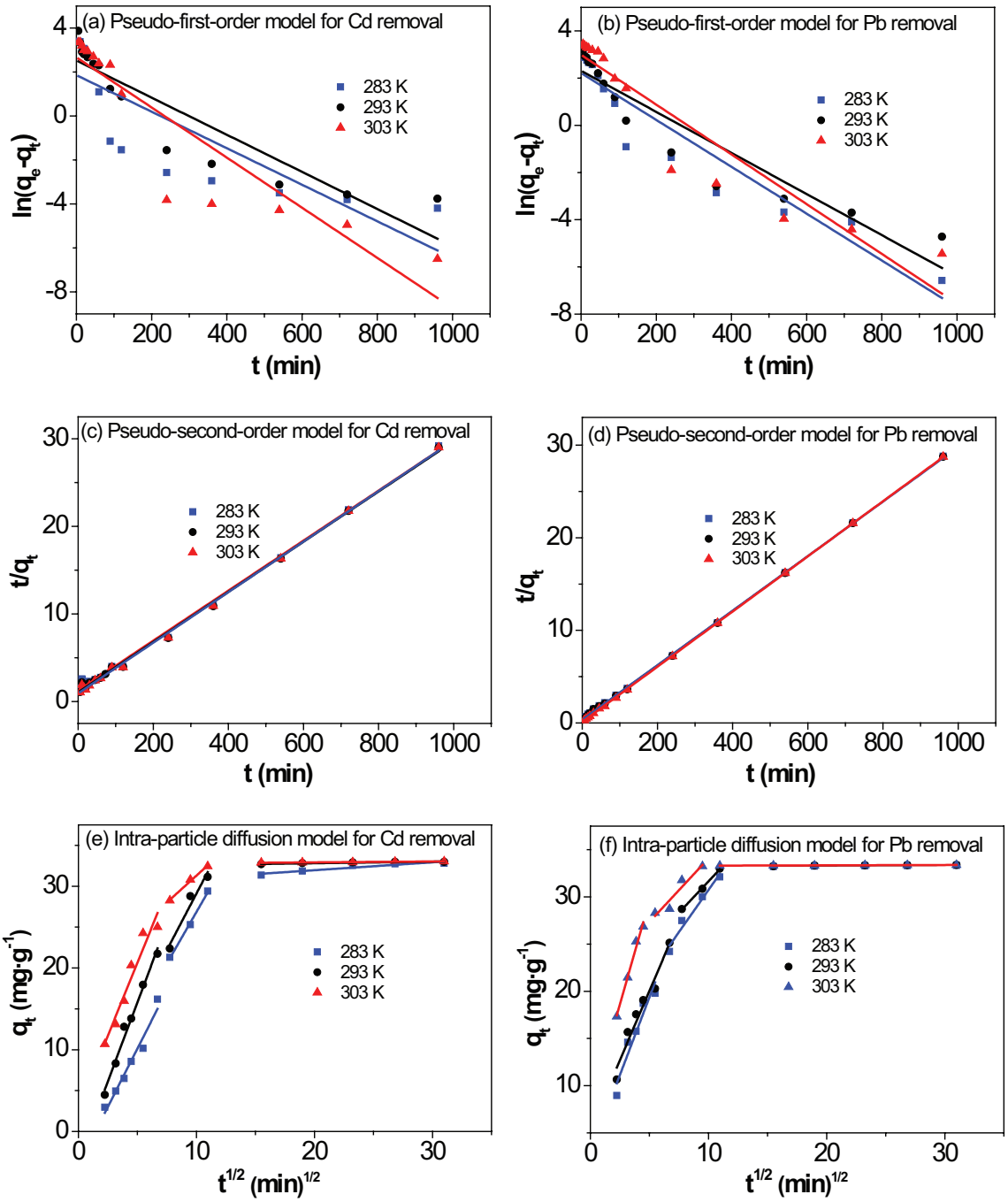

Fig. 4 Kinetics of of Cd (II) and Pb (II) adsorption onto EFB at different temperature (the initial Cd (II) or Pb (II) concentration = 10 mg·L^{-1}, adsorbent dosage = 0.3 g·L^{-1}, and pH = 6.0).

$$\ln q_e = \ln Q_{\max} - K_{DR}\varepsilon^2 \quad (14)$$

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \quad (15)$$

$$E = \left[\frac{1}{\sqrt{-2K_{DR}}}\right] \quad (16)$$

where K_{DR} (mol^2·KJ^{-2}) is a constant; ε is the Polanyi potential; R (8.314 J·mol^{-1}·K^{-1}) is the gas constant; E (KJ·mol^{-1}) is the mean sorption energy.

The value of E is shown in Table 2. If the E-value is more than 8 KJ·mol^{-1}, the chemical adsorption prevails. The physical adsorption can be indicated by E less than 8 KJ·mol^{-1} [40]. For Cd (II) and Pb (II) removal, the chemical adsorption will play an important role, indicated by the E-values of 14.434 KJ·mol^{-1} and 35.355 KJ·mol^{-1}.

Table 1
Kinetic parameters for the adsorption of Cd (II) and Pb (II) onto *EFB*

Kinetic models	Cd (II)			Pb (II)		
	Temperature (°C)			Temperature (°C)		
	10	20	30	10	20	30
Pseudo-first-order						
$q_{e,exp}$ (mg·g^{-1})	32.562	33.139	33.482	31.156	31.879	32.782
k_1 (min^{-1})	0.011	0.014	0.011	0.010	0.009	0.007
$q_{e,cal}$ (mg·g^{-1})	8.333	16.005	18.379	9.170	10.090	19.839
R^2	0.698	0.881	0.830	0.901	0.883	0.669
Pseudo-second-order						
k_2 (g·mg^{-1}·min^{-1})	0.0007	0.0008	0.0009	0.0021	0.0025	0.0079
$q_{e,cal}$ (mg·g^{-1})	30.450	31.916	32.026	30.568	31.044	32.190
R^2	0.998	0.997	0.997	0.999	0.999	1.000
Intra-particle diffusion						
K_{w1} (mg·g^{-1}·min$^{1/2}$)	2.845	3.859	3.563	3.298	2.937	4.396
C_1	–4.080	–3.500	2.826	2.886	5.370	7.632
R_1^2	0.956	0.981	0.925	0.927	0.946	0.984
K_{w2} (mg·g^{-1}·min$^{1/2}$)	2.515	2.760	1.311	1.783	1.331	1.347
C_2	1.697	1.505	18.183	12.911	18.339	20.613
R_2^2	0.993	0.912	0.990	0.950	0.996	0.889
K_{w3} (mg·g^{-1}·min$^{1/2}$)	0.097	0.019	0.011	0.0068	0.0074	0.0033
C_3	30.027	32.436	32.708	33.124	33.169	33.280
R_3^2	0.868	0.879	0.935	0.945	0.869	0.959

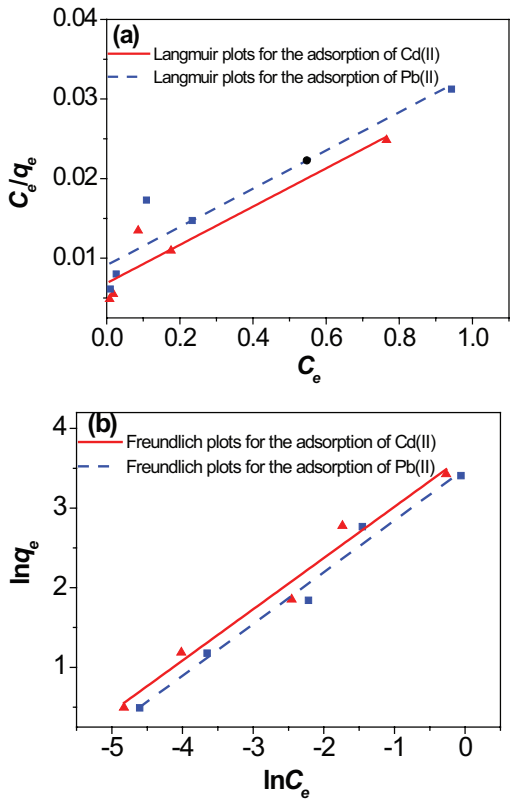

Fig. 5 Adsorption isotherms of Cd (II) and Pb (II) adsorption onto EFB (the initial Cd (II) or Pb (II) concentration = 0.5, 1, 2, 5, 10 mg·L^{-1}, adsorbent dosage = 0.3 g·L^{-1}, pH = 6.0, contact time = 720 min, and the temperature = 25 ± 1°C).

Table 2
Adsorption isotherm parameters for the adsorption of Cd (II) and Pb (II) onto *EFB*

Adsorption isotherm models	Parameters	Cd (II)	Pb (II)
Langmuir isotherm	Q_{max} (mg·g^{-1})	41.580	41.597
	b (L·mg^{-1})	3.501	2.636
	R^2	0.853	0.850
Freundlich isotherm	K_F (mg$^{1-1/n}$·L$^{1/n}$·g^{-1})	38.864	32.949
	n	1.554	1.538
	R^2	0.970	0.977
Dubinin–Radushkevich (DR) isotherm	Q_{max} (mg·g^{-1})	32.353	31.003
	K_{DR} (mol^2·KJ^{-2})	–0.004	–0.0024
	E (KJ·mo L^{-1})	35.355	14.434
	R^2	0.932	0.919

3.5. Adsorption thermodynamics

The thermodynamic behavior of *EFB* was analyzed by three thermodynamic parameters including entropy change (ΔH, KJ ·mol^{-1}), enthalpy change (ΔS, KJ ·mol^{-1}) and standard free energy (ΔG, KJ ·mol^{-1}), which were estimated from the Eqs. (17) and (18) [41].

$$\Delta G = -RT\ln K_F \tag{17}$$

$$\ln K_F = -\left(\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right) \tag{18}$$

where K_F ($mg^{1-1/n} \cdot L^{1/n} \cdot g^{-1}$) is the Freundlich adsorption equilibrium constant; R (8.314 $J \cdot mol^{-1} \cdot K^{-1}$) is the gas constant; T (K) is the absolute temperature in Kevin; ΔH (KJ mol^{-1}) is the intercept of the linear plot of $\ln K_F$ vs. $1/T$; ΔS (J mol^{-1} K^{-1}) is the slope of the linear plot of $\ln K_F$ vs. $1/T$.

Table 3 listed the thermodynamic parameters.

The ΔG values were found to decrease as temperature rose, indicating that adsorption process of Cd (II) and Pb (II) is more favorable at higher temperatures [42]. The thermodynamically favorable and spontaneous nature of Cd (II) and Pb (II) adsorption onto *EFB* was indicated by the negative ΔG values. The positive ΔH (3.008 KJ mol^{-1} for Cd (II) and 4.231 KJ mol^{-1} for Pb (II)) confirmed an endothermic nature of the process. In addition, an amplificatory randomness of Cd (II) and Pb (II) adsorption was indicated by a positive ΔS of 40.517 J mol^{-1} K^{-1} for Cd (II) and 43.260 J mol^{-1} K^{-1} for Pb (II) [43].

Table 3
The thermodynamic parameters for the adsorption of Cd (II) and Pb (II) on the adsorbent

	Temperature (K)	Thermodynamic parameters		
		ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Cd (II)	298.15	–9.073		
	303.15	–9.274	3.008	40.517
	313.15	–9.680		
Pb (II)	298.15	–8.663		
	303.15	–8.889	4.231	43.260
	313.15	–9.314		

3.6. Characterization of adsorbents

The surface morphologies of *EFB* before and after adsorption were characterized by SEM, and the relevant plots are shown in Fig. 6. The SEM micrograph of the raw *EFB* (Fig. 6(a)) showed the irregular and loose structure. After the adsorption procedure, some white particles were observed on the surface of the Cd-loaded and Pb-loaded *EFB* (shown in Figs. 6(b) and (c)).

3.7. Mechanism of adsorption

The chemisorption is believed to be the dominant adsorption mechanism. The Cd (II) and Pb (II) adsorption process can be interpreted by an ion-exchange between metal ions

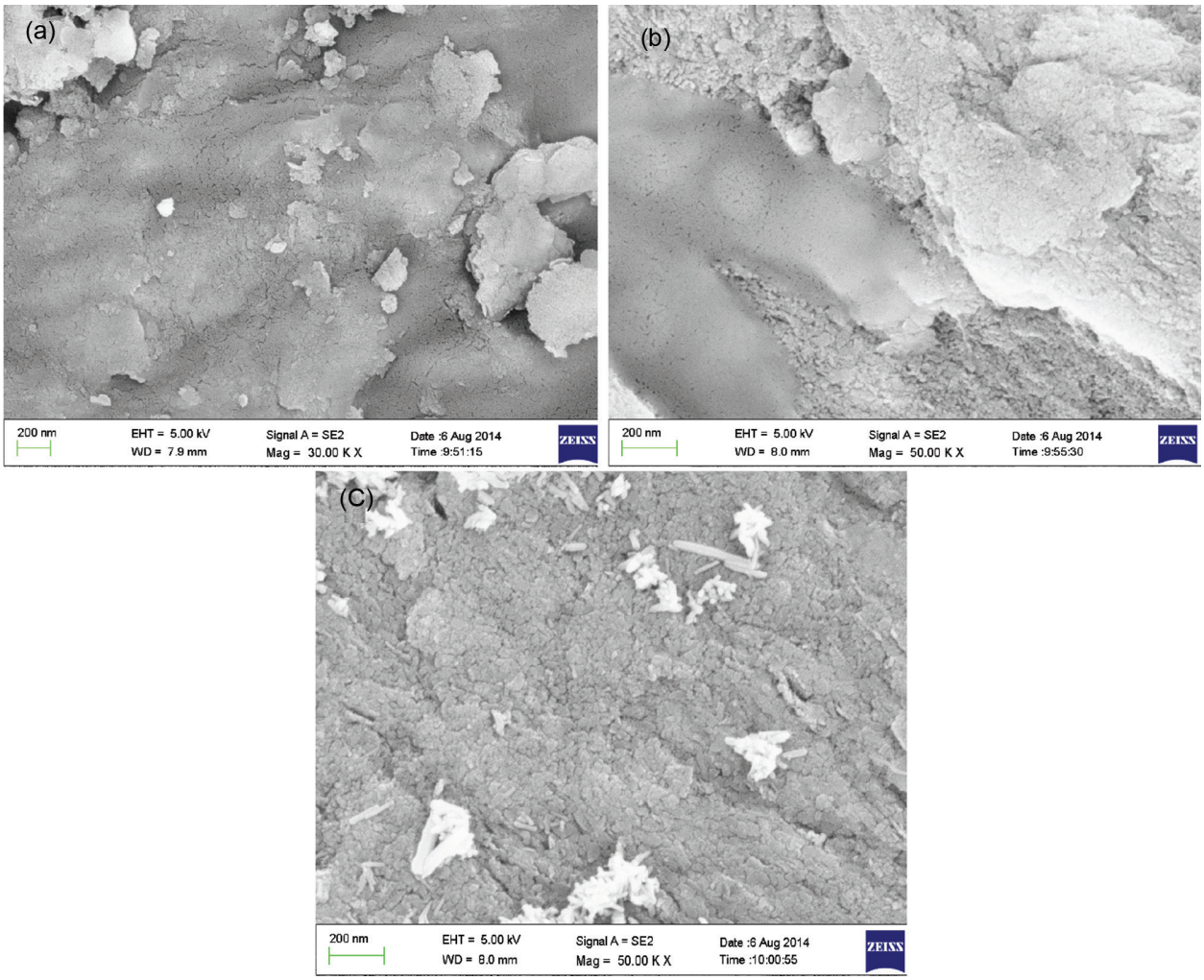

Fig. 6 SEM morphology of (a) EFB, (b) Cd-loaded EFB, and (c) Pb-loaded EFB.

Table 4
Comparison of *EFB* adsorption capacities for Cd (II) with other adsorbents reported

Metal	Adsorbents	Adsorption capacities ($mg \cdot g^{-1}$)	Reference
Cd (II)	Peanut hull pellets	6	[44]
	Sawdust of Pinus sylvestris	19.08	[45]
	Tea-industry waste	11.29	[46]
	Marine alga Ecklonia maxima	83.5	[47]
	Crop milling waste	39.99	[26]
	Sulphuric acid-treated wheat bran	101.0	[48]
	Sugarcane bagasse	69.06	[49]
	Mercapto-acetic acid modified orange peel	136.05	[49]
	Mango peel waste	68.92	[50]
	Banana peels	5.71	[51]
	Rice husk	103.09	[52]
	Bentonite	9.320	[53]
	Saw dust	5.37	[54]
	Baggase fly ash	2.00	[55]
	Dye-Attached Sawdust	8.093	[56]
	Ethanol-treated fish bone waste	41.580	This work

Table 5
Comparison of *EFB* adsorption capacities for Pb (II) with other adsorbents reported

Metal	Adsorbents	Adsorption capacities ($mg \cdot g^{-1}$)	Reference
Pb (II)	Hazel nut shell	1.78	[57]
	Peanut Hulls	30.43	[44]
	Saw dust	3.00	[58]
	Cocoa shells	33.0	[59]
	Orange peels	4.0	[60]
	Sawdust of Pinus sylvestris	22.22	[45]
	Baggase fly ash	2.50	[61]
	Coffee residue	20.0	[62]
	Tree fern	40.0	[63]
	Palm kernel fiber	49.9	[64]
	crop milling waste	49.97	[26]
	Rice husk	11.0	[65]
	Grape stalk	49.89	[66]
	Olive stone waste	9.15	[67]
	Tea waste	65.1	[68]
	Coir	48.83	[69]
	Rice husk ash	91.74	[27]
	Mango peel waste	99.05	[50]
	Banana peels	2.18	[51]
	Cotton waste	196.07	[70]
	Modified areca waste	3.37	[71]
	Ash	25	[72]
	Fe nanoparticles loaded ash	30	[72]
	Solanum melongena leaves	71.42	[73]
	Waste Biomass from Biotrickling Filters	160.0	[74]
	Dye-Attached Sawdust	11.59	[56]
	Ethanol-treated fish bone waste	41.597	This work

and calcium ions of HAP, the major ingredient in fish bone. This phenomenon was confirmed by other adsorption behavior properties such as the variety of adsorption capacities at different pHs. Furthermore, the clear changes in surface structure, which was observed by further SEM analyses (Fig. 6), was probably due to the reaction of ion exchange.

Besides chemisorption, physisorption also plays a significant role in the Cd (II) and Pb (II) removal process. In the process, the specific surface area (BET) decreased from 28.412 m^2/g for *EFB* to 2.451 m^2/g for Pb-loaded *EFB* and 2.232 m^2/g for Cd-loaded *EFB*. The significant reduction of the surface area confirmed the physisorption nmechanism.

3.8. Comparison of EFB with others

For the Cd (II) and Pb (II) removal, the *EFB* adsorption capacities were compared with different adsorbents and the results are listed in Tables 4 and 5.

4. Conclusions

New ethanol pretreated fish bone (*EFB*) adsorbent was used to remove aqueous Cd (II) and Pb (II) as a sustainable way to mitigate water pollution. Optimal adsorbent removal dosages were found to be 1.0 and 0.3 $g \cdot L^{-1}$ for Pb (II) and Cd (II). The maximum adsorption amount of Cd (II) or Pb (II) was achieved at pH 6.0 and was 33.05 and 32.67 $mg \cdot g^{-1}$, respectively. The pseudo-second-order model well fitted the Cd (II) or Pb (II) adsorption data on *EFB*. The pseudo-second-order rate constant was increased as the temperature increased to 40°C, implying an endothermic adsorption process occurred. In the removal process of the Cd (II) and Pb (II), the adsorption is the boundary layer accompanied by intra-particle diffusion. The *EFB* exhibited the multilayer adsorption for Cd (II) or Pb (II), indicated by the good fitting results with the Freundlich equation. The sorption energy, which was determined from Dubinin-Radushkevich isotherm, indicated that the Cd (II) and Pb (II) adsorption process is chemical in nature. And the thermodynamic equilibrium indicated that the removal process presents spontaneous, favorable, and endothermic with randomness. The SEM analysis indicated large amounts of Cd (II) and Pb (II) were adsorbed on the surface of *EFB*. The maximum adsorption capacities of *EFB* were compared with other adsorbents reported. The results highlighted that *EFB* could be applied as a potential absorbent in the removal of Cd (II) or Pb (II) from aqueous solution.

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