Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1006258

57 (2016) 6452–6462
March

Taylor & Francis
Taylor & Francis Group

Removal of Cd(II) and Pb(II) from aqueous solutions by modified polyvinyl alcohol

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Received 17 June 2014; Accepted 3 January 2015

ABSTRACT

In this study, modified polyvinyl alcohol (PVA) was prepared and characterized by element analysis, scanning electron microscopy, Fourier transform infrared spectroscopy, and surface area and proximity analysis. The isotherms and thermodynamic parameters of the modified PVA adsorption process were estimated. The data indicate that the adsorption process is exothermic, feasible, spontaneous, and fit to the Langmuir isotherm model. The maximum adsorption capacities for Cd(II) and Pb(II) were calculated to be 1.19 and 1.48 mmol/g, respectively. Sorption was rapid, with the removal percentage higher than 98% after 10 min. Adsorption behavior mechanisms were analyzed using pseudo-first-order and pseudo-second-order models, which were highly fitted to pseudo-second-order model. This suggests the main adsorption mechanism is a chemical adsorption, involving ion exchange and valence forces through sharing or exchange of electrons between metal ions and modified PVA. The modified PVA is a good reusable sorbent, enhancing the economics of practical application for the removal of Cd(II) and Pb(II) from water and wastewater.

Keywords: Polyvinyl alcohol; Adsorption; Equilibrium isotherms; Adsorption kinetic; Thermodynamics

1. Introduction

Heavy metal ions are among the most commonly encountered and hard to treat environmental pollutants, due to their mobility in natural water ecosystems and their toxicity. Heavy metal ions are found in the waste streams of industrial processes [1], such as metal plating, mining activities, smelting, battery manufacture, petroleum refining, alloy manufacture, tanneries, pesticides, printing, and photographic industries [2]. Heavy metal ions have significant ecological impact on ecosystem and can modify the physical and chemical properties of water by affecting the aquatic flora and fauna [3,4], since these pollutions accumulate in living tissues throughout the food chain causing serious health problems [5].

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Cadmium and lead have been recognized for their toxicity even at low concentrations and have been shown to bioaccumulate. Adverse health effects due to cadmium or lead are well documented and reported to cause renal disturbances, lung insufficiency, bone lesions, cancer, and hypertension in humans [6,7]. The permissible limits discharge in wastewater (according to integrated wastewater discharge standard GB 8978-1996) and drinking water (according to drinking water sanitary standard GB 5749-2006) are0.1 and 0.005 mg L^{-1} for cadmium, and 1.0 and 0.01 mg L^{-1} for lead, respectively. Thus, the concentration of toxic metals in usual water sources frequently needs a remediation operation [8,9]. Methods for removing metals from a water stream include ion exchange, chemical precipitation, electrolytic recovery techniques, membrane filtration, reverse osmosis, [10–12] and adsorption. Although adsorption of metal ions in wastewater stream has attracted much interest, the adsorbents are limited for high-operational cost and slow speed in the removal of heavy metal ions in the stream.

Polyvinyl alcohol (PVA) has the advantages of high strength, resistance to microbial decomposition, non-toxic characteristics of micro-organisms, and low toxicity to organisms [13–16]. On the other hand, PVA is low tendency in the gastrointestinal tract, not easy to bioaccumulate [14,15]. It has been widely used in fermentation industry, organic wastewater treatment, and other fields. Modified PVA has been reported to have high potential for the adsorption of metal ions [17–19]. To improve its adsorption capacity and enhance the adsorption rate, the design and exploration of novel adsorbents are necessary. Researchers have been paid close attention to the modification of PVA for enhancing the adsorption performance based on introducing the active groups [20–22], such as carboxyl, epoxy, amino, and mercapto, which can upgrade the capacity of adsorption.

In this study, a modified PVA was prepared with large capacity, easily regenerable, cheap, and fast adsorption rate characteristics in removal of Cd(II) and Pb(II) ions from aqueous solutions. The adsorbent can easily collected from aqueous media using a porous boxes and displayed high uptake capacity and fast speed even in low concentration. The factors affecting the removal behavior were studied. Thermodynamic and kinetic properties of the adsorption process were also clarified to evaluate the adsorption interaction between adsorbent and metal ions and to establish the rate-limiting step of Cd(II) and Pb(II) ions adsorption.

2. Materials and methods

2.1. Materials

All the chemicals were of analytical grade products and used as received. Poly (vinyl alcohol) 1788 and degree of alcoholysis (this means the alcoholization of poly (vinyl alcohol) 1788) was 87.0 ~ 89.0% (mol/mol), which was Aladdin Industrial Corporation product. Cadmium and lead solutions were prepared from reagent grade $CdCl_2$ and $PbCl_2$ using deionized water. Cis-butenedioic anhydride, butyl acetate, 1,2-dichloroethane solution, and absolute ethyl alcohol were Guangzhou Chemical Reagent Factory products.

2.1.1. Preparation of modified polyvinyl alcohol

Cis-butenedioic anhydride (60 g) was dissolved in butyl acetate (250 mL) and then mixed with PVA (30 g). The reaction mixture was stirred at 90℃ for 4 h. The polymer between cis-butenedioic anhydride (MA) and PVA obtained was filtered off, washed with absolute ethanol, and then kept to dry, which was named as PVA/MA.

In 1,2-dichloroethane solution, 30 g PVA/MA was dipped for over 10 h. In the mixture, 400 mL concentrated sulfuric acid was added, and the process was performed unceasingly at 90℃ for over 6 h. At the end of the reaction, the polymers were filtered and extracted with ethanol in a Soxhlet apparatus for 8 h and then washed by deionized water, 3% hydrochloric acid, deionized water, 3% sodium hydroxide, and deionized water three times alternately. Finally, the polymers were dried at 70℃ before being used as shown in Fig. 1.

2.1.2. Characterization of modified PVA

The texture of the studied modified PVA was analyzed using nitrogen adsorption measurements at

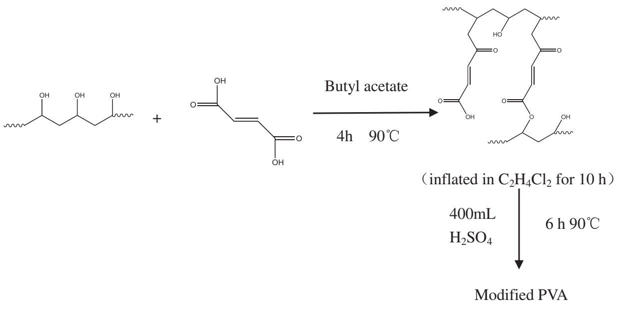

Fig. 1. Modified PVA synthetic route.

77 K with Surface Area and Proximity Analyzer and Micromeritics ASAP 2020. The apparent surface areas were determined from the adsorption isotherms using the BET equation.

Surface morphology was studied with the scanning electron microscope (PHILIPS XL-30ESEM, Holland). Characterization of the modified PVA using scanning electron microscopy operated at a typical accelerating voltage 10 kV.

The IR spectrums of the modified PVA with Cd(II) or Pb(II) were recorded on a Perkin Elmer FTIR (WQF-410, The Second Beijing Optical Instrument Factory, China). For FTIR studies, the dried modified PVA (about 0.1 g) was mixed with KBr (0.1 g) and compacted in pellet form.

2.2. Modified PVA sorption batch experiments

Batch systems of Cd(II) and Pb(II) were used in the adsorption experiments. These solutions were prepared with chloride of Cd(II) and Pb(II) and deionized water. The effects of metal ions initial concentration, agitation time, solution pH value, and temperature on the adsorption uptake were investigated. Experiments were performed by shaking 0.20 g modified PVA with 50 mL metal ion solution for 3 h at 120 rpm. The concentrations of metal ions in the solutions before and after adsorption were analyzed by ICP-OES 8300 (PerkinElmer) or Nexion 300X ICP-Mass Spectrometer (PerkinElmer). The amount of metal ions adsorbed onto unit mass of modified PVA (sorption capacity, mmol/g) was calculated by Eq. (1):

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

where C_0 and C_e are the initial and final concentration (mmol/L or mg/L) of heavy metal ions in the solution, respectively; V is the volume (L) of metal ion solution used for adsorption experiments; m is the adsorbent amount (g); and q_e is the amount of adsorbed metal ions at equilibrium (mmol/g or mg/g).

2.2.1. Effect of solution pH

The effect of solution pH on the heavy metal ions removal was investigated by varying the initial pH of the solutions from pH 2 to 6. The pH was adjusted using 0.1 M hydrochloric acid or 0.1 M sodium hydroxide and was measured using pH meter (Shanghai Precision Scientific Instrument Co., Ltd). The initial concentration of heavy metal ions was fixed at 400 mg/L of Cd(II) or 600 mg/L Pb(II), with modified PVA dosage of 0.20 g/50 mL and solution temperature at 30℃. The percent removals of heavy metal ions were calculated using Eq. (2):

$$\text{Removal } (\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

2.2.2. Thermodynamics

Batch adsorption experiments were performed from 50 to 1,400 mg/L for Cd(II) or 100 to 1,600 mg/L for Pb(II). All adsorption isotherms were adjusted solution pH by adding sodium hydroxide or hydrochloric acid. Specifically, heavy metals adsorption studies were performed by reciprocally shaking (120 rap/min) a fixed mass of adsorbent (0.02 g) with fixed volumes of solution (50 mL) at four different temperatures, i.e. 20, 30, 40, and 60℃ to assess the effect of temperature. Equilibrium time was 3 h. The amount of metal ions adsorbed onto unit mass of modified PVA was calculated by Eq. (1).

2.2.3. Kinetics

Kinetic adsorption parameters were determined using metal solutions at different temperatures. At designed temperature, 2.00 g of modified PVA was contacted with 500 mL of metal ion solution ($C_{\mathrm{Cd(II)}} =$ 400 or $C_{\mathrm{Pb(II)}} = 600$ mg/L). In each experiments, 5 mL aliquots were removed at appropriate times (1, 2, 5, 10, 15, 20, 30, 60, 90, 120, and 180 min) and analyzed by ICP-OES 8300. The pH of adsorption kinetic equilibrium experiments was the natural value of the multi-component solutions, which ranged from 5.0 to 5.8. Note that these conditions are below the onset for hydrolysis of Cd(II) and Pb(II) in order to prevent metal precipitation. The instantaneous adsorption capacity of the modified PVA q_t (mg/g) was calculated by the following Eq. (3):

$$q_\tau = \frac{(C_0 - C_\tau)V}{m} \tag{3}$$

Where C_τ is the metal concentration (mg/L) in aqueous phase after time τ and q_τ is the amount of adsorbed metal ions at time τ (mg/g).

2.2.4. Regeneration of modified PVA

For the regeneration studied, 0.20 g modified PVA was loaded with 50 mL (Cd(II) 1,400 mg/L, at pH 6.0 or Pb(II) 1,600 mg/L, at pH 5.0) metal ion solution at 30℃, 120 rpm, and contact time of 3 h. Metal ion-modified PVA were collected and gently washed with distilled water to remove any unabsorbed metal ions. The modified PVA was then agitated with 50 mL HNO_3 (concentration of 5%) for 2 h. The final concentration of metal ions in the aqueous phase was determined by ICP-OES. Desorption ratio of metal ions from modified PVA was calculated using Eq. (4):

$$D\% = \frac{C_{HNO_3}}{C_{ad}} \times 100 \quad (4)$$

where C_{HNO_3} is the metal ions desorbed to the HNO_3 solution (mmol/L) and C_{ad} is the metal ions adsorbed onto modified PVA (mmol/L).

The modified PVA was separated from the HNO_3 solution, washed with distilled water until neutral, then dried at 70°C in an oven and then added into an Erlenmeyer flask containing 50 mL metal ion solution, which concentration of Cd(II) was 1,400 mg/L or Pb (II) was 1,600 mg/L. The flask was kept in the water-bath shaker at the same temperature for the same time as the adsorption test. This adsorption–desorption cycle was repeated six times using the same adsorbent. The percent removals of heavy metal ions were calculated using Eq. (2).

3. Results and discussion

3.1. Characterization of modified PVA

The polymer surfaces were characterized by Boehm titration method [23]. According to this method, we found that hydroxyl and carboxyl groups have been connected on a carbon surface. The total amounts of surface groups per unit mass of the carbon at certain time are summarized in Table 1.

The nitrogen physisorption experiment data of modified PVA confirmed that there is scarcely any porous structure in it, because $SBET < 0.2\ m^2\ g^{-1}$ and $V_{micro} < 0.005\ m^3\ g^{-1}$. This characterization is also approved by the SEM images shown in Fig. 2, which had a smooth, featureless surface, and some crevices.

The main bands observed in the IR spectra of PVA and PVA–MA were according to the previous report [24,25]. The IR spectra of the PVA–MA presented a strong adsorption bands at 3,422, 1,732, and 1715 cm^{-1} which are attributed to the COOH, C=O, and COOR of the inserted maleic anhydride moieties, respectively.

The modified PVA was also analyzed by FT-IR spectrum as shown in Fig. 3. It is found that the absorption peak of bond S=O is formed at 1,032 cm^{-1}, which indicates that sulfonic group is grafted on PVA–MA. Moreover, the mass fraction of element S is changed from 0 to 4.36%, which indirectly indicates that sulfonic group is grafted on modified PVA by the reaction between PVA–MA and concentrated sulfuric acid.

In the presence of sulfuric acid, C=C bond is broke, because the adsorption band of modified PVA at 858 cm^{-1} disappeared. Other absorption peaks of function group do not make obvious changes, showing that the modified PVA reserves intrinsic function groups.

The active groups of the modified PVA are COOH, C=O, COOR, and SO_3H. The active groups of COOH and SO_3H can make H^+ ions exchange with heavy metals; C=O and COOR groups are make effect by valence forces between O and heavy metals.

3.2. Metal ions uptake studies

3.2.1. Effect of pH

Fig. 4 shows the relationship between solution pH and metal ions percent removal on modified PVA. As can be seen from these plots, the adsorption capacities of Cd(II) or Pb(II) increase with the increase in the solution pH and then flatten out with the further increase in the pH of the solution. In addition, the optimum adsorption pH of the modified PVA for Cd (II) or Pb(II) was 3–6. The adsorption capacities decrease dramatically when $pH < 3$, which are the similar of the peat adsorption of Cd(II) and Pb(II) [26]. At low pH, along with the concentration of H^+ increases and the dissociation degree of exchange group (–COOH) decreases, the exchange capacities between H^+ and Cd(II) or Pb(II) decrease. Synchronously, the stability of coordination compound is weakened. So, the adsorption capacities decrease. According to our control experiment, at $pH > 6$ of Cd(II) or $pH > 5$ of Pb(II) started to deposit as $Cd(OH)_2$ or $Pb(OH)_2$. The different maximum adsorption pH of Pb and Cd

Table 1
Texture parameters of the studied modified PVA

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	S_{micro} (m^2/g)	Hydroxyl groups (mmol/g)	Carboxyl groups (mmol/g)
Modified PVA	0.1893	0.0043	10.9856	1.0374	1.7857

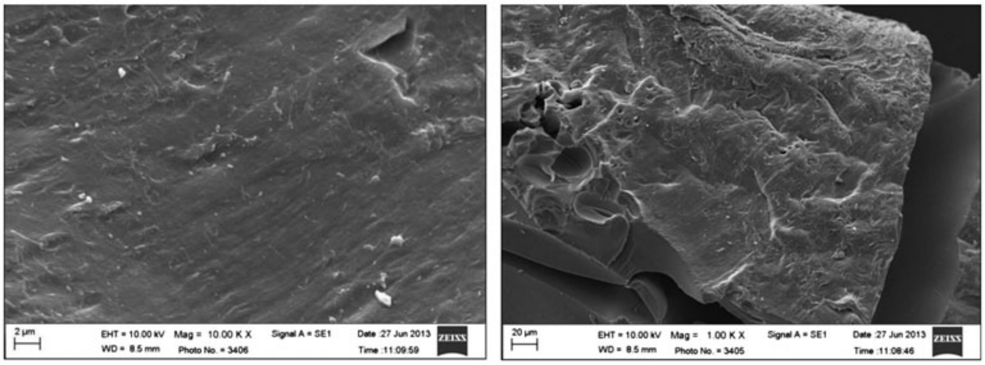

Fig. 2. The SEM photographs of modified PVA (PHILIPS XL–30ESEM, 10kV).

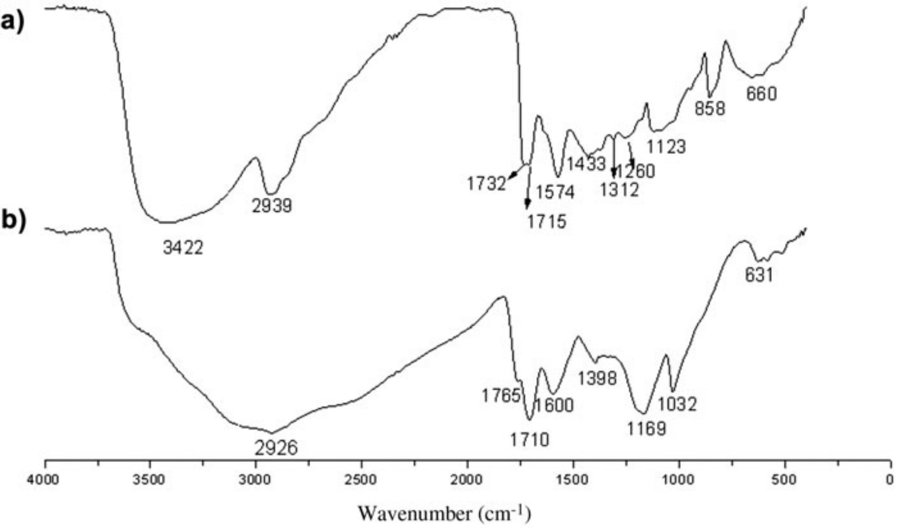

Fig. 3. FTIR spectra of: (a) PVA–MA and (b) modified PVA.

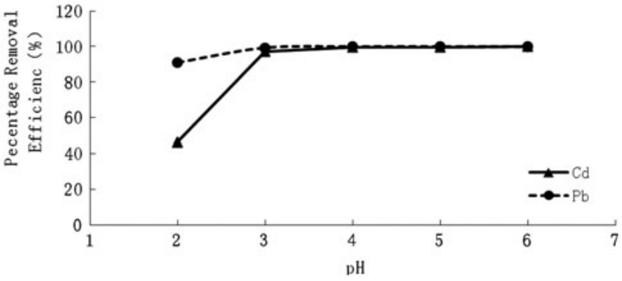

Fig. 4. Effect of pH on adsorption capacity for metal ions by modified PVA (400 mg/L Cd(II) or 600 mg/L Pb(II), 0.20 g modified PVA/50 mL solution, 30℃).

highlights the importance of pH in the treatment of wastewaters-containing different metals. In the following adsorption isotherms and kinetic models studied, the pH values of the systems were adjusted to 6.0 of Cd(II) and 5.0 of Pb(II), respectively.

3.2.2. Adsorption isotherms

Batch adsorption experiments were performed from 50 to 1,400 mg/L for Cd(II), at pH 6.0; 100 to 1,600 mg/L for Pb(II), at pH 5.0. Specifically, heavy metals adsorption studies were performed by shaking (120 rap/min) a fixed mass (0.02 g) of adsorbent with fixed volumes (50 mL) of solution at four different temperatures, i.e. 20, 30, 40, and 60℃ to assess the effect of temperature. Equilibrium time was 3 h.

According to the experiments, when the original concentrations of Cd(II) were less than or equal to 400 mg/L, the removal rates were more than 99%. Adsorbent reached adsorption saturation. Speaking to the adsorption of Pb(II), adsorption curve (adsorption capacity-original concentration) increased first and then flattened out, and the boundary point of the original concentrations was 1,200 mg/L at four different temperatures. The adsorption capacities of both ions were decreased with the increasing temperature, which indicated low temperature was advantage for the adsorption.

The capacity of adsorption can be described by equilibrium sorption isotherms, which are characterized by certain constants whose values express the surface properties. The equilibrium isotherms were investigated using Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models given in Table 2. The experimental data of adsorption isotherms of Cd(II) or Pb(II) on modified PVA are well fitted by Langmuir adsorption model. The relative values calculated from the three models are listed in Table 3.

Table 3 shows that at all the four temperatures studied, the best fitting is obtained by the Langmuir model with the highest R^2 values which are greater than 0.99. For the better correlation coefficient and the fact that the equilibrium adsorption capacities (q_m) obtained from Langmuir model were close to the experimentally observed saturation capacities, indicating that the monolayer Langmuir model is more suitable to explain the adsorption of Cd(II) and Pb(II) onto modified PVA. The maximum adsorption capacity (q_m) calculated by Langmuir model for Pb(II) is 1.48 mmol/g, which is higher than Cd(II) 1.19 mmol/g, and q_m are found to be decreased when the temperature increases from 293.5 to 333.5 K, suggesting on exothermic process. On the other hand, Table 4 presents the comparison of adsorption capacity (q_m). The adsorption capacities of modified PVA for Cd(II) or Pb(II) are higher than that of the majority of other adsorbent mentioned. Therefore, it can be noteworthy that the modified PVA is a promising adsorbent for the removal of Pb(II) and Cd(II) ions from aqueous solutions.

The Dubinin–Radushkevich model also described the experimental data, but not better than the Langmuir model. It is interesting to find that the q_m derived from the Langmuir (1.19 mmol/g of Cd(II), 1.48 mmol/g of Pb(II)) is lower than that derived from D–R model (1.70 mmol/g of Cd(II), 2.52 mmol/g of Pb(II)). Because in Langmuir model, q_m represents the maximum adsorption of metal ions at monolayer coverage, while in D–R model, it represents the maximum adsorption of metal ions at the total specific micropore volume of the sorbent [37]. The magnitude of E is useful for estimating the type of adsorption. If E value is below 8 kJ/mol, the adsorption type can be explained by physical adsorption between 8 and 16 kJ/mol. If the adsorption is governed by chemical ion exchange and over 16 kJ/mol, the adsorption type can be explained by a stronger chemical adsorption than ion exchange [36]. As shown in Table 3, almost all of the E values at four temperatures are slightly more than 16 kJ/mol, which indicate the orders of a stronger chemical adsorption. It insists with the active groups deducing from the characterization of modified PVA.

3.2.3. Kinetic studies

At a designed temperature, 2.00 g of modified PVA was contacted with 500 mL of metal ion solution ($C_{\mathrm{Cd(II)}} = 400$ or $C_{\mathrm{Pb(II)}} = 600$ mg/L). In each experiments, 5 mL aliquots were removed at appropriate times (1, 2, 5, 10, 15, 20, 30, 60, 90, 120, and 180 min), analyzed by ICP-OES 8300. The pH of adsorption kinetic equilibrium experiments was the natural value of the multi-component solutions, which ranged from 5.0 to 5.8.

The prediction of adsorption rate gives the important information for designing batch adsorption systems. Fig. 5 shows the kinetics of the adsorption of metal ions Cd(II) and Pb(II) by modified PVA. The kinetic curves for Cd(II) or Pb(II) ions showed that the

Table 2
Isotherm models

Isotherm models	Linearized equations	References
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \times q_m}$	[27,28]
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	[29]
Dubinin–Radushkevich	$\ln q_e = \ln q_m - \beta\varepsilon^2 \varepsilon = \mathrm{RT} \ln\left(1 + \frac{1}{C_e}\right) E = \frac{1}{\sqrt{2\beta}}$	[30,31]

Notes: where q_m is the maximum adsorption capacity of adsorbents (mmol/g or mg/g); K_L is the Langmuir isotherm constant (L/mmol); K_F is the Freundlich isotherm constant $((\mathrm{mmol\,g^{-1}})/(\mathrm{mmol\,L^{-1}})^{1/n})$; n is the Freundlich isotherm exponent; R is the gas constant (8.314 J/mol K); T is the absolute temperature (K); β is the activity coefficient related to mean sorption energy ($\mathrm{mol^2/kJ^2}$); ε is the Polanyi potential; and E is the adsorption energy (kJ/mol).

Table 3
Isotherm parameters and regression data for Cd(II) and Pb(II) sorption on modified PVA

		Cd(II) (K)				Pb(II) (K)			
Models	Parameters	293.5	303.5	313.5	333.5	293.5	303.5	313.5	333.5
Langmuir	q_m (mmol/g)	1.19	1.16	1.00	0.96	1.48	1.39	1.29	1.13
	K_L (L/mmol)	290.52	169.55	102.39	15.32	118.63	101.49	66.39	48.49
	R^2	0.9999	0.9999	0.9987	0.9989	0.9991	0.9998	0.9991	0.9994
Freundlich	n	5.74	5.25	5.53	5.76	4.57	3.28	5.43	4.52
	K_F (mmol g^{-1})/(mmol L^{-1})$^{1/n}$	1.01	1.03	1.19	1.27	1.66	1.73	1.30	1.03
	R^2	0.7620	0.8068	0.8812	0.7989	0.7916	0.6971	0.8019	0.6962
D–R	β (mol/kJ)^2	0.0015	0.0016	0.0014	0.0012	0.0015	0.0020	0.0015	0.0014
	q_m (mmol/g)	1.70	1.74	1.43	1.34	2.52	2.99	2.21	1.80
	E (kJ/mol)	18.26	17.68	18.90	20.41	18.26	15.81	18.26	18.90
	R^2	0.8144	0.8709	0.9475	0.8793	0.8476	0.8624	0.8103	0.8207

Table 4
Comparison of individual Cd(II) and Pb(II) ion adsorption capacities of different adsorbents

Adsorbent	Cd(II) (mmol/g)	Pb(II) (mmol/g)	Conditions	References
Natural bentonite	–	0.070	pH 3.00; room	[32]
Modified Al_2O_3	0.741	0.483	pH 6.00; room	[33]
HMO	1.275	1.565	pH 6.00; room	[34]
CNTs	0.097	0.468	pH 5.00; room	[35]
Nano hydroxyapatite	1.271	4.822	pH 6.00; 20℃	[36]
MX-80 bentonite	–	0.331	pH 3.50; 18℃	[37]
Titanate nanotube	2.13	2.64	pH 5.00; 20℃	[38]
Amanita rubescens	0.243	0.185	pH 5.00; 20℃	[39]
Modified PVA	1.19	1.48	pH 6.00; 20℃	Present work

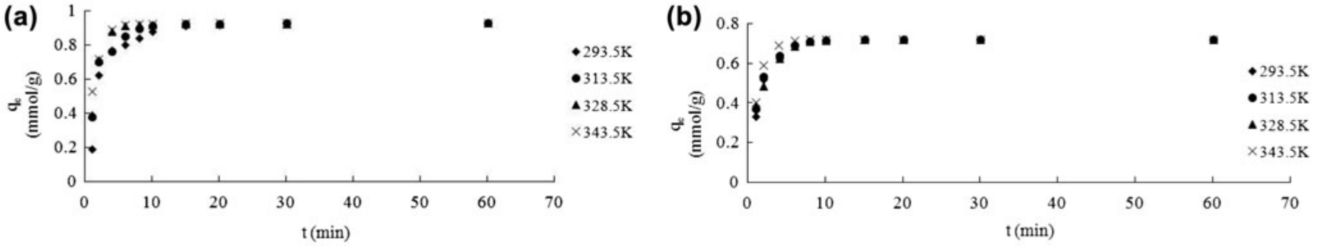

Fig. 5. Adsorption kinetics metal ions on adsorbent of different temperatures: (a) $C_{Cd(II)} = 400$ mg/L and (b) $C_{Pb(II)} = 600$ mg/L, pH 5.0–5.8, 2 g modified PVA/500 mL solution 120 rap/min.

adsorption are initially rapid and reached equilibrium after approximately 6 min. In order to clarify the adsorption kinetics of Pb(II) and Cd(II) ions onto modified PVA, two kinetic models, which are pseudo-first-order and pseudo-second-order models [39], were applied to fit the experimental data. The following Eqs. (5) and (6) are the pseudo-first-order and pseudo-second-order kinetic models, respectively:

$$\ln\,(q_e - q_\tau) = \ln q_e - k_{p1}\tau \tag{5}$$

$$\frac{\tau}{q_\tau} = \frac{1}{k_{p2}{q_e}^2} + \frac{1}{q_e}\tau \tag{6}$$

where k_{p1} is the pseudo-first-order rate constant (min^{-1}) and k_{p2} is the pseudo-second-order rate constant (g/mg min).

A good correlation of the kinetic data explains the adsorption mechanism of the metal ions on the solid phase [40]. The data of adsorption equilibrium of Cd(II)

Table 5
Kinetic parameters for Cd(II) and Pb(II) ions adsorption by modified PVA

		Pseudo-first-order model			Pseudo-second-order model		
Metals	Temperature (K)	k_{p1} (min^{-1})	q_{e1}^{cal} (mg/g)	R^2	k_{p2} (g/mg min)	q_{e2}^{cal} (mg/g)	R^2
Cd(II)	293.5	0.1687	43.49	0.9333	0.0065	108.70	0.9970
	313.5	0.1918	28.86	0.8805	0.0138	106.38	0.9996
	328.5	0.1327	12.56	0.6256	0.0201	106.38	0.9996
	343.5	0.2120	11.89	0.7993	0.0322	105.26	0.9998
Pb(II)	293.5	0.3114	42.02	0.9177	0.1320	151.52	0.9996
	313.5	0.2700	36.64	0.8840	0.0156	151.52	0.9998
	328.5	0.3129	41.43	0.9002	0.0136	151.52	0.9997
	343.5	0.3492	10.61	0.7561	0.0256	151.52	0.9998

and Pb(II) on modified PVA are well fitted by pseudo-second-order model. The relative values calculated from the two models are listed in Table 5.

During the first 10 min, the uptake capacities were higher than 98%, and the kinetic rates are independent of the temperature. The adsorption of Cd(II) and Pb (II) on modified PVA may be considered as the instantaneous adsorption or external surface adsorption. In order to examine the controlling mechanism of adsorption process, pseudo-first-order and pseudo-second-order models are used to test the experimental data. The pseudo-first-order kinetic model is not applicable since R^2 values are rather low, and the theoretical q_{e1}^{cal} values calculated from it are far away from the experimental q_e^{exp} values. In contrast, the theoretical q_{e2}^{cal} values calculated from the pseudo-second-order kinetic model are much close to the experimental q_e^{exp} values with $R^2 \geq 0.997$. This suggests the main adsorption mechanism is a chemical adsorption, involving ion exchange and valence forces through sharing or exchange of electrons between metal ions and modified PVA. The adsorption

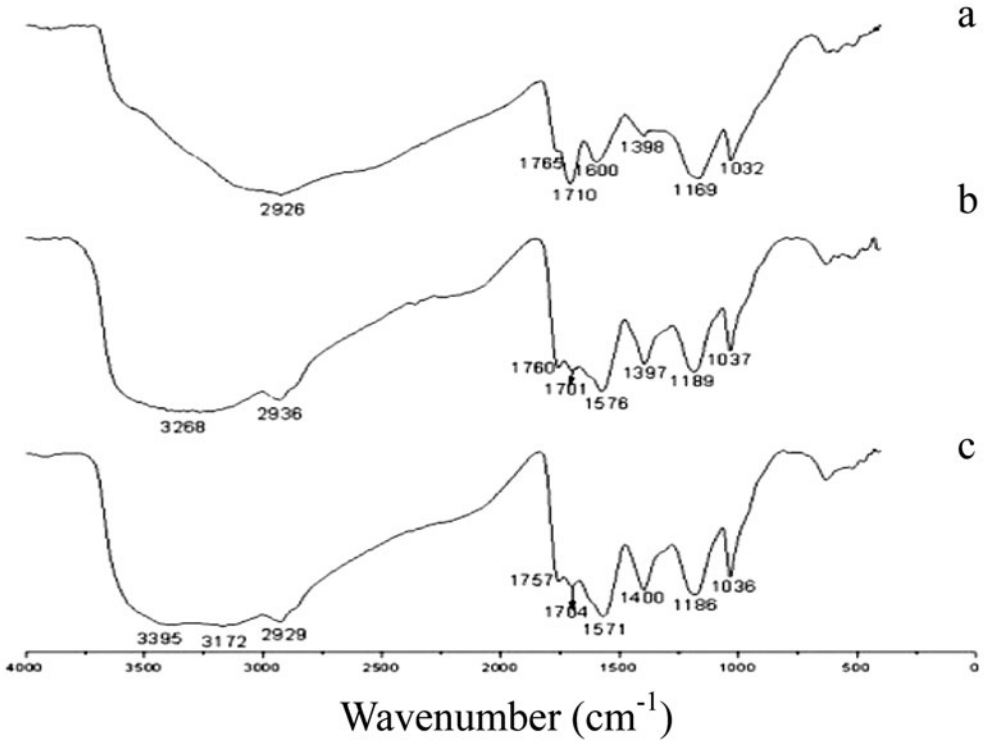

Fig. 6. FTIR spectra of modified PVA: (a) before metal ions adsorption, (b) after Cd(II) adsorption, and (c) after Pb(II) adsorption (Perkin Elmer FTIR (WQF-410), PVA was mixed with KBr and compacted in pellet form).

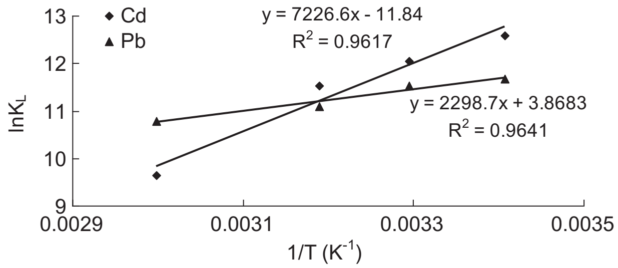

Fig. 7. Influence of temperature on the thermodynamic behavior of adsorption of Cd(II) and Pb(II) on modified PVA: (a) $C_{Cd(II)}$ = 50–1,400 mg/L, pH 6.0, and (b) $C_{Pb(II)}$ = 100–1,600 mg/L, pH 5.0, 0.2 g modified PVA/50 mL solution, 120 rap/min.

mechanism can be certified by the FTIR spectra of the modified PVA before and after adsorption of metal ions presented in Fig. 6.

As shown in Fig. 6, the strong peaks at about 1,765, 1,710, and 1,032 cm^{-1} which correspond to COOR, C=O, and S=O bonds, respectively. The peaks of active functional groups move to 1,760, 1,701, and 1,037 cm^{-1} after Cd(II) adsorption, and move to 1,757, 1,704, and 1,036 cm^{-1} after Pb(II) adsorption. The peak at 2,926 cm^{-1} of COOH disappeared after metal ions adsorption since the proton exchange with the metal ions.

3.2.4. Thermodynamic studies

The thermodynamic nature of uptake process was obtained from the plotting of binding constant (K_L) against temperature according to Vant't Hoff [41] Eq. (7):

$$\log K_L = \frac{-\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \qquad (7)$$

where K_L is the distribution coefficient calculated by Langmuir isotherm equation, since Langmuir model is superior fit with the experimental data; R is the universal gas constant (8.314 J/(mol k)); T is the absolute temperature (K); ΔH° and ΔS° are the enthalpy and entropy change of adsorption process. From the straight lines obtained in Fig. 7, the values of ΔH° and ΔS° were calculated from the slope and intercept, respectively. On the other hand, the free energy of uptake reaction was obtained from the following Gibbs free energy [42] Eq. (8):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (8)$$

The calculated values of ΔH°, ΔS°, and ΔG° are given in Table 6. The negative value of enthalpy change ΔH° is (−60.08) or (−19.11) kJ/mol for Cd(II) or Pb(II), respectively, indicating the overall adsorption processes seem to be exothermic. The result also supports the capacities of adsorption increase with decreasing temperature. The negative values of ΔG° for all metal ions indicate the spontaneous nature of uptake reaction, and that the degree of spontaneity of the reaction increases with decreasing temperature. The negative ΔH° and ΔS° values mean a chemical exothermic process accompanied by a lowering in the entropy due to the adsorption of the metal ions on the modified PVA surface. The thermodynamic data indicate that the adsorption of Cd(II) and Pb(II) on modified PVA are spontaneous process, and the processes are unfavorable at high temperature. The results are consistent with the batch results.

3.3. Desorption and repeated use

The consecutive adsorption–desorption procedure was repeated for six cycles to investigate the repeated

Table 6
Thermodynamics parameters of adsorption

		Thermodynamics parameters			
Metals	T (K)	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)	$T\Delta S^\circ$ (kJ/mol)
Cd(II)	293.5	−60.08	−98.44	−30.70	−28.89
	303.5			−30.38	−29.88
	313.5			−30.07	−30.86
	333.5			−26.72	−32.83
Pb(II)	293.5	−19.11	−32.16	−28.51	−9.44
	303.5			−29.09	−9.76
	313.5			−28.94	−10.08
	333.5			−29.92	−10.73

Table 7
Adsorption capacities and desorption rate of modified PVA

Recycle times	1	2	3	4	5	6
Adsorption capacity (mmol/g)						
Cd(II)	1.21	1.21	1.20	1.21	1.19	1.18
Pb(II)	1.51	1.50	1.50	1.48	1.48	1.44
Desorption ratio (%)						
Cd(II)	99.11	99.34	99.82	97.24	96.98	95.37
Pb(II)	98.86	98.40	98.02	96.37	95.52	95.17

use capability of the modified PVA. Each adsorption or desorption equilibrium time was 3 h. The results are listed in Table 7. The adsorption capacities of the modified PVA show a slight decrease, whereas remain stable, demonstrate that the modified PVA is a good reusable sorbent in removal of Cd(II) and Pb(II) from its single-metal ion solution.

4. Conclusions

The present studies showed that the modified PVA is a promising adsorbent to be used in removal of Cd(II) and Pb(II) from aqueous solutions. Adsorption experiments are found to be effective in the pH range from 3 to 6 and at low temperature. Three isotherm models are used to describe the equilibrium isotherm data, and then Langmuir model is found to be highly appropriated with high R^2. Kinetic study shows that the pseudo-second-order model is more suitable for the adsorption process, and at the setting concentration, the adsorption rate is independent of the temperature. All of the thermodynamic parameters ΔH°, ΔS°, and ΔG° are negative, which mean the adsorption processes are feasible, spontaneous, and exothermic. The mechanism of adsorption includes mainly ion exchange and valence forces between metal cations and modified PVA. The adsorption capacity after six consecutive adsorption–desorption cycles remains stable, showing the modified PVA is a good reusable sorbent, resulting to enhance the economics of practical application for the removal of Cd(II) and Pb(II) from water and wastewater.

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