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Removal of Metal Ions From Aqueous Solutions Using Sawdust Modified with Citric Acid or Tartaric Acid

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This study describes the adsorption of heavy metal ions (Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II)) from aqueous solutions by pine (*Pinus densiflora*) sawdust modified with citric acid (CA) or tartaric acid (TA). The optimal parameters, contact time, and pH were determined and the adsorption isotherms were obtained. The removal efficiency of the modified sawdust increased as the pH increased. The maximum adsorption capacity of sawdust modified with CA or TA was 14 to 57 times higher than that of unmodified sawdust. These results indicate that either CA or TA can be used to enhance the removal of heavy metals using sawdust.

Keywords adsorption; citric acid; heavy metals; sawdust; tartaric acid

INTRODUCTION

Heavy metal ions are among the most important pollutants in source and treated water, and they are becoming a severe public health problem (1). They are both toxic and non-biodegradable (2). Heavy metal ions can be accumulated through the food chain and are harmful to aquatic life. Thus, water contamination by heavy metal ions is a serious threat to human health. Therefore, adequate and cost-effective treatment technologies are needed to remove heavy metal ions from aqueous solutions.

To accomplish this, various technologies have been developed, including electrochemical and chemical treatments, biological treatments, membrane processes, and adsorption. Of these, adsorption is the most convenient and popular method for removing heavy metals from industrial effluents (1,3–10). Recently, cheaper and more effective adsorbents have been studied. The use of environmentally-friendly natural materials as adsorbents has been widely investigated for removing metal ions from aqueous solutions (1–2,7–10).

Sawdust is a waste material derived from the wood industry and is a green and economical sorbent for the removal of heavy metals from aqueous solutions. Recently, many researchers have investigated metal adsorption onto sawdust (2,4,11–17), but untreated sawdust has a low adsorption capacity. Therefore, the capacity has been improved by treatment with NaOH, H_3PO_4, formaldehyde, sulphuric acid, citric acid, tartaric acid, or succinic anhydride (11–13,16–18).

In this study, sawdust treated with organic acid (citric acid or tartaric acid) was used to remove heavy metal ions from aqueous solutions. The adsorption kinetics and isotherms of several metals were tested, and the adsorption mechanism was investigated using various adsorption kinetic models and isotherm equations.

MATERIALS AND METHODS

Sawdust

The sawdust, originating from *Pinus densiflora*, was first sieved (20–50 mesh), then washed with de-ionized water, and dried in an oven at 60°C (raw sawdust, RS). Next, 40 g of RS was mixed in a beaker with 100 mL of 6 mol/L citric acid (CA) or tartaric acid (TA) solution, and allowed to soak for 1 h. The sample was then dried in an oven at 60°C for 4 h to remove excess water. The sample was reacted at 120°C for 2 h. It was next washed with de-ionized water until the pH was neutral, and finally dried overnight in an oven at 60°C. The sawdust treated with CA is denoted CA-SD and that treated with TA is denoted TA-SD. The final sawdust was sieved with 20–50 mesh to remove fine particles.

The change in the functional groups and surface morphology of the sawdust was investigated using several analytical methods. The surface functional groups of RS, CA-SD, and TA-SD were determined using attenuated

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total reflectance Fourier transform infrared (ATR-FTIR, Nicolet iS10, Thermo Scientific, USA) spectroscopy. The surface images of the sawdust were analyzed by a field emission scanning electron microscope (FE-SEM, Hitachi Su-70, Japan). The specific surface areas of the apatite particles were measured by the Brunauer-Emmet-Teller (BET) method with a Micrometrics TriStar 3000 (Micrometrics Instrument Corp., Norcross, GA, USA).

Reagents

Stock solutions (10 mM) of heavy metal ions were prepared with $Cd(NO_3)_2 \cdot 4H_2O$, $CuSO_4 \cdot 5H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$, and $Zn(NO_3)_2 \cdot 6H_2O$, which were obtained from Sigma-Aldrich (USA). Sodium hydroxide and nitric acid were purchased from Samchun Pure Chemical Co. Ltd. (Korea). CA and TA were obtained from Junsei Chemical Co. (Japan). De-ionized water was prepared using a Millipore water purification system (Millipore, USA).

Adsorption Experiments

Adsorption kinetic experiments of heavy metal ions (Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II)) onto sawdust were conducted with 0.5 g of sawdust in 0.6 L of 0.3 mM metal ion solution at pH 4.5 ± 0.5 and 25°C. The solution was mixed with an overhead stirrer at 200 rpm and 5 mL was taken and filtered at specified times (0, 1, 5, 10, 15, 20, 30, 60, 90, 120, 180, 240, 300, 360, and 1,080 min). The metal ions concentration in the filtrates was analyzed by an inductively coupled plasma-optical emission spectrophotometer (ICP-OES, 730-ES, Varian Inc., USA).

The effect of pH on metal adsorption onto sawdust was investigated with 0.1 g of sawdust and 30 mL of 0.3 mM metal ion solution. The solution pH was adjusted from 1.5 to 6.5 using HNO_3 and NaOH. The solution was shaken at 25°C and 120 rpm for 12 hours. Then it was filtered with a 0.45 µm syringe filter and the metal ions concentration in the filtrate was analyzed using ICP-OES.

Adsorption isotherm experiments were conducted at 25°C and pH 4.5 to avoid precipitation of the metal ions. Generally, 0.1 g of sawdust was added to a 50 mL conical tube containing 30 mL of metal ion solution (0–1 mM). The pH of the solution was adjusted to pH 4.5 using NaOH and HNO_3. The samples were equilibrated for 24 h at 120 rpm in an orbital shaker and then filtered through a 0.45 µm membrane filter. Because the solution pH was varied during the experiment, the pH of the solution was re-adjusted to pH 4.5 after 12 h shaking. The final pH and metal ion concentrations of the solutions were measured by a pH meter and ICP-OES, respectively.

Analysis of Heavy Metal Ions

The aqueous solution was filtered using a 0.45-µm membrane filter, and the metal ion concentration was then determined using ICP-OES. The amount of metal ions adsorbed onto the sawdust was calculated using the following equation:

$$q = \frac{(C_0 - C_f)}{m} \times V$$

where q is the adsorption amount (mmol/g), C_o and C_f are the initial and final metal ion concentrations in the solution (mM), respectively, V is the solution volume (L), and m is the mass of the sawdust (g).

RESULTS AND DISCUSSION

Characterization of Sawdust

The components of sawdust are cellulose, hemicelluloses, and lignin; lignin is an active ion-exchange compound (2). The surface morphology of the sawdust was analyzed using SEM (Fig. 1). The surface of the sawdust treated with CA or TA was rougher than that of the untreated sawdust. The BET surface area of RS, CA-SD, and TA-SD was $0.3721\,m^2\,g^{-1}$, $0.6380\,m^2\,g^{-1}$, and $0.5809\,m^2\,g^{-1}$, respectively. The changes in the structure and roughness of the sawdust surface were probably caused by the organic acid treatment. The functional groups of the sawdust were determined using the FT-IR spectrum (Fig. 2). Bands of carbonyl (C=O) and hydroxyl (-OH) of the carboxyl group (-COOH) occurred at 1727 and $1608\,cm^{-1}$, respectively (19). The intensities of the bands increased after CA or TA treatments. It reflected the result of organic acid esterification. Figure 3 shows the reaction scheme for the sawdust modification. The hydroxyl group of the sawdust reacted with the carboxyl group of the organic acid by esterification and created adsorption sites. The phenolic or carboxylic group offer adsorption sites for heavy metal ions. These surface and functional group studies reveal that the carboxyl groups of modified sawdust are able to bind with heavy metal ions.

Kinetic Adsorption of Heavy Metal Ions by Modified Sawdust

Figure 4 shows the effect of contact time on the metal ion adsorption. For 30 min, the adsorption increased rapidly and then the metal ions in the aqueous phase equilibrated with the metal ions adsorbed onto the sawdust. This relatively fast adsorption (within 60 min) has been commonly observed in the adsorption of heavy metal ions onto sawdust (2,11,19). The adsorption is fast because the main adsorption mechanism is ion exchange. A detailed analysis of the adsorption mechanism is given in a later section. In addition, adsorption onto TA-SD was slightly faster than adsorption onto CA-SD. However, there were no significant differences in the adsorption kinetics of the different metal ions.

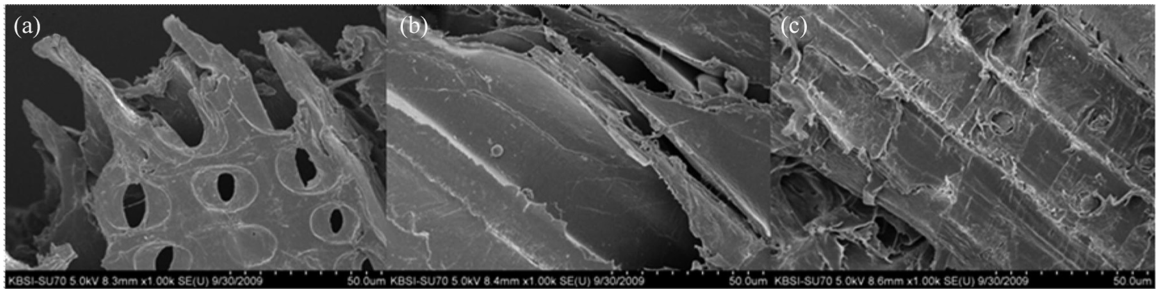


FIG. 1. SEM images of (a) raw, (b) citric-acid treated, and (c) tartaric-acid treated sawdust.

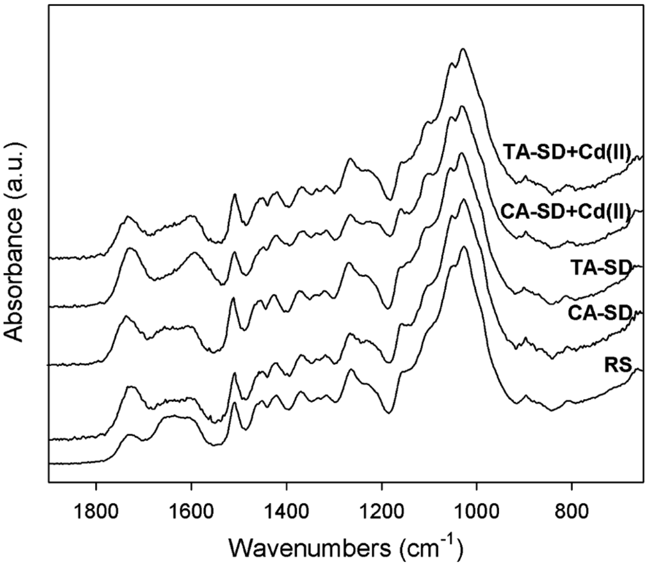


FIG. 2. FT-IR spectrum of sawdust.

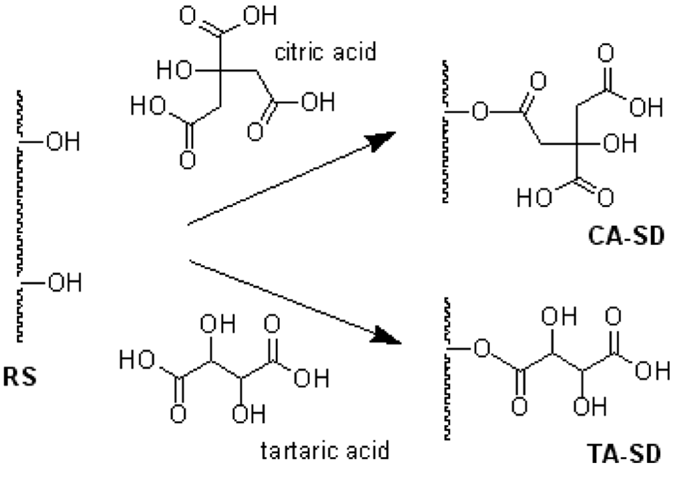
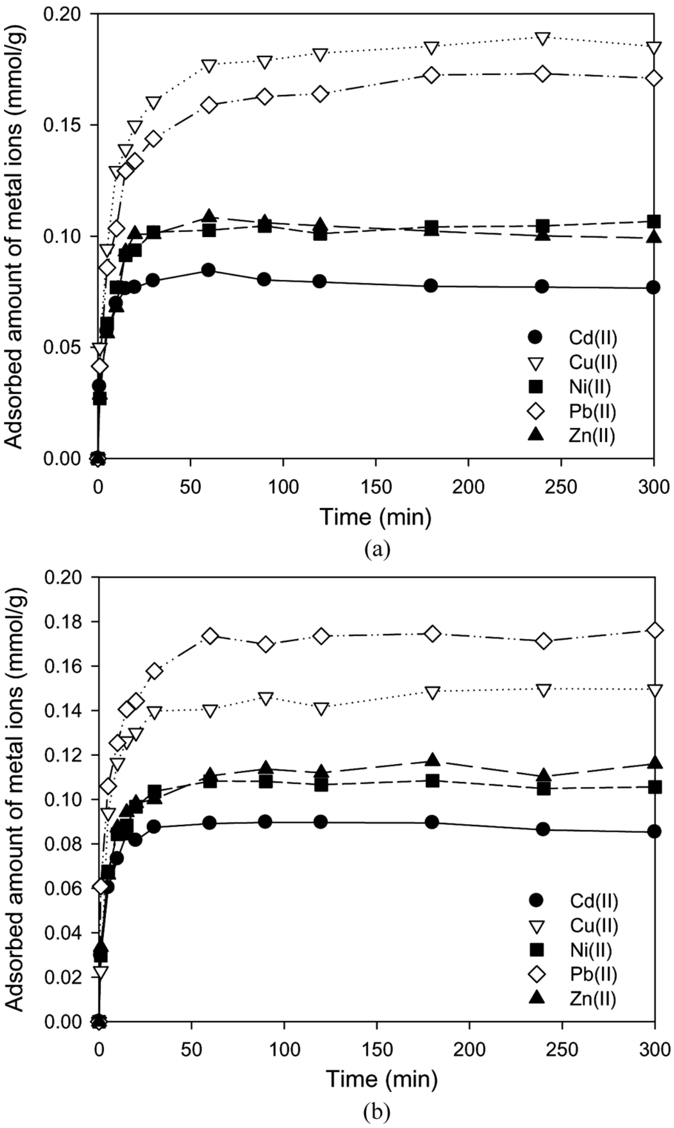


FIG. 3. Scheme for synthesis of CA-SD and TA-SD from RS.



(a)

(b)

FIG. 4. Effect of contact time on adsorption of heavy metal ions onto (a) CA-SD and (b) TA-SD.

Four kinetic adsorption models were fitted to the data: the pseudo-first-order model, the pseudo-second-order model, the intraparticle diffusion model, and the pore diffusion model. The kinetic rate equation for the pseudo-first-order model can be written as (20–22):

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

where k_1 is the pseudo-first-order rate constant of adsorption ($\mathrm{g\,mmol^{-1}\,min^{-1}}$), q_e is the amount of metal ions adsorbed at equilibrium ($\mathrm{mmol\,g^{-1}}$), and q_t is the amount of metal ions on the surface of the adsorbent at any time t ($\mathrm{mmol\,g^{-1}}$). The equation was integrated with boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ and a linearized form was obtained:

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

The kinetic rate equation for the pseudo-second-order model can be written as (20,23):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

where k_2 is the pseudo-second-order rate constant of adsorption ($\mathrm{g\,mmol^{-1}\,min^{-1}}$). After integration with boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation can be rearranged to obtain a linear form (20):

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

with

$$h = k_2 q_e^2$$

where h is the initial adsorption rate ($\mathrm{mmol\,g^{-1}\,min^{-1}}$).

The adsorption kinetics were not well matched with the pseudo-first-order model (Figs. 5(a) and 6(a)). Generally, the pseudo-first-order model could be applied at the initial adsorption phase. The pseudo-second-order model fitted the experimental data well (Figs. 5(b) and 6(b)). The pseudo-second-order kinetic model constants are summarized in Tables 1 and 2. The coefficient of determination was over 0.999 for all the metal ions. The k_2 values for the metal ions were in the range 0.985–35.05 ($\mathrm{g\,mmol^{-1}\,min^{-1}}$) for CA-SD, and 1.709–6.528 ($\mathrm{g\,mmol^{-1}\,min^{-1}}$) for TA-SD. The h values for the metal ions were in the range 0.030–0.356 ($\mathrm{mmol\,g^{-1}\,min^{-1}}$) for CA-SD and 0.035–0.074 ($\mathrm{mmol\,g^{-1}\,min^{-1}}$) for TA-SD. Larger values for k_2 and h indicate faster adsorption. However, the ranking of the metal ions by k_2 and h values depended on the organic acid. For CA-SD the ranking was Zn(II) > Cd(II) > Ni(II) > Cu(II) > Pb(II) whereas for TA-SD it was Ni(II) > Cd(II) > Zn(II) > Pb(II) > Cu(II).

In the kinetic data, there might be a rate-limiting step in the initial adsorption stage. In fluid-solid mass transfer, there are four major rate-determining mechanisms: fluid-phase external mass transfer, fluid-phase pore diffusion, reaction at the phase boundary, and solid-phase diffusion (24). Fluid-phase pore diffusion and solid-phase diffusion are also known as pore diffusion and intraparticle diffusion, respectively. To find the main rate-determining step, the intraparticle and pore diffusion models were fitted to the experimental data.

The intraparticle diffusion model is expressed as (25,26):

$$R = k_{id}t^{\alpha}$$

and

$$\log R = \log k_{id} + \alpha_{id}\log t$$

where R is the percentage of metal adsorbed, k_{id} is the rate constant of intraparticle diffusion, and α_{id} is the gradient of the linear plot. Larger values of k_{id} indicate a faster rate of adsorption, whereas larger α_{id} values indicate a better adsorption mechanism, which is related to an improved bonding between the metal ions and the adsorbent (25). In the initial adsorption stage (0–10 min), the pore diffusion model described the experimental data well. However, the value of α_{id} was always less than 0.50, indicating that intraparticle diffusion might not be the only rate-determining step (25).

The pore diffusion model, also known as Bangham's model, is expressed as (27,28):

$$\log\left(\frac{C_0}{C_0 - q_t m'}\right) = \log\left(\frac{k_B m'}{2.303V}\right) + \alpha_B \log t$$

where m' is the mass of the adsorbent in the solution ($\mathrm{g\,L^{-1}}$), and k_B and α_B are the rate constants. This model also described the experimental data well in the initial adsorption stage (0–10 min). These results indicate that adsorption resistance at the initial stage was caused by both intraparticle diffusion and pore diffusion. However, sawdust is not a highly porous material and so diffusion of metal ions in the inner part of sawdust is not a rate-determining step after 10 min.

pH Effect

It is well known that the pH of the solution is an important parameter for the adsorption of heavy metal ions. At high pH heavy metal ions precipitate as metal hydroxides, and at low pH they compete with hydrogen ions for

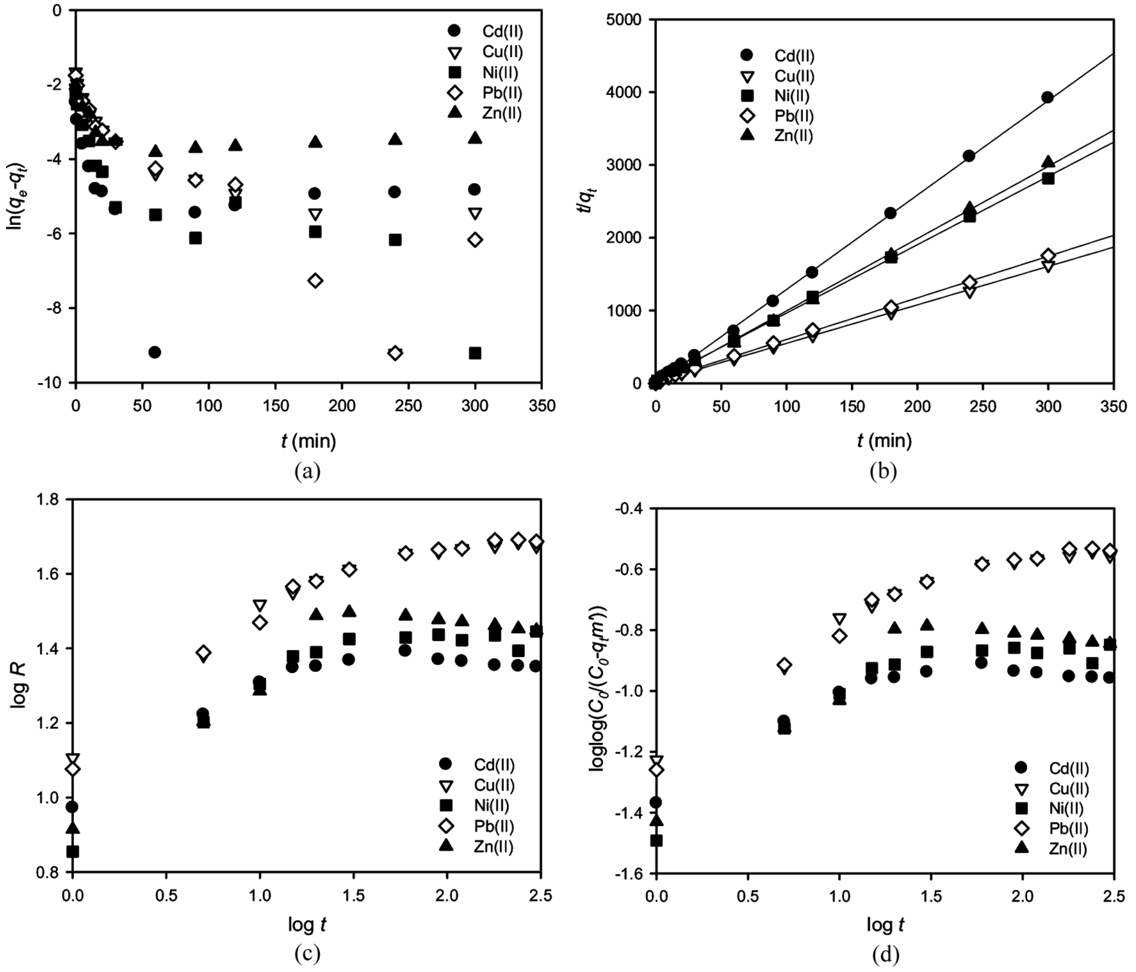


FIG. 5. Kinetic modeling of adsorption of heavy metal ions onto CA-SD with (a) pseudo-first-order, (b) pseudo-second-order, (c) intraparticle diffusion, and (d) pore diffusion equations.

available adsorption sites. Thus, the removal efficiency is low at low pH and high at high pH.

To minimize the precipitation of heavy metal ions and to find the adsorption efficiency of the sawdust, the pH effect was tested in the range 1.5–7 (Fig. 7). When the pH < 2, the metal removal was negligible. When the pH is above 6, the removal efficiency was over 90%. There is no significant difference between CA-SD and TA-SD. With 0.3 mM of metal ions and 1 g sawdust/300 mL, removal of 50% of the Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) was achieved with CA-SD at pH 3.99, 3.19, 3.95, 3.06, and 3.95, respectively, and achieved with TA-SD at pH 3.60, 3.05, 3.60, 2.83, and 3.51, respectively. Removal of 90% of the Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) was achieved with CA-SD at pH 4.71, 4.07, 5.67, 3.72, and 5.34, respectively, and with TA-SD at pH 4.51, 3.89, 4.65, 3.50, and 4.39, respectively. At lower pH values, the removal efficiency of the metal ions had the following order: Pb(II) > Cu(II) > Zn(II) ≈ Cd(II) ≈ Ni(II). The stability constants (log K) of citrate-Cd(II), citrate-Cu(II), citrate-Ni(II), citrate-Pb(II), and citrate-Zn(II) are 4.98, 7.57, 6.59, 7.27, and 6.21, respectively (29). The stability constants of tartrate-Cd(II), tartrate-Cu(II), tartrate-Ni(II), tartrate-Pb(II), and tartrate-Zn(II) are 2.70, 3.97, 3.46, 3.98, and 3.43, respectively (29). Because a higher stability constant means stronger complexation was formed, the removal efficiencies of Pb(II) and Cu(II) in low pH were higher than those of Cd(II), Ni(II), and Zn(II).

Adsorption Isotherm

Adsorption isotherms are important for describing the adsorption mechanism and maximum adsorption capacity. In this study, four adsorption isotherm equations were used to describe the metal adsorption: the Langmuir isotherm equation, the Freundlich isotherm equation, the Redlich-Peterson isotherm equation, and the Dubinin-Radushkevich isotherm equation.

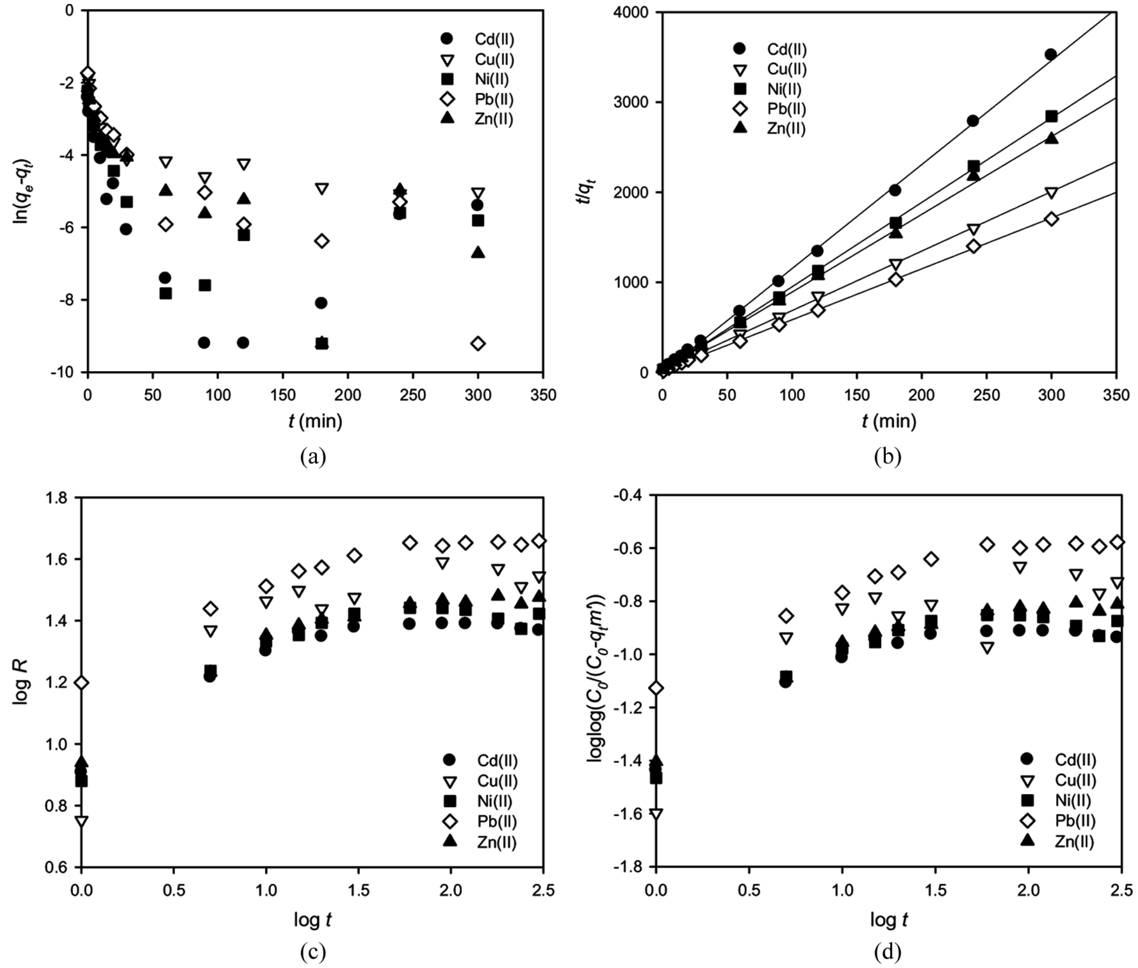


FIG. 6. Kinetic modeling of adsorption of heavy metal ions onto TA-SD with (a) pseudo-first-order, (b) pseudo-second-order, (c) intraparticle diffusion, and (d) pore diffusion equations.

The Langmuir isotherm equation can be written as:

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

where q_{max} is the maximum amount of metal ions adsorbed at equilibrium (mmol g^{-1}), C_e is the equilibrium concentration of metal ions in the aqueous phase (mmol L^{-1}), and K_L is a constant reflecting the affinity of the sawdust for the metal ions (L mmol^{-1}). The equation can be rearranged into a linear form:

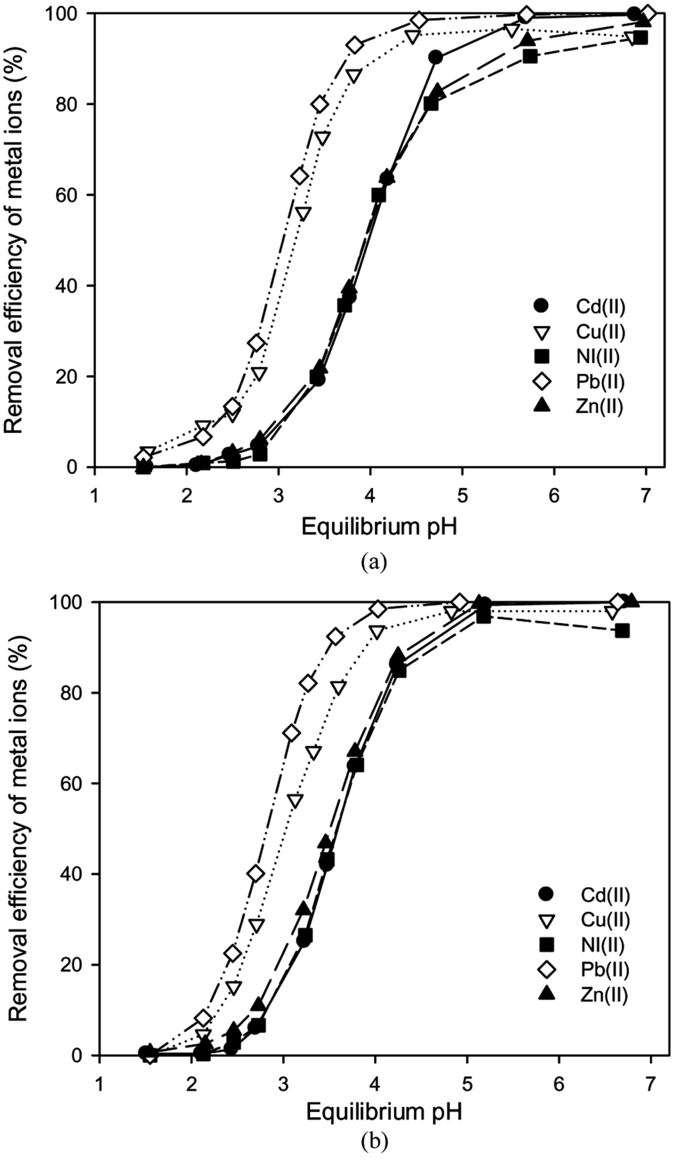
$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e$$

TABLE 1
The pseudo-second-order kinetics constants for adsorption of heavy metal ions onto CA-SD

	Pseudo-second-order constants				
Metal ions	k_2 (g mmol^{-1} min^{-1})	q_e (mmol g^{-1})	$q_e(exp)$ (mmol g^{-1})	h (mmol g^{-1} min^{-1})	R^2
Cd(II)	7.109	0.077	0.077	0.042	0.999
Cu(II)	1.117	0.190	0.185	0.040	1.000
Ni(II)	2.941	0.107	0.107	0.033	1.000
Pb(II)	0.985	0.175	0.173	0.030	1.000
Zn(II)	35.05	0.101	0.108	0.356	0.999

TABLE 2
The pseudo-second-order kinetics constants for adsorption of heavy metal ions onto TA-SD

	Pseudo-second-order constants				
Metal ions	k_2 (g mmol^{-1} min^{-1})	q_e (mmol g^{-1})	$q_e(exp)$ (mmol g^{-1})	h (mmol g^{-1} min^{-1})	R^2
Cd(II)	5.396	0.087	0.085	0.040	0.999
Cu(II)	1.709	0.151	0.150	0.039	1.000
Ni(II)	6.528	0.107	0.108	0.074	1.000
Pb(II)	1.740	0.177	0.175	0.054	1.000
Zn(II)	2.614	0.116	0.117	0.035	0.999



(a)

(b)

FIG. 7. Effect of pH on heavy metal ions adsorption onto (a) CA-SD and (b) TA-SD.

The dimensionless equilibrium parameter (R_L), which can be used to predict the affinity between sawdust and metal ions, is expressed by (30):

$$R_L = \frac{1}{1 + K_L C_0}$$

The Freundlich isotherm equation can be expressed as (31):

$$q_e = K_F C_e^{1/n}$$

or

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where K_F and $1/n$ are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively (32).

The Redlich-Peterson isotherm equation is a combination of the Langmuir and Freundlich isotherms and can be expressed as (33):

$$q_e = \frac{K_{RP} C_e}{1 + b_{RP} C_e^g}$$

and

$$K_{RP} = q_{\max} b_{RP}$$

where K_{RP}, b_{RP}, and g, which ranges from 0 to 1, are the Redlich-Peterson parameters.

The constants of the adsorption isotherm equations are summarized in Tables 3 and 4. The Langmuir isotherm equation describes monolayer adsorption and the Freundlich isotherm equation describes heterogeneous adsorption. The Redlich-Peterson isotherm equation is a combination of the two. The coefficient of determination was in the range 0.875–0.996 for the Langmuir isotherm equation, 0.901–0.981 for the Freundlich isotherm

TABLE 3
Isotherm constants for the adsorption of heavy metal ions on CA-SD

	Langmuir constants			Redlich-Peterson constants			
Metal ions	q_{max} (mmol g^{-1})	K_L (L mmol^{-1})	R^2	q_{max} (mmol g^{-1})	b_{RP} (L^g mmol^{-g})	g	R^2
Cd(II)	0.114	38.46	0.969	0.133	101.4	0.822	0.990
Cu(II)	0.237	28.57	0.983	0.237	28.3	1.000	0.983
Ni(II)	0.167	9.80	0.996	0.178	12.7	0.850	0.999
Pb(II)	0.234	66.67	0.932	0.299	282.8	0.789	0.979
Zn(II)	0.140	17.86	0.993	0.149	23.3	0.880	0.997

	Freundlich constants			Dubinin-Radushkevich constants			
Metal ions	$1/n$	K_F (mmol$^{(1-1/n)}$ g^{-1} L$^{1/n}$)	R^2	q_{max} (mmol g^{-1})	β_{DR} (mol^2 kJ^{-2})	E (kJ mol^{-1})	R^2
Cd(II)	0.428	0.219	0.954	0.636	0.0025	14.0	0.982
Cu(II)	0.678	0.905	0.901	6.376	0.0040	11.2	0.935
Ni(II)	0.645	0.320	0.960	2.574	0.0040	11.2	0.982
Pb(II)	0.384	0.480	0.957	0.985	0.0023	14.8	0.982
Zn(II)	0.541	0.262	0.953	1.381	0.0033	12.4	0.980

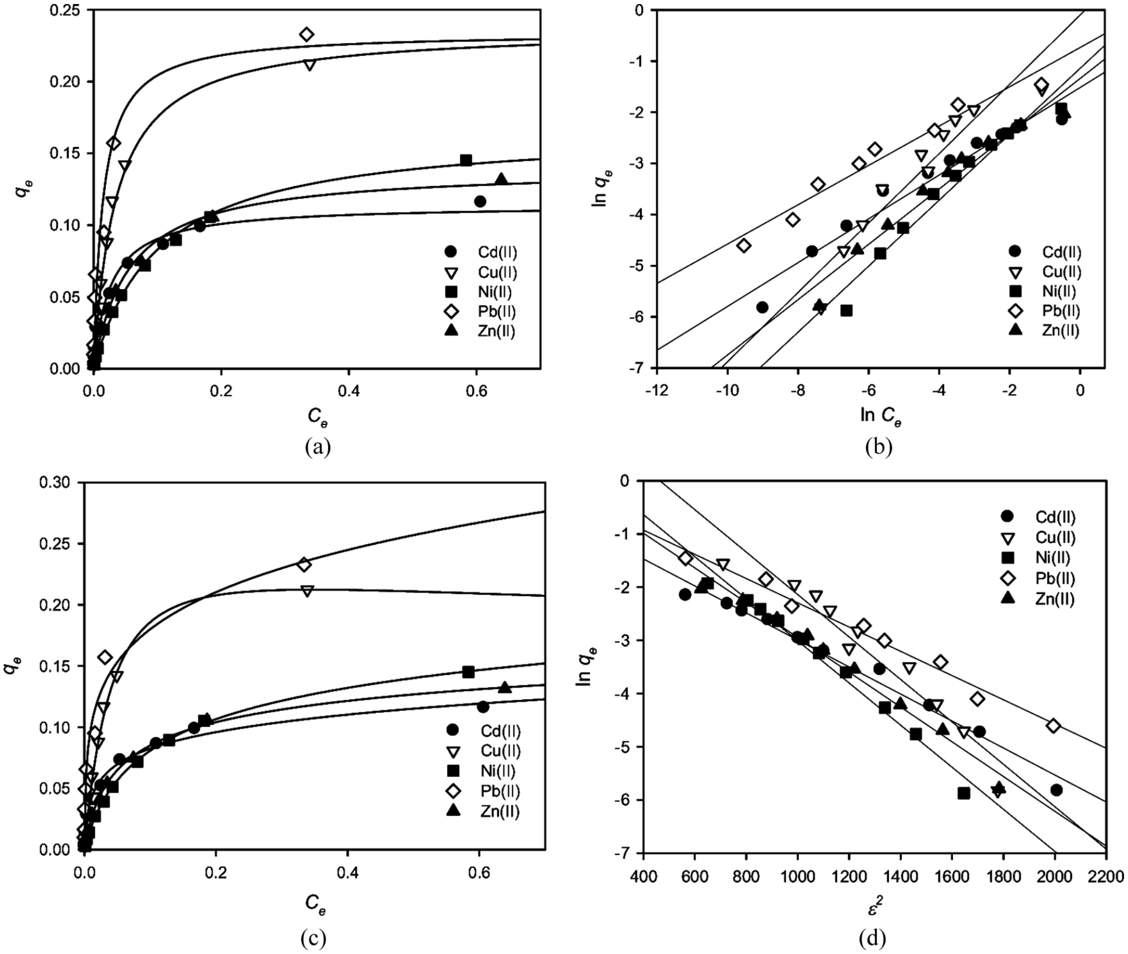
equation, and 0.983–0.998 for the Redlich-Peterson isotherm equation. The g values for the Redlich-Peterson isotherm equation were in the range 0.789–1.000. Since the g values are close to 1, this equation is similar to the Langmuir isotherm equation.

The metal adsorption onto CA-SD was in the range 0.114–0.234 mmol g^{-1} and that onto TA-SD was in the range 0.105–0.185 mmol g^{-1}. The maximum adsorbed amount of unmodified sawdust (SS) was in the range 0.0028–0.0110 (data not shown). The maximum adsorption capacity of sawdust modified by CA or TA was 14 to 57 times higher than that of unmodified sawdust. Wong et al. (34) reported that the adsorption amount of Cu and Pb by tartaric acid modified rice husk was 29 (0.46 mmol) and 109 (0.53 mmol) mg g^{-1}, respectively. Lu et al. (19) reported that the maximum adsorption capacity of citric acid modified lawny grass for Pb(II) was 1.55 mmol g^{-1}. Zhu et al. (35) obtained that the maximum adsorption capacity of the citric

TABLE 4
Isotherm constants for the adsorption of heavy metal ions on TA-SD

	Langmuir constants			Redlich-Peterson constants			
Metal ions	q_{max} (mmol g^{-1})	K_L (L mmol^{-1})	R^2	q_{max} (mmol g^{-1})	b_{RP} (L^g mmol^{-g})	g	R^2
Cd(II)	0.105	83.33	0.954	0.132	235.6	0.826	0.996
Cu(II)	0.176	45.45	0.972	0.207	77.7	0.843	0.986
Ni(II)	0.130	55.56	0.955	0.162	143.7	0.804	0.997
Pb(II)	0.185	500.0	0.875	0.224	3586.9	0.838	0.986
Zn(II)	0.141	65.50	0.934	0.175	214.9	0.791	0.998

	Freundlich constants			Dubinin-Radushkevich constants			
Metal ions	$1/n$	K_F (mmol$^{(1-1/n)}$ g^{-1} L$^{1/n}$)	R^2	q_{max} (mmol g^{-1})	β_{DR} (mol^2 kJ^{-2})	E (kJ mol^{-1})	R^2
Cd(II)	0.375	0.209	0.951	0.495	0.0021	15.3	0.981
Cu(II)	0.490	0.442	0.904	1.661	0.0028	13.4	0.934
Ni(II)	0.428	0.269	0.920	0.896	0.0024	14.4	0.948
Pb(II)	0.214	0.282	0.981	0.429	0.0013	20.0	0.994
Zn(II)	0.322	0.216	0.970	0.579	0.0019	16.1	0.990



(a) (b)

(c) (d)

FIG. 8. Adsorption isotherm modeling of heavy metal ions onto CA-SD with (a) Langmuir, (b) Freundlich, (c) Redlich-Peterson, and (d) Dubinin-Radushkevich isotherm models.

acid modified soybean straw for Cu(II) was 0.77 mmol g^{-1}. The adsorption capacities of sawdust in this study was lower than published data. But the adsorption capacities was obtained at pH 4.5 and with 20–50 mesh sawdust. It is expected that the adsorption capacities increase when the solution pH increases and the size of adsorbent decreases.

The order of adsorption onto CA-SD was Cu(II) > Pb(II) > Ni(II) > Zn(II) > Cd(II) and for TA-SD it was Pb(II) > Cu(II) > Zn(II) > Ni(II) > Cd(II). It is related to the stability constants of organic acid-metal ions. The order of stability constants of citrate-metal ions and tartrate-metal ions is Cu(II) > Pb(II) > Ni(II) > Zn(II) > Cd(II) and Pb(II) > Cu(II) > Ni(II) > Zn(II) > Cd(II), respectively, which is the same order of adsorption capacity for CA-SD and TA-SD. It means that the adsorption capacities of sawdust could be changed according to the modifier.

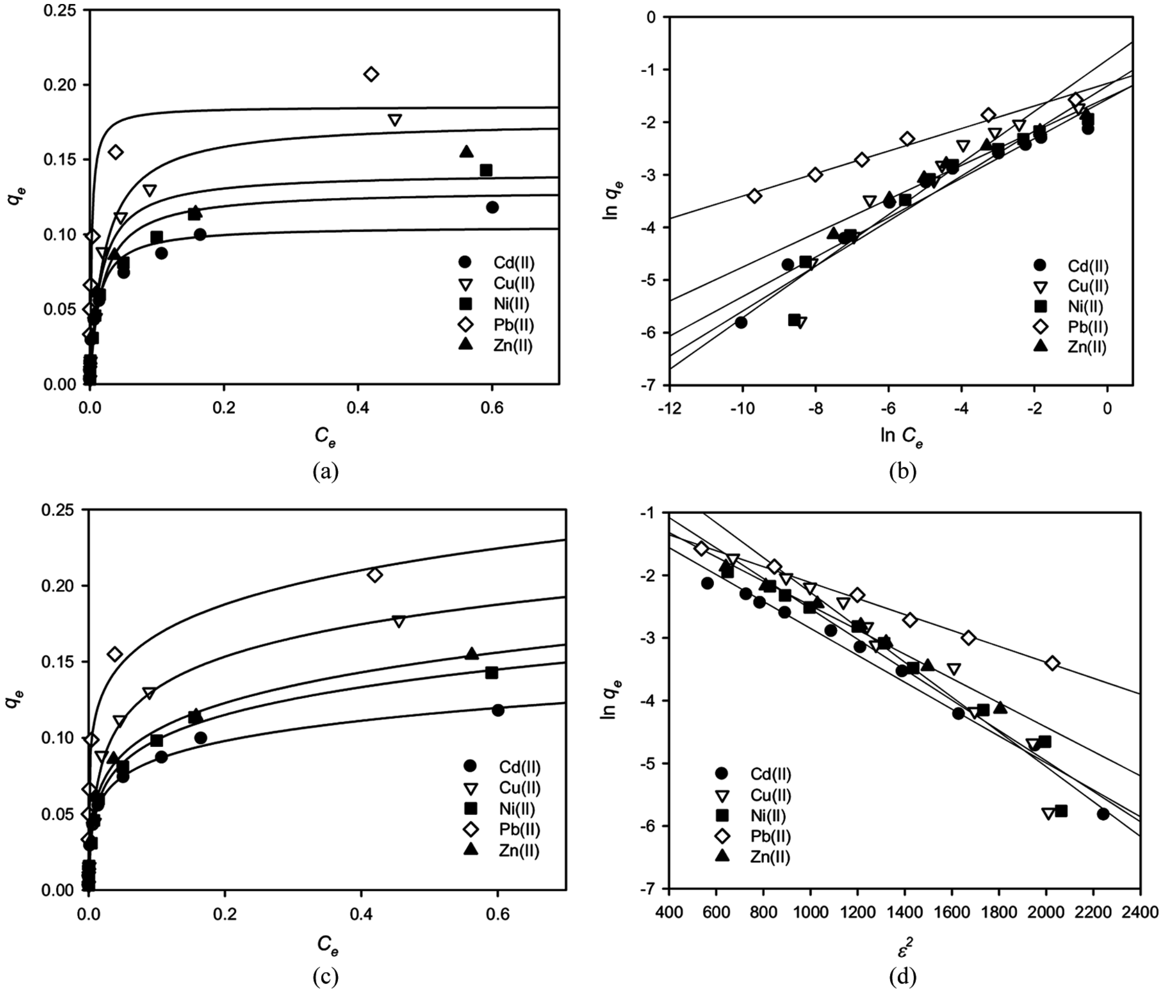
The parameter R_L indicates whether or not the adsorption is favorable: (a) $R_L > 1$: adsorption is unfavorable, (b) $R_L = 1$: adsorption is linear, (c) $0 < R_L < 1$: adsorption is favorable, and (d) $R_L = 0$: adsorption is irreversible (12). The values of R_L in the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) onto CA-SD were 0.03–0.72, 0.03–0.77, 0.09–0.91, 0.01–0.57, and 0.57–084, respectively. Those for Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) onto TA-SD were 0.01–0.55, 0.02–0.68, 0.02–0.63, 0.00–0.15, and 0.01–0.60, respectively. These results indicate that the adsorption of heavy metals onto modified sawdust was favorable, and the adsorption became close to irreversible as the metal concentration decreased.

The Dubinin-Radushkevich isotherm equation is expressed as (36,37,38):

$$q_e = q_{\max}\exp(-\beta_{DR}\varepsilon^2)$$

where β_{DR} is the activity coefficient (mol^2 kJ^{-2}) and ε is the Polanyi potential (kJ mol^{-1}) which can be expressed as (38,39):

$$\varepsilon = RT\ln\left(1+\frac{1}{C'_e}\right)$$



(a) (b)

(c) (d)

FIG. 9. Adsorption isotherm modeling of heavy metal ions onto TA-SD with (a) Langmuir, (b) Freundlich, (c) Redlich-Peterson, and (d) Dubinin-Radushkevich isotherm models.

where C_e' is the equilibrium metal concentration ($g\,g^{-1}$), R is the gas constant ($0.00831447\,kJ\,K^{-1}\,mol^{-1}$), and T is the absolute temperature (297.15 K). The Dubinin-Radushkevich equation has a linear form:

$$\ln q_e = \ln q_{\max} - \beta_{DR}\varepsilon^2$$

The value of the coefficient of determination was in the range 0.934–0.990 and this indicates that the Dubinin-Radushkevich isotherm equation fits the experimental data well. However, the calculated maximum metal adsorption capacity (q_{max}) obtained using the Dubinin-Radushkevich isotherm equation (0.495–$6.376\,mmol\,g^{-1}$) was much higher than those obtained using the Langmuir (0.105–$0.234\,mmol\,g^{-1}$) and Redlich-Peterson isotherm equations ($0.0.132$–$0.299\,mmol\,g^{-1}$).

The mean free energy E ($kJ\,mol^{-1}$) can be computed from β as follows (40):

$$E = \frac{1}{\sqrt{2\beta_{DR}}}$$

For $E < 8\,kJ\,mol^{-1}$, physical adsorption dominates the sorption mechanism. If E is between 8 and $16\,kJ\,mol^{-1}$, ion exchange is the dominant factor. In this study, the E values were in the range 11.19–14.81 for CA-SD and 13.41–19.98 for TA-SD. The E values for CA-SD were lower than those for TA-SD. In the case of Zn(II) and Pb(II) adsorption onto TA-SA, the E values were over $16\,kJ\,mol^{-1}$ and the others were in the range 8–$16\,kJ\,mol^{-1}$. This shows that the metal ion adsorption mechanism was predominantly ion exchange.

CONCLUSIONS

The adsorption of heavy metal ions (Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II)) onto sawdust modified with CA or TA was investigated. Four kinetic models and four isotherm equations were fitted to the experimental data to elucidate the adsorption mechanism. The metal ions were easily adsorbed onto the modified sawdust within 60 min, and pore and intraparticle diffusion were the rate-limiting steps in the initial adsorption stage. Of the kinetic models, the pseudo-second-order equation provided the best fit to the data. The metal ion adsorption increased with pH and 90% of the metal ions were adsorbed in the pH range 3.72–4.72. The adsorption of heavy metal ions was a favored reaction and the main adsorption mechanism is ion exchange. The maximum metal ion adsorption capacity onto CA-SD and TA-SD at pH 4.5 was 0.114–0.234 and 0.105–0.185 mmol g^{-1}, respectively. These results show that modifying sawdust with organic acids significantly increases the metal ion adsorption capacity, and that modified sawdust could be used as an adsorbent for heavy metal ions removal from aqueous solutions.

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