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Deli Liu<sup>a</sup>; Dezhi Sun<sup>a</sup>; Yangqing Li<sup>b</sup>

<sup>a</sup> School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin, P.R.

China <sup>b</sup> Department of Bioengineering, Harbin Institute of Technology, Weihai Campus, Weihai, Shandong, P.R. China

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# Removal of Cu(II) and Cd(II) From Aqueous Solutions by Polyaniline on Sawdust

Deli Liu,<sup>1</sup> Dezhi Sun,<sup>1</sup> and Yangqing Li<sup>2</sup>

<sup>1</sup>*School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin, P.R. China*

<sup>2</sup>*Department of Bioengineering, Harbin Institute of Technology, Weihai Campus, Weihai, Shandong, P.R. China*

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The present work deals with the removal of Cu(II) and Cd(II) ions from aqueous solutions in a batch mode system using polyaniline doped sawdust (PANI/SD). The effects of various experimental conditions such as pH, initial metal ion concentration, time, and temperature were studied. The sorption system follows a second-order kinetic model, and adsorption equilibrium was achieved within 40 min. The maximum adsorption capacities obtained from the Langmuir isotherm model are 208.77 mg/g and 136.05 mg/g for Cu(II) and Cd(II), respectively, at pH 5.0 and a temperature of 293 K. Thermodynamic parameters such as  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  were evaluated for the adsorption process, and the results show that the adsorption of Cu(II) and Cd(II) is spontaneous and endothermic. Desorption of metal ions and regeneration of adsorbent is achieved in 2 M hydrochloric solution. It is therefore reasonable that PANI/SD could be used for the removal of Cu(II) and Cd(II) ions from waste water.

**Keywords** adsorption; desorption; polyaniline; sawdust

## INTRODUCTION

Large quantities of heavy metals, e.g., cadmium, chromium, cobalt, copper, and lead are discharged into the environment due to the development of industrialization. Heavy metals constitute a serious environmental problem because these substances are non-biodegradable. Their high toxicity in living organisms causes various diseases and disorders (1). Human intake of excessively large doses of copper, for example, leads to severe mucosal irritation and corrosion, hepatic and renal damage, widespread capillary damage, and central nervous system irritation followed by depression (2). Longer-term exposure to cadmium primarily affects the kidneys and leads to serious diseases such as renal damage, anemia, hypertension, and itai-itai (3).

The effective removal of heavy metals from industrial wastewater has great scientific and practical interest. Various technologies have been developed: chemical precipitation (4), membrane separation (5,6), solvent extraction (7), ion-exchange (8,9), adsorption (10), and biosorption (11,12). Each of these methods has some significant drawbacks in practice. Adsorption in particular has proven to be an effective and versatile method for the removal of heavy metals when combined with appropriate desorption and metal recovery steps. The advantage of adsorption is the operation's relative ease and the low cost of most natural adsorbents. Many novel adsorbents have been studied for Cu(II) and Cd(II) removal from aqueous solution, e.g., chelating resin(13), fiber (14,15), cellulose (16), titanate nanotubes (17), agricultural by-products (18–21), bacteria (22), and hydrogel (23).

Polyaniline, a dark-blue powder, has been given considerable attention in recent years because of its high environmental stability, high electrical conductivity, and easy synthesis. It can be used in battery electrodes (24), sensors (25), corrosion inhibitors (26), and magnetic recording (27). Additionally, polyaniline is expected to have a strong affinity for metal ions due to its multitude of amine and imine functional groups. Few studies have been reported about the removal of toxic heavy metal ions by polyaniline (28,29). Unfortunately, polyaniline itself cannot be directly employed for the removal of heavy metals in fixed-bed or any other flow-through systems due to the excessive pressure drop resulting from its fine particle sizes. To obtain a cheap, highly-efficient and homogeneous adsorbent of excellent mechanical performance, support materials are required. These support materials must also be cheap and extensive. Several materials have been used to support polyaniline such as polystyrene (30), jute fiber (31), and sawdust (32). Wood sawdust, a solid waste product obtained from mechanical wood processing, can be used as an adsorbent of heavy metals directly. It has been used for the removal of heavy metals in fixed-bed and

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Address correspondence to Deli Liu, School of Municipal and Environmental Engineering, Harbin, China. Tel.: +86 631 5687037; Fax: +86 631 5687230. E-mail: rensiyan2004@126.com

flow-through systems, but its adsorption capacity is relatively low (33,34). Little attention has hitherto been paid to the adsorption of Cu(II) and Cd(II) by polyaniline. In this research, polyaniline was directly synthesized on the surface of sawdust for use as an adsorbent material. PANI/SD has better mechanical performance and can be directly employed for the removal of heavy metals in fixed-bed or any other flow-through systems.

The objective of the present study is to investigate the possible use of PANI/SD as an alternate adsorbent material for the removal of Cu(II) and Cd(II) ions from wastewater. The adsorption of Cu(II) and Cd(II) ions from solution was investigated using PANI/SD in batch mode. These tests were conducted to examine the effects of pH, temperature, metal ion concentration, and contact time. Emphasis was also given to the evaluation of adsorption isotherms, kinetics, thermodynamics, desorption, and regeneration of the adsorbent. The results show that PANI/SD has the better adsorbability to the Cu(II) and Cd(II) ions, and can be used as an effective adsorbent for the removal of metal ions from real wastewater.

## EXPERIMENTAL SECTION

### Materials

Commercial grade aniline was purified by distilling at its boiling point temperature, and the oxidizing agent ammonium peroxydisulfate was used as received. Solutions of Cu(II) and Cd(II) ions were prepared by dissolving weighed quantities of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ . All chemicals and reagents were of analytical grade. Deionized water was used for all dilutions and reagent preparations. Sawdust was obtained from the local timber processing plant. It was first washed to move dust and other contaminants before being dried at about 60°C. The pH of each test solution was adjusted to the required value with  $\text{H}_2\text{SO}_4$  or NaOH solutions prior to mixing with the adsorbent.

### Synthesis of Polymer on the Surface of the Sawdust

Polyaniline was synthesized by the traditional route using a 1:1 molar ratio of aniline to oxidizing agent in 1 M hydrochloric acid (35). Sawdust was added to acidic aniline solution in a quantity equal to aniline. Polymerization was then initiated by the addition of ammonium peroxydisulfate solution in 1 M hydrochloric acid under continuous stirring at room temperature. The insoluble precipitate was filtered and washed with water until the filtrate became colorless. The dark-green colored polyaniline containing sawdust was then dried at 50°C in an oven.

### Batch Adsorption Experiments

Batch adsorption experiments were performed to investigate the effects of different conditions (e.g., aqueous pH,

initial metal ion concentration, temperature, and adsorption time) on metal ion adsorption. PANI/SD was added to 100 mL solutions of Cu(II) and Cd(II) of varying concentration for adsorption experiments. Each experiment was conducted in an electric-heated, thermostatic water bath with magnetic stirring. After reaching equilibrium, the mixture was filtered, and the concentration of the filtrate was analyzed.

The amount of adsorption was calculated according to the difference of metal ion concentration before and after adsorption. The adsorption capacity ( $q_t$ , mg/g) and, the removal rate (R) were calculated according to the following equations:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$R = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (2)$$

where  $C_0$  and  $C_t$  are the concentration of metal ions (mg/L) initially and at time  $t$ , respectively. V is the initial volume of the solution (L), and m is the mass of PANI/SD (g) used in the experiment.

### Desorption and Regeneration Experiments

Initially, 100 mL samples, each containing 50 mg/L of Cu(II) or Cd(II) ions, were treated with 4 g/L of PANI/SD for 2 h at pH of 5.0. The mixture was then filtered, and the filtrate was analyzed to calculate the amount of metal ions adsorbed on the PANI/SD. The Cu(II) or Cd(II) loaded-adsorbent was washed with water before being treated with 100 mL of hydrochloric acid or nitric acid of varying concentration. After equilibrating by stirring for 2 h, this mixture was filtered. The collection and metal analysis of the filtrate was then carried out. Finally, the adsorbent was washed three times with water, and then dried for reuse. The adsorption-desorption process was conducted a total of five times. All experiments were performed in two sets, and average values were considered in the data analysis.

### Analytical Procedure

The specific surface area of sawdust is measured using BET surface area analyzer. The values for the specific surface area and pore diameter were  $1.06 \text{ m}^2 \text{ g}^{-1}$  and  $0.68 \mu\text{m}$ , respectively. The average particle diameter of sawdust was 1.85 mm.

The adsorbent was characterized by UV-visible spectroscopy and X-ray diffraction (XRD). The UV-visible characterization was performed with a NEWLABO 2200 UV-visible spectrophotometer using a cell of 1 cm optical path length. The spectrum was recorded in the wavelength range of 300–800 nm. The XRD patterns were recorded on

a XD-2 diffractometer with Cu K $\alpha$  operated at 30 kV and 20 mA. The scanning scope and scanning speed were 10°–90° and 2°/min, respectively. Metal ions were estimated by atomic absorption spectrometry (AA 370 mc China) operated with an air-acetylene flame.

## RESULTS AND DISCUSSIONS

### Characterizations of Adsorbent

PANI/SD was dissolved in N,N'-dimethylformamide solvent, and the UV-visible spectrum was recorded (Fig. 1). It can be seen that the polyaniline solution spectrum presents absorption bands at 635 and 330 nm, which are most predominant in the emeraldine salt form of polyaniline. These absorption bands are assigned to the charge transfer from benzenoid to quinoid rings and  $\pi$ – $\pi^*$  transitions, respectively (36). It can be concluded that the use of sawdust does not affect the synthesis of polyaniline.

The XRD spectra of PANI/SD are shown in Fig. 2. The XRD pattern obtained for PANI/SD containing cupric ions is not significantly different from that of PANI/SD without any metal ions. This indicates that the crystallinity of polyaniline is not significantly affected by the adsorbed metal ion.

### Effects of pH

Solution pH is an important parameter that affects the adsorption capacity for heavy metals. Adsorption of Cu(II) and Cd(II) on the sorbent was studied over the pH range of 1.0–8.0 with a constant PANI/SD amount of 1 g/L and metal ion concentration of 40 mg/L at 293 K. At the same time, sawdust was examined for the removal of Cu(II) and Cd(II) under the same conditions. Sawdust is principally made up of lignin, cellulose, hemicellulose, and carbohydrate. The functional groups present in the sawdust are

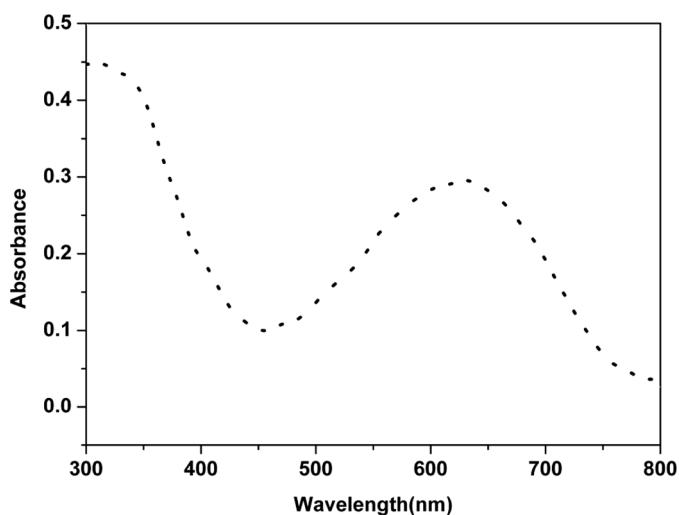


FIG. 1. UV spectra of PANI/SD.

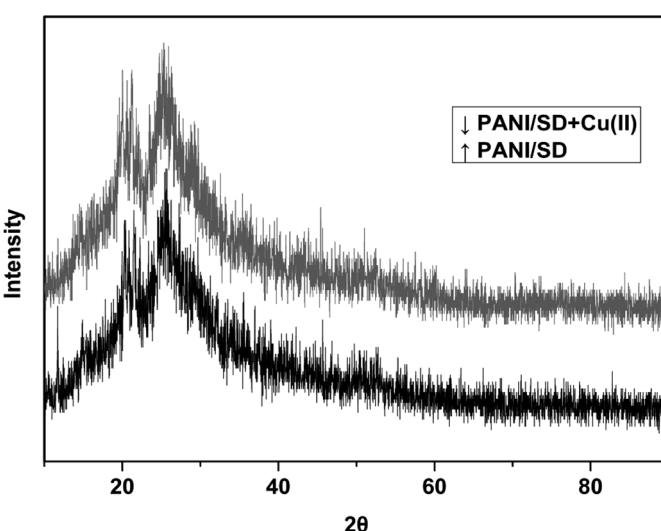


FIG. 2. XRD patterns of PANI/SD before and after interacting with Cu(II).

carbonyl, hydroxyl, and amino groups. These functional groups are likely to be the sites for adsorption (33). The influence of pH on adsorption behavior is illustrated in Fig. 3. The sawdust exhibited low metal ions removal at reaction pH range of 1.0–8.0. It can be understood that the adsorption of metal ions is mainly by polyaniline.

It can be easily seen that the removal ratio for Cu(II) and Cd(II) increased with the increase of solution pH with a maximum at pH 5.0. Increasing the solution pH above 6.0 caused the removal ratio to decrease. It is generally accepted in the literature that nitrogen atoms on polyaniline surfaces are responsible for metal ions adsorption (37). The mechanism of adsorption of Cu(II) and Cd(II)

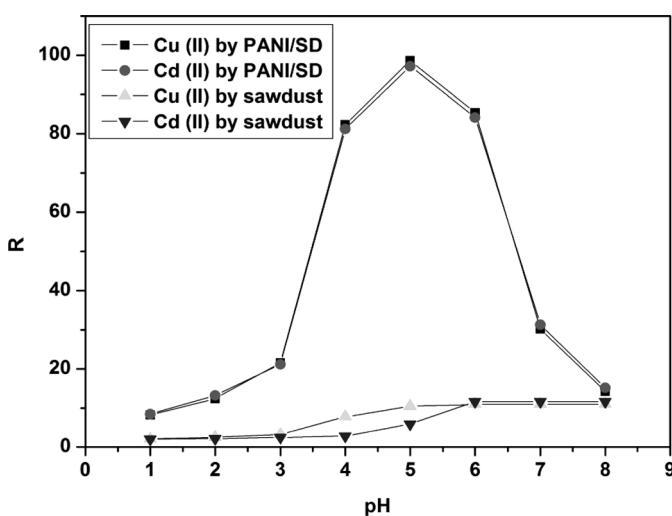
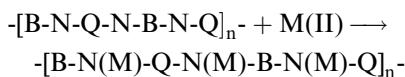


FIG. 3. Effect of pH on Cu(II) and Cd(II) removal (initial metal ion concentration of 40 mg/g, adsorbent amount of 1 g/L, adsorption time of 4 h).

on polyaniline may be as follows



where B are benzenoid rings, Q are quinoid, and M is Cu(II) or Cd(II). At lower pH values, the uptake of Cu(II) and Cd(II) ions was inhibited, and this can be attributed to the presence of  $H^+$  ions competing with the metal ions for the adsorption sites. When the pH was less than 4.0, nitrogen atoms of the imine functional groups in polyaniline were competitively bound by protons. These protons were released from the imine groups at higher pH values, which allowed the metal ions to have a higher affinity for the nitrogen-containing binding sites. In contrast, increasing pH values above 6.0 led to the replacement of hydrogen ions on the nitrogen atoms by hydroxyl; thus, the physicochemical properties of polyaniline were changed and the extent of adsorption decreased. Therefore, further experiments were carried out with initial pH values of 5.0 for Cu(II) and Cd(II). The adsorption of Cu(II) and Cd(II) on rice straw has been observed to be dependent on solution pH (1). The most adequate sorption pH was 5.0 for both Cu(II) and Cd(II). The optimum pH being above 4.0 was also reported in the removal of Cu(II) by poly(acrylamide)/attapulgite composite (38) and by poly(hydroxyethyl methacrylate) nanobeads (39).

### Effects of Initial Metal Ion Concentration and Adsorption Isotherm

To further characterize the adsorption behavior of Cu(II) and Cd(II) on PANI/SD, adsorption equilibrium experiments were conducted with 100 mL metal ions solutions of different concentrations (40 to 500 ppm) in the presence of 100 mg of PANI/SD at 293 K. Figure 4 shows the amount of Cu(II) and Cd(II) adsorbed on PANI/SD as a function of the equilibrium concentration of the metal ions in solution. The increase in the initial concentration of Cu(II) and Cd(II) from 40 to 500 mg/L, led to an increase in adsorption amount over a constant adsorption time (4 h). The sorption data obtained for various metal ion concentrations were analyzed using isotherm models given by the Freundlich isotherm equation and the Langmuir isotherm equation.

$$\text{Freundlich equation: } \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

$$\text{Langmuir equation: } \frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (4)$$

In these equations  $q_e$  and  $C_e$  are the amounts of the metal ions adsorbed (mg/g) and the concentration of solution at equilibrium, respectively.  $K_F$  and  $n$  are the Freundlich constants that indicate the adsorption capacity

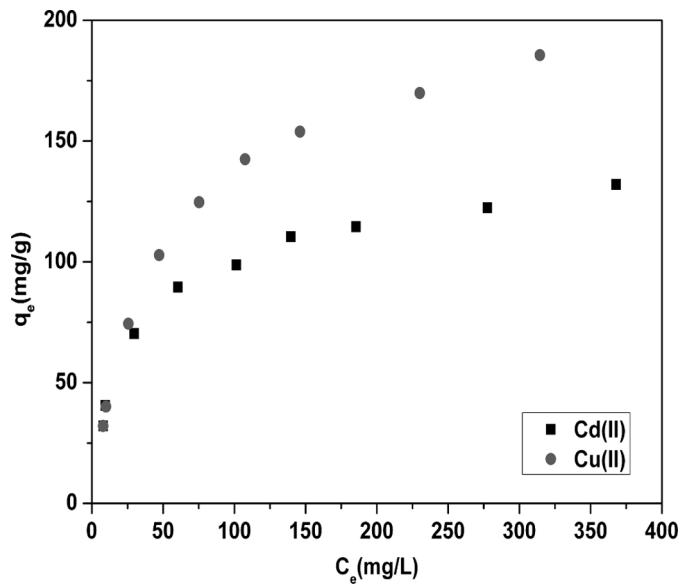


FIG. 4. Effect of initial concentration on metal ion uptake (temperature of 293 K, PANI/SD amount of 1 g/L, adsorption time of 4 h).

and the adsorption intensity, respectively. Under good adsorption conditions, the value of  $n$  is between 1 and 10. The parameter  $q_{\max}$  is the monolayer adsorbent capacity.  $K_L$  is the energy constant of adsorption.

The experimental data corresponding to Fig. 4 were fitted to Eq. (3) and Eq. (4). Parameters of the two models were calculated from the intercepts and slopes of  $C_e/q$  versus  $C_e$  and  $\log q_e$  versus  $\log C_e$  plots. The results are shown in Table 1.

To select the best fitting isotherm model, Chi square was calculated by the following equation:

$$\chi^2 = \sum \frac{(q_e - q_{\text{em}})^2}{q_{\text{em}}} \quad (5)$$

where  $q_e$  is the calculated amount of the metal ions adsorbed at equilibrium, and  $q_{\text{em}}$  is calculated using the isotherm models. Compared values of  $\chi^2$  and  $R^2$  for the two isotherms can be found in Table 1. The results indicate that the Langmuir model is best suited for the adsorption of Cu(II) and Cd(II) by PANI/SD. This model assumes that monolayer adsorption occurs, and it predicts the maximum mono-layer adsorption capacity of the adsorbent (40). A dimensionless separation factor, as defined in Eq. (6), is required for the model to indicate the favorability of adsorption.

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

Other researchers (41) have shown that  $R_L$  indicates the shape of the isotherm itself, and that a value of  $R_L < 1$  represents favorable adsorption conditions. Because the

TABLE 1  
Regression data of isotherm models

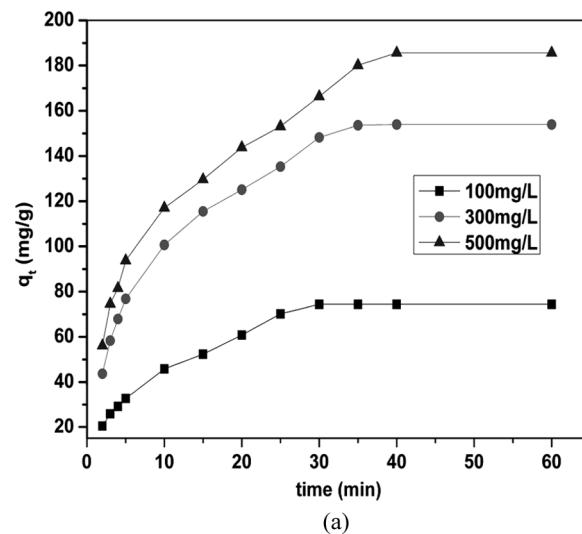
Metal ions	Frendlich				Langmuir			
	K <sub>F</sub> (mg/g)	n	R <sup>2</sup>	x <sup>2</sup>	q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	x <sup>2</sup>
Cu(II)	14.29	2.11	0.962	13.55	208.77	0.021	0.998	0.97
Cd(II)	18.59	2.86	0.953	7.14	136.05	0.032	0.996	4.18

value of  $K_L$  is positive, the values of  $R_L$  are all less than 1. The  $R_L$  values for the adsorption of Cu(II) and Cd(II) were 0.54 and 0.44 respectively at an initial concentration of 40 mg/L whereas the values were 0.09 and 0.06 respectively at an initial concentration of 500 mg/L. The values of  $q_{max}$ , estimated to be 208.77 mg/g for Cu(II) and 136.05 mg/g for Cd(II) adsorption, match well with experimental values. All these indicate that the Langmuir isotherm model is able to provide a better fit to the experimental data than the Freundlich isotherm model. In a previous study, the adsorption of Cu(II) ions from aqueous solution by recycled tire rubber (42) was found to follow the Langmuir adsorption equation. The Cu(II) and Cd(II) maximum adsorption capacity by PANI/SD in present study is compared with the adsorption capacities for some adsorbents reported in the literature (Table 2).

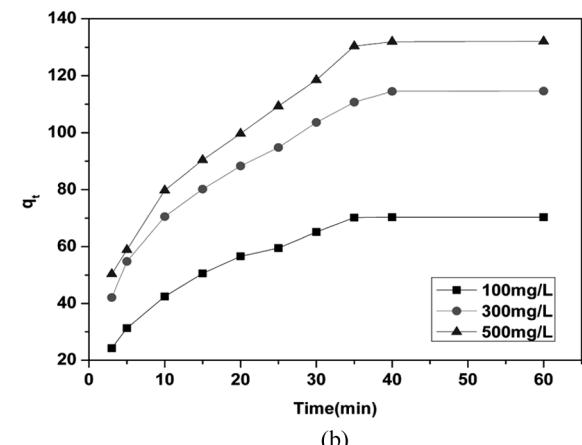
### Effects of Time and Adsorption Kinetics

The adsorption of Cu(II) and Cd(II) on PANI/SD was studied as a function of time, and the removal trends are shown in Figs. 5a and 5b. It can be seen from Figs. 5a and 5b that the  $q_t$  of Cu(II) and Cd(II) increased up to about 40 min, and without further change with the increase of contact time, attained an equilibrium state. The results

indicate that the amount adsorbed at equilibrium increased from 34.5 mg/g to 185.6 mg/g for Cu(II) and 32.1 mg/g to 132.1 mg/g for Cd(II) with a range of metal ion concentration varying from 100 mg/L to 500 mg/L. The results also show that Cu(II) was adsorbed in higher amounts than Cd(II) at the same initial metal ion concentration and contact time. The difference was enlarged by increasing the initial metal ion concentration. For example, 74.4 mg/g



(a)



(b)

FIG. 5. Effect of adsorption time on (a) Cu(II) adsorption by PANI/SD, (b) Cd(II) adsorption by PANI/SD (PANI/SD amount of 1 g/L, temperature of 293 K).

TABLE 2  
Cu(II) and Cd(II) adsorption capacities for some adsorbents reported in the literature

Adsorbent	Adsorption capacity (mg/g)		
	Cu(II)	Cd(II)	Ref.
Present Study	208.77	136.05	
Citrus <i>reticulata</i> waste biomass	87.75		15
Titanate nanotubes	120		17
Peanut hull	21.25		18
Banana peels		5.71	19
Bark modified by Fenton	55.25	35.34	20
Saw dust		26.73	21
Hydrogels	100.86	134.66	23
Magnetic hydrogels	105.61	130.96	23

of Cu(II) and 70.3 mg/g of Cd(II) were adsorbed at a concentration of 100 mg/L, and 185.6 mg/g Cu(II) and 132.1 mg/g Cd(II) were adsorbed at a concentration of 500 mg/L.

To analyze the kinetics and the rate of adsorption of Cu(II) and Cd(II) by PANI/SD, experimental data (Figs. 5a and 5b) were further treated with Lagergren's pseudo-first order kinetic model (Eq. (7)) and the pseudo-second-order kinetic model (Eq. (8)).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Where  $q_e$  and  $q_t$  are the amount of metal ions adsorbed on PANI/SD at equilibrium and time  $t$ , respectively,  $k_1$  and  $k_2$  are the first and second model constants. The values of reaction rates and correlation coefficient are shown in Table 3.

As shown in Table 3, the values of  $R^2$  for the two kinetic models are all satisfactory ( $>0.97$ ). The data were further analyzed with the Chi-square test to indentify the appropriate kinetic model as shown in Eq (9).

$$\chi^2 = \sum \frac{(q_t - q_{tm})^2}{q_{tm}} \quad (9)$$

Here  $q_t$  and  $q_{tm}$  (m/ g) are experimental and calculated values according to the kinetic model at time  $t$ , respectively. It was found that the values of  $\chi^2$  for the pseudo first-order and second-order kinetic models were similar. However, there was a large difference for  $q_e$  between the experimental value and the calculated one according to the first-order kinetic model. The calculated  $q_e$  value agreed with the experimental data in the case of the second-order equation.

This suggested that the adsorption data were well represented by pseudo second-order kinetics. This has also been reported for Cu(II) and Cd(II) adsorption by Hao Chen (43) and Naiya (44).

### Effects of Temperature and the Thermodynamics of Adsorption

Temperature can affect the process of metal ion removal. Experiments were performed under different temperatures (ranging from 293 K to 333 K) to examine the effect of temperature on adsorption by PANI/SD. Adsorption of metal ions increased as the temperature increased from 298 to 328 K, and the adsorbed amount increased from 74.4 mg/g to 86.5 mg/g for Cu(II) and from 70.3 mg/g to 80.7 mg/g for Cd(II). The Gibbs free energy change ( $\Delta G^\circ$ ) is the fundamental criterion of spontaneity of a process and can be determined using the equilibrium constant as below:

$$\Delta G^\circ = -RT\ln K \quad (10)$$

The change in enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) associated with the adsorption process were calculated by the following equation.

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

Here,  $R$  (8.3145 J/mol · K) is the ideal gas constant, and  $T$  (K) is the temperature.  $K$  ( $q_e/c_e$ ) is the distribution coefficient. According to Eq. (11),  $\Delta H^\circ$  and  $\Delta S^\circ$  parameters can be calculated from the linear plot of  $\ln K$  versus  $1/T$  (shown in Fig. 6), and the results are shown in Table 4. The free energy change ( $\Delta G^\circ$ ) can be determined from Eq. (12).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

TABLE 3  
Kinetic parameters for the adsorption of Cu(II) and Cd(II) on PANI/SD

Metal ions	mg/L	First-order kinetic model				Experimental value	Second-order kinetic model					
		$q_e$ (mg/g)	$k_1$ (min <sup>-1</sup> )	$R^2$	$x^2$		$q_e$ (mg/g)	$q_e$ (mg/g)	$k_2$ (g/mg. min)	$R^2$		
Cu	100	61.02	0.073	0.994	0.198	0.019	74.4	77.28	$2.04 \times 10^{-3}$	0.990	0.506	0.010
	300	117.45	0.073	0.974	1.923	0.024	153.9	162.34	$1.09 \times 10^{-3}$	0.998	0.328	0.003
	500	134.80	0.061	0.986	2.626	0.035	182.4	186.92	$1.02 \times 10^{-3}$	0.993	2.381	0.005
Cd	100	54.74	0.067	0.996	0.185	0.017	70.3	75.76	$1.87 \times 10^{-3}$	0.996	0.223	0.008
	300	86.98	0.064	0.981	1.393	0.043	114.6	121.40	$1.26 \times 10^{-3}$	0.991	1.153	0.009
	500	101.89	0.063	0.984	2.443	0.039	132.1	139.90	$1.03 \times 10^{-3}$	0.987	2.383	0.009

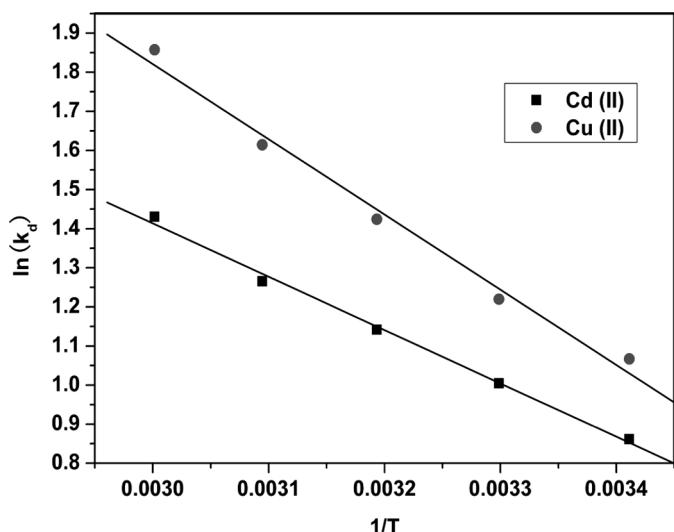


FIG. 6. Effect of temperature (initial ion concentration of 50 mg/L, PANI/SD amount of 1 g/L, adsorption time of 40 min).

The value of  $\Delta H^\circ$  for Cu(II) is 15.99 kJ/mol and 11.34 kJ/mol for Cd(II). These values show that the adsorption processes for both ions are endothermic in nature. Similar findings were observed during the adsorption of mercury ions onto a composite of polyaniline with polystyrene (30). The positive value of entropy change ( $\Delta S^\circ$ ) shows the increased randomness at the solid/solution interface during the adsorption of Cu(II) and Cd(II) on PANI/SD. The free energy change ( $\Delta G^\circ$ ) of the process decreases with an increase in temperature. The values of  $\Delta G^\circ$  at all

temperature are negative for both ions. It can therefore be concluded that the adsorption process is spontaneous and that spontaneity increases with the rise in temperature.

### Desorption and Regeneration

The recovery of metal ions from the loaded adsorbent is necessary for disposal as well as for the reuse of the adsorbent. After adsorption of the metals on PANI/SD, the adsorbent was washed with water. Then, the adsorbent was treated with 100 mL of water over a period of 24 h. The mixture was filtered, and the concentration of the filtrate was analyzed for any leaching of metal ions. It was found that no metal ions were released from the adsorbent. The loaded adsorbent was treated with 100 mL of hydrochloric acid or nitric acid at various concentrations. The final metal ion concentration in the filtrate was analyzed for metals desorbed. The desorption ratio was calculated from the amount of metal ions adsorbed on the PANI/SD and the final metal ion concentration in the desorption medium. The results are shown in Table 5.

It can be clearly observed from Table 5 that the desorption ratio increases slightly with the increase of acid concentration. The desorption ratio is sufficiently high for the 2 M hydrochloric acid, yet desorption itself is still incomplete even at this concentration. This can be explained by the formation of chemical bonds between the metal ions and the nitrogen atoms of polyaniline.

Five successive cycles of adsorption and desorption of the test metals were carried out in a batch system to assess the reusability of PANI/SD for metal adsorption. The results are shown in Fig. 7. The percentage of adsorption

TABLE 4  
Thermodynamic parameters for the adsorption of Cd(II) and Cu(II) at different temperatures

Metal ions	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol · K)	$\Delta G^\circ$ (kJ/mol)				
			293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
Cu(II)	15.99	0.063	-2.51	-3.14	-3.77	-4.40	-5.03
Cd(II)	11.34	0.046	-2.08	-2.54	-2.99	-3.45	-3.91

TABLE 5  
Desorption of Cu(II) and Cd(II) by desorbing agent

Metal agent	Concentration	Ratio (%)			
		0.5 M	1 M	1.5 M	2 M
Cu(II)	HCl	78.5	85.3	92.6	95.4
	HNO <sub>3</sub>	50.2	63.3	70.4	78.1
Cd(II)	HCl	79.1	87.6	94.3	96.2
	HNO <sub>3</sub>	54.6	65.7	73.2	79.6

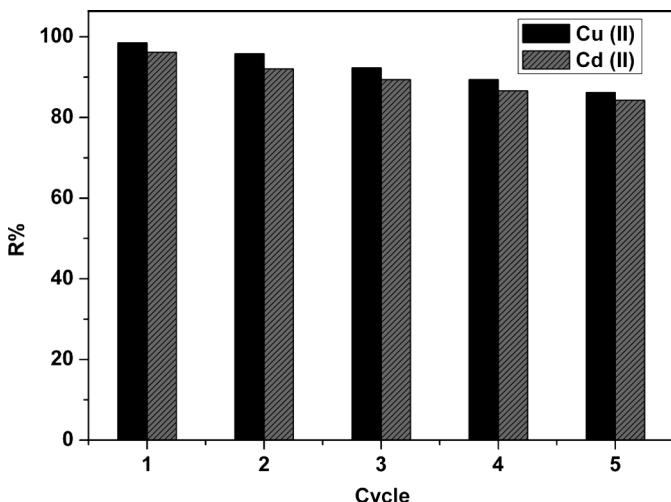


FIG. 7. Effect of cycle times (initial ion concentration of 50 mg/L, PANI/SD amount of 4 g/L, and adsorption time of 40 min).

of the recycled adsorbent was 98.5% and 96.2% at the first cycle for Cu(II) and Cd(II), respectively. After five adsorption–desorption cycles, the adsorption of Cu(II) and Cd(II) decreased by 11.3% and 10.2%. The results indicate that PANI/SD is an effective and recyclable adsorbent for the removal of Cu(II) and Cd(II) ions.

## CONCLUSION

In this study, polyaniline was synthesized on the surface of sawdust, and this material was used as an adsorbent for removing Cu(II) and Cd(II) metal ions from aqueous solutions. The uptake process follows a second-order rate law and obeys the Langmuir isotherm model. With the rise in reaction temperature, Cu(II) and Cd(II) adsorption increased, which indicated that adsorption is endothermic in nature. The maximum monolayer adsorption capacities obtained from the Langmuir isotherm model are 208.77 mg/g and 136.05 mg/g for Cu(II) and Cd(II), respectively, at pH 5.0 and a temperature of 293 K. Experimental studies show that PANI/SD can be used as an effective material to remove high amounts of toxic Cu(II) and Cd(II) ions from waste water.

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