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Adsorption of Cu(II) and Cr(VI) onto Treated *Shorea dasyphylla* Bark: Isotherm, Kinetics, and Thermodynamic Studies

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The efficacy of treated *Shorea dasyphylla* bark for Cu(II) and Cr(VI) adsorption was assessed in a batch adsorption system as a function of pH, agitation period, and initial metal concentration. The equilibrium nature of Cu(II) and Cr(VI) adsorption was described by the Freundlich, Langmuir, and Dubinin-Radushkevich isotherms. The maximum monolayer capacities of treated *Shorea dasyphylla* bark, estimated from the Langmuir equation were 184.66 and 42.72 mg/g for Cu(II) and Cr(VI), respectively. The experimental results were fitted using pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models; the pseudo-second order showed the best conformity to the kinetic data. Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) were determined by applying the Van't Hoff equation. The adsorption of Cu(II) and Cr(VI) onto treated *Shorea dasyphylla* bark was found to be spontaneous and exothermic. The adsorption mechanism was confirmed by means of Fourier transform infrared (FTIR) and Energy dispersive X-ray (EDX) spectroscopy. The dimensionless constant separation factor (R_L), indicated that treated *Shorea dasyphylla* bark was favorable for Cu(II) and Cr(VI) adsorption.

Keywords adsorption; isotherm; kinetics; remediation; thermodynamic; treated bark

INTRODUCTION

Heavy metals are ubiquitous contaminants in the aqueous environment and have increased tremendously due to rapid global industrialization. Water pollution by heavy metals has received serious attention because unlike organic pollutants, which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (1). Copper is introduced into streams by several industries, such as plating, fertilizer, paints and pigments, wood and leather preservatives, refineries, paper and pulp. Excessive intake of copper by humans (more than 1.0 mg/L in drinking water) may lead to severe mucosal irritation, central nervous system irritation, necrotic changes in the liver and kidney, and gastrointestinal disease (2). In aqueous solutions, chromium is generally present in oxidation states ranging from Cr^{2+} to Cr^{6+}. Cr(III) is regarded as an essential micronutrient for organisms and plants, whereas Cr(VI) is known to be toxic even at low concentrations. The major detrimental effects of high levels of Cr(VI) to human health are kidney damage, chronic ulceration, perforation of the nasal septum and asthma (3). Potential primary sources of chromium in industrial effluents are leather tanning, electroplating, dyeing, steel fabrication, paints, textile, cement, and photography industries. The recommended limit of Cr(VI) in potable water is only 0.05 mg/L (4). Thus, treatment of the effluents to reduce or remove unwanted contaminants before discharging into the environment becomes important and inevitable.

Numerous low-cost adsorbents such as coir pith (5), sissoo wood sawdust (6), rubber (*Hevea brasiliensis*) leaf (7), peanut shell pellets (8), grape stalk (9), maize leaf (10), and papaya wood (11) have been used for both heavy metal (12,13) and organic compound (14,15) removal. Adsorption of heavy metals and organic compounds by agricultural waste materials has been attributed to their proteins, carbohydrates, and phenolic compounds containing carboxyl, hydroxyl, sulfate, phosphate, and amino groups that can bind metal ions and organic compounds (16). However, pretreatment of agricultural waste is essential in order to enhance the adsorption capacity as well as the chelating efficiency (17). In Malaysia, bark is a waste by-product of the timber industry and abundantly available at very low economic value. The use of bark in water treatment converts the agricultural waste into a cost-effective adsorbent and reduces the cost of residues disposal.

The overall goal of this work was to evaluate the potential of untreated and treated *Shorea dasyphylla* bark to

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remove Cu(II) and Cr(VI) from aqueous solution. In this study, an attempt to modify raw *Shorea dasyphylla* bark with an inexpensive and simple method by using hydrochloric acid and sodium hydroxide was investigated. This study not only provides information on adsorption behavior, but also on the interaction between heavy metal ions and *Shorea dasyphylla* bark. Information on adsorption behavior and mechanisms are very crucial in the treatment of metal laden effluents.

EXPERIMENTAL

Preparation of Adsorbent

Shorea dasyphylla bark was supplied by Hong Huat Sawmill, Butterworth, Penang. Bark was rinsed thoroughly with distilled deionized water to remove dirt adhered on the surface, and finally dried at 70°C for 6 h. After drying, the bark was crushed and sieved through 150–250 µm size fraction using an American Society for Testing and Materials (ASTM) standard sieve.

Treatment and Physical Characterization of Adsorbent

The dried dark was treated with 0.5 M HCl in the ratio 1:2 (w/v), heated to a temperature 60°C for 2 h, and stirred continuously using a magnetic stirrer. After 2 h, the reacted mass was allowed to cool and the NaOH solution was added to neutralize the acid. The mass was then filtered under vacuum and rinsed with distilled deionized water until the washings were free from alkalinity. The wet mass was dried in an oven at 70°C for 6 h. The lumps were crushed and sieved through 150–250 µm size fraction ASTM standard sieve. The resulting powdered materials were used as the adsorbents for Cu(II) and Cr(VI) removal.

Some physical and chemical properties of untreated and treated *Shorea dasyphylla* bark were characterized using FTIR, SEM, EDX, and BET surface area analyses. FTIR spectra were recorded on a Perkin-Elmer System 1600 FTIR spectrophotometer using a KBr disc technique. SEM images and EDX elemental data of the adsorbent were obtained using a scanning electron microscope equipped with energy dispersive X-ray spectroscopy (Leica Cambridge S360). Surface area and average pore diameter analyses were carried out on a Micromeritics ASAP 2010 gas adsorption surface analyzer according to the Brunauer, Emmett, and Teller (BET) multipoint technique. In this study, the pH of the zero point of charge (pH_{zpc}) of adsorbents was determined by the acid-base titration approach outlined by Huang and Ostovic (18) and Jha et al. (19). The characteristics of the raw and treated adsorbents are given in Table 1.

TABLE 1
Physical characteristics of *Shorea dasyphylla* bark

Physical properties	Untreated	Treated
Color	Dark reddish-brown	Light brown
Moisture content (%)	8.25	6.47
Ash content (%)	4.31	3.92
Bulk density (g/cm^3)	0.83	1.59
BET surface area (m^2/g)	9.42	28.86
Average pore diameter (Å)	1.87	7.39
Cation exchange capacity (meq/g)	14.38	21.28
Surface charge density (meq m^2)	1.53	0.74

Preparation of Adsorbate Solutions

Analytical grade of $CuCl_2 \cdot 2H_2O$ and $K_2Cr_2O_7$ salts were acquired from Fluka. Salts were dissolved in distilled deionized water to prepare 1000 mg/L stock solutions. The solutions were further diluted to the required concentrations before use.

Batch Adsorption and Desorption Experiments

Isotherm studies were carried out by suspending 500 mg of adsorbent in 50 mL of each of the metal ion solutions of desired concentration at optimum conditions. At the end of the predetermined time interval, the adsorbent was removed by filtration. The equilibrated metal concentration in the supernatant was measured by means of a Perkin-Elmer 3100 atomic absorption spectrophotometer.

To study the effect of pH, the pH of the adsorption system was varied between 1.0 and 8.0 using either 0.1 mol/L HCl or 0.1 mol/L NaOH. The effect of time was conducted by contacting 500 mg of adsorbent with 50 mL of 200 mg/L metal ion solutions at room temperature. The suspensions were stirred at a constant speed of 150 rpm for a period of time (between 5 and 180 min). The effect of initial metal ion concentration on adsorption was studied by placing 500 mg of adsorbent in contact with metal ion solutions of concentrations ranging between 50 and 500 mg/L, pH adjusted to 6.0 and 3.0 for Cu(II) and Cr(VI) respectively. The effect of temperature on Pb(II) and Cu(II) adsorption was performed by agitating 500 mg of adsorbent with 50 mL of 200 mg/L metal ion solution at a range of temperatures (300, 310 and 320 K).

The adsorption capacity, q_e (mg/g) (20) was estimated according to Eq. (1):

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where, C_o and C_e (mg/L) are the initial and final or equilibrium Cu(II) and Cr(VI) concentration, respectively.

V (mL) is the volume of the metal solution, and W (mg) is the weight of adsorbent.

In each experiment, metal and adsorbent free blanks were run as controls. Each adsorption and desorption experiment was performed in triplicate and the mean values are presented in this work. The error obtained was ±3%.

RESULTS AND DISCUSSION

Effect of pH

The amount of Cu(II) and Cr(VI) removed by untreated and treated bark as a function of pH is shown in Fig. 1. The adsorption of Cu(II) increased with increasing pH of the solution. This can be explained by the fact that in acidic medium, more H^+ ions are available to compete with Cu(II) ions for the adsorption sites of the adsorbents. However, the adsorption of Cu(II) ions increased at higher pH values and this was due to the weak inhibitory effect of H^+ ions. It was observed that Cu(II) precipitation occurred simultaneously at pH values higher than 7.0. Therefore, pH 6.0 was chosen as the optimum pH for the adsorption of Cu(II) ions to avoid the formation of Cu(II) hydroxide which will affect the adsorption by adsorbents.

In contrast to Cu(II) adsorption, the adsorption of Cr(VI) increased with an increase in the pH of the solution until an optimum point was reached at about pH 3.0. A gradual drop in the adsorption capacity was observed after pH 3.0 and might be attributed to the weak electrostatic force attraction between the oppositely charged adsorbate and adsorbent. Cr(VI) exists in anionic forms in aqueous solution as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, and $HCr_2O_7^-$; depending on chromium concentration and pH. The adsorption of Cr(VI) ions on bark is dependent on the stability and affinity of the Cr(VI) species. At low concentrations with pH values between 2.0 and 4.0, the main fraction is $HCrO_4^-$, whereas the CrO_4^{2-} species increases with an increase in pH value and becomes the main form at a pH value above 7.0 (21). These anions can interact effectively with functional groups of the adsorbent at low pH because the adsorption surfaces are highly protonated in the acidic medium. As the pH increased beyond 6.0, a significant decrease in adsorption capacity of Cr(VI) was observed. This was due to the competition between OH^- and CrO_4^{2-} ions for adsorption sites.

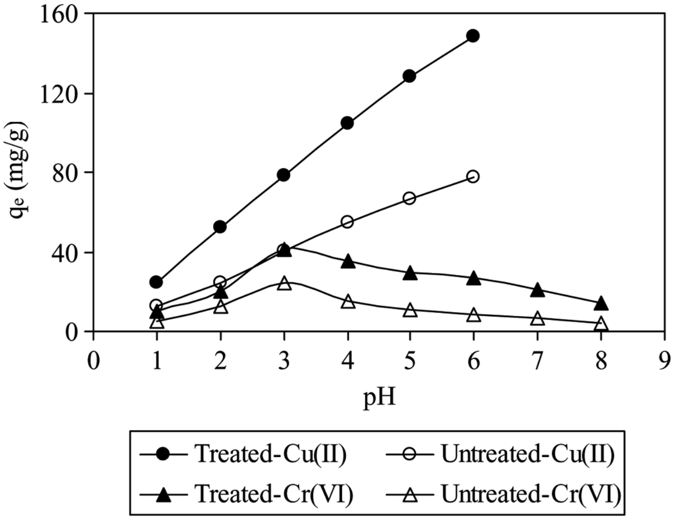


FIG. 1. Effect of pH on the adsorption of Cu(II) and Cr(VI) on bark.

The pH of the zero point of charge (pH_{zpc}) describes the behavior and ability of a substrate to adsorb pollutants from aqueous environment. According to Mall et al. (22), adsorption of cations is favored at $pH > pH_{zpc}$, while the adsorption of anions is favored at $pH < pH_{zpc}$. In this study, pH_{zpc} obtained for untreated and treated bark are 5.1 and 4.2, respectively. As can be seen from Fig. 1, the maximum adsorption of Cu(II) and Cr(VI) onto untreated and treated bark was at pH 6.0 (higher than pH_{zpc} value) and 3.0 (lower than pH_{zpc} value), respectively.

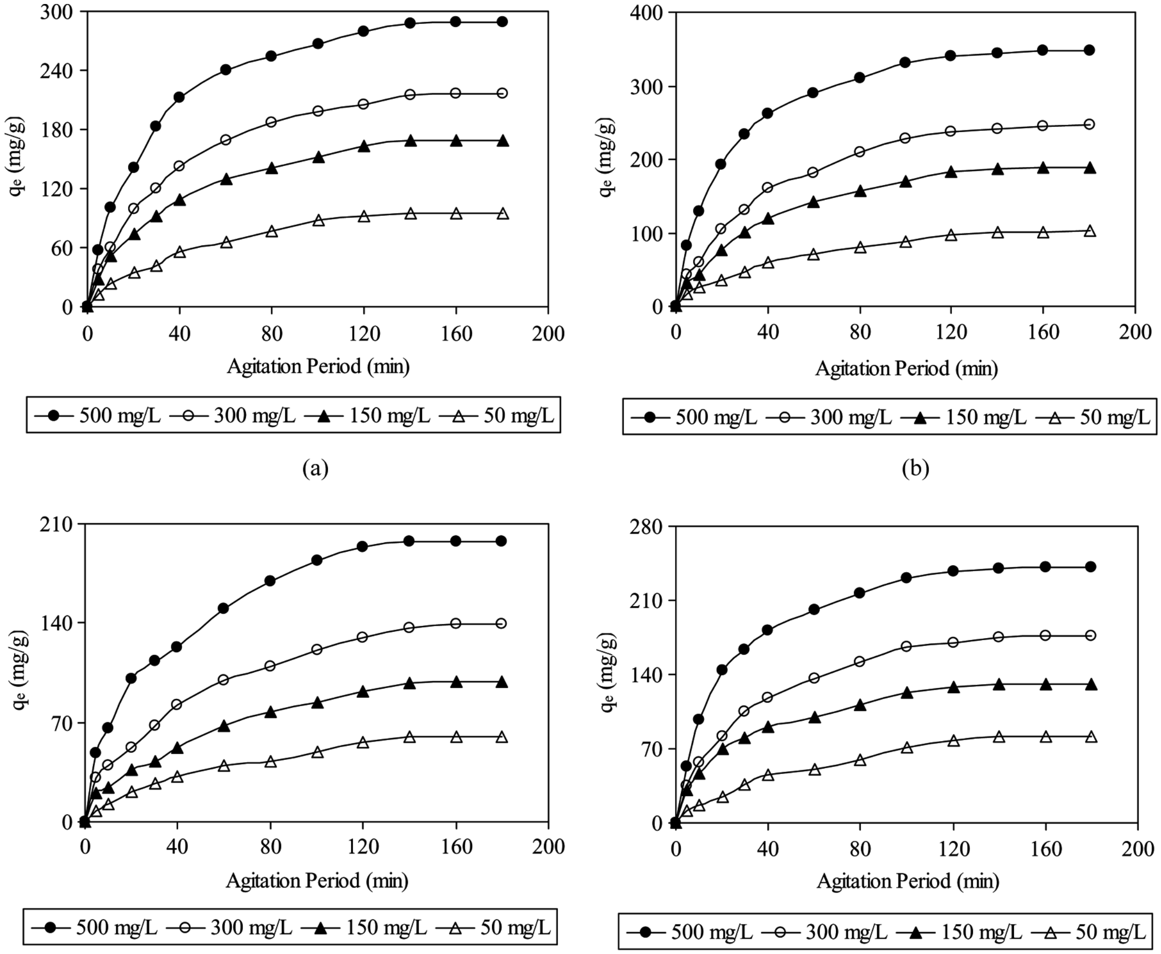
Effect of Initial Concentration and Agitation Period

The effect of initial metal concentration and agitation period on the adsorption of Cu(II) and Cr(VI) are shown in Figs. 2(a–d). It was seen that the absolute amount of metal ions removed by untreated and treated bark increased with increasing initial metal concentration. A higher initial metal concentration not only enhances the probability of collision between metal ions and the adsorbent surface, but also accelerates the diffusion of metal ions onto adsorbents. Thus, an increase in the initial metal concentration results in an increased driving force and reduces the mass transfer resistance (23). The typical form of saturation curves (Fig. 2), reveal that the kinetics of Cu(II) and Cr(VI) adsorption mainly consist of two stages—an initial rapid stage and a slower gradual adsorption stage. The high adsorption rate during the initial period of the removal process is due to the number of available adsorption sites on the bare surface of adsorbents. As these sites became progressively covered, the rate of adsorption decreases. Treated bark attained equilibrium in a shorter period of time (120 min) than untreated bark (140 min). This might be due to its better surface characteristics, such as surface area and morphology as compared to untreated bark.

Adsorption Equilibrium Isotherm

Equilibrium adsorption isotherm describes the interactive behavior between adsorbate and adsorbent. In this study, the Freundlich, Langmuir, and Dubinin-Radushkevich isotherm models were used to describe equilibrium adsorption isotherms.

The Freundlich expression is an empirical model based on adsorption onto a heterogeneous surface. The



(a) (b) (c) (d)

FIG. 2. (a) Effect of agitation period and initial concentration on the adsorption of Cu(II) on untreated bark; (b) Effect of agitation period and initial concentration on the adsorption of Cu(II) on treated bark; (c) Effect of agitation period and initial concentration on the adsorption of Cr(VI) on untreated bark; (d) Effect of agitation period and initial concentration on the adsorption of Cr(VI) on treated bark.

linearized form of the Freundlich isotherm (24) is given by Eq. (3):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (2)$$

where, q_e (mg/g) is the amount of Cu(II) or Cr(VI) adsorbed per unit weight of untreated and treated bark at equilibrium concentration, C_e (mg/L) is the equilibrium concentration of Cu(II) or Cr(VI), K_F (mg/g) is the maximum adsorption capacity, and n is the Freundlich constant indicating adsorption intensity. According to theory, adsorption conditions can be considered favorable if the n value, is higher than 1.

The Langmuir equation initially derived from kinetic studies, was based on the assumption that on the adsorbent surface there is a definite and energetically equivalent number of adsorption sites. The binding of adsorbates to the adsorption sites can be either chemical or physical, but it must be sufficiently strong to prevent displacement of adsorbed adsorbates on neighboring sites (25). The most widely used Langmuir equation (26), which is valid for monolayer sorption on to a surface with a finite number of identical sites and is rendered as Eq. (4):

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \qquad (3)$$

where, Q (mg/g) is the maximum adsorption at monolayer, C_e (mg/L) is the equilibrium concentration of Cu(II) or Cr(VI). q_e (mg/g) is the amount of Cu(II) or Cr(VI) adsorbed per unit weight of untreated and treated bark at equilibrium concentration. b (mL/mg) is the Langmuir constant related to the affinity of binding sites and is a measure of the energy of adsorption. As shown in Fig. 3, there was a gradual increase of adsorption of Cu(II) and

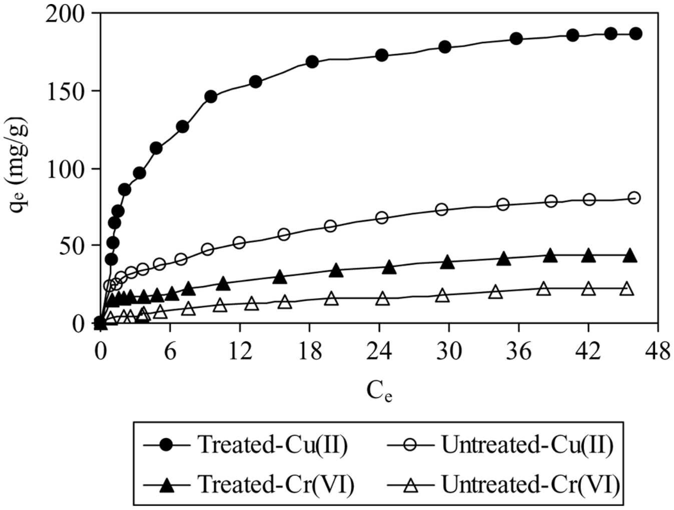


FIG. 3. Adsorption isotherms of Cu(II) and Cr(VI) on bark.

Cr(VI) until equilibrium was attained at about 45 mg/L for the bark.

The Dubinin-Radushkevich equation (27) is expressed as Eq. (4):

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{4}$$

where, ε (Polanyi potential) is equal to $RT\ln(1 + 1/C_e)$, q_m (mg/g) is the maximum adsorption capacity, K is related to the mean free adsorption energy per molecule of adsorbate, E (kJ/mol). E provides information about chemical and physical adsorption, and can be determined according to Eq. (5).

$$E = \frac{1}{\sqrt{-2K}} \tag{5}$$

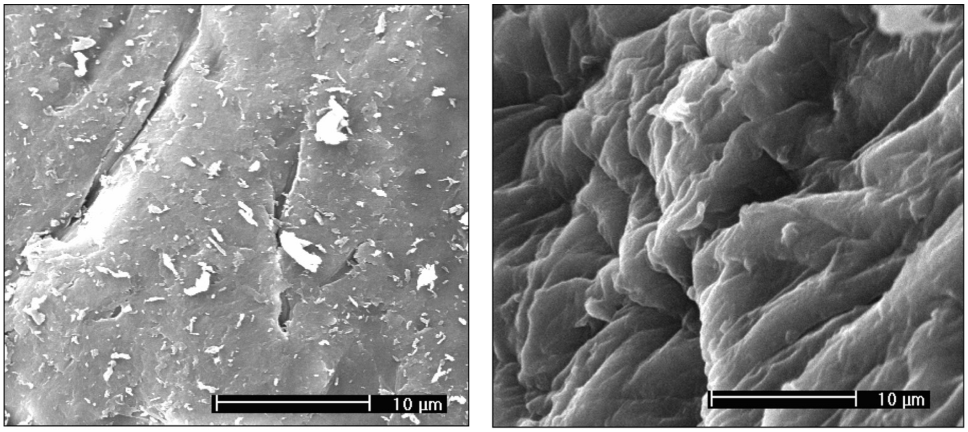
The calculated results of the Freundlich, Langmuir, and Dubinin-Radushkevich isotherm constants are given in Table 2. As presented in Table 2, the E values of the Dubinin-Radushkevich isotherm obtained lie between 8 and 16 kJ/mol indicating that the ion exchange mechanism governs the Cu(II) and Cr(VI) ion uptake (28). The adsorption of Cu(II) and Cr(VI) on untreated and treated *Shorea dasyphylla* bark were correlated well ($R > 0.99$) with the Langmuir isotherm model. Based on the Langmuir equation, the Q_{max} of Cu(II) by natural and treated bark was 75.18 and 184.66 mg/g, while 18.95 and 42.72 mg/g of Cr(VI) adsorbed onto natural and treated bark, respectively. The maximum adsorption capacity for treated bark was comparatively higher than untreated bark. The improvement in adsorption capacity may be owing to the change of surface properties after chemical treatment. Based on Table 1, it can be seen that BET surface area and average pore diameter of bark increased about 3–4 times after treatment. There is a significant difference in surface morphology of the two forms of bark as depicted in Fig. 4. A striking feature of this image is the appearance of rough and groove texture on the surface of the treated bark. Presumably, this propitious feature offers more adsorption sites for adsorbates.

It was found that the concentration of Cu(II) adsorbed onto both adsorbents was comparatively higher than that computed for Cr(VI). According to Tarley and Arruda (29), ionic radius affects metal ion adsorption onto adsorbents, where ions with a greater ionic radius are preferentially adsorbed. The higher adsorption of Cu(II) as compared to Cr(VI) on adsorbents could be due to the greater ionic radius of Cu(II) relative to Cr(VI), 0.73 and 0.44 Å, respectively. In addition, the higher adsorption capacity for Cu(II) ions could also be related to the stronger attraction due to the higher electronegativity (30). The electronegativity values for Cu(II) and Cr(VI) are 1.90 and 1.66, respectively, thus corroborating the adsorption profile of these metal ions.

This was further proved by results obtained from EDX analysis. The EDX elemental analysis data of natural and treated bark after Cu(II) and Cr(VI) adsorption are presented in Table 3. The EDX microanalysis revealed the appearance of carbon, calcium, oxygen, sodium, magnesium, and silica at the energy values of 0.277, 0.341, 3.690, 0.525, 1.041, 1.253, and 1.739 KeV. Carbon, calcium, oxygen, sodium, magnesium, and silica are the major constituents on bark. About 2–7% of Au M_α and Au L_α were detected at 2.121 and 9.712 KeV. In this study, samples

TABLE 2
Langmuir, Freundlich, and Dubinin-Radushkevich isotherm constants and correlation coefficients

		Freundlich			Langmuir			Dubinin-Radushkevich		
Ion	Bark	K_F (mg/g)	n	R	Q (mg/g)	b (mL/mg)	R	q_m (mg/g)	E (kJ/mol)	R
Cu(II)	Untreated	88.16	4.85	0.8522	75.18	835	0.9991	70.57	9.28	0.8476
	Treated	143.91	2.33	0.9584	184.66	1172	0.9987	137.16	9.93	0.8524
Cr(VI)	Untreated	35.26	8.99	0.8827	18.95	252	0.9989	12.75	11.27	0.9743
	Treated	68.71	6.74	0.9731	42.72	594	0.9992	32.56	13.04	0.9855



(a) (b)

FIG. 4. SEM images of (a) untreated and (b) treated *Shorea dasyphylla* bark at 2500X.

were coated with gold to prevent charging and to increase electric conduction. Exposure to copper solution has resulted in the presence of two energy lines of copper, namely Cu L_α and Cu K_α at the energy values of 0.930 and 8.040 KeV, respectively. Interaction with copper solution led to the presence of Cl K_α at 2.621 KeV. This observation may be due to the deposition of chloride ions during the contact with $CuCl_2 \cdot 2H_2O$ solution. In contrast to copper, only one energy line related to Cr K_α was detected at 5.411 KeV after Cr(VI) adsorption, while another two energy lines appeared at 0.294 and 3.312 KeV represent K L_α and K K_α deposited from $K_2Cr_2O_7$ solution. As presented in Table 3, the total weight percentage for Cu is relatively higher than Cr, suggesting that Cu was adsorbed in preference to that of Cr.

TABLE 3
EDX elemental analysis of adsorbents after Cu(II) and Cr(VI) adsorption

		Weight (%)			
		After Cu(II) adsorption		After Cu(IV) adsorption	
Element	Energy (KeV)	Untreated	Treated bark	Untreated	Treated bark
C K_α	0.277	32.8	31.7	35.3	33.8
K L_α	0.294	N.D	N.D	4.2	3.6
Ca L_α	0.341	16.6	11.9	15.7	11.2
O K_α	0.525	19.5	16.4	17.3	16.3
Cu L_α	0.930	8.6	15.4	N.D	N.D
Na K_α	1.041	2.4	1.3	2.5	1.8
Mg K_α	1.253	1.9	1.1	2.1	1.3
Si K_α	1.739	3.4	2.5	3.6	3.1
Au M_α	2.121	4.2	4.7	6.4	7.1
Cl K_α	2.621	2.2	3.8	N.D	N.D
K K_α	3.312	N.D	N.D	3.1	2.7
Ca K_α	3.690	3.8	2.4	1.7	1.5
Cr K_α	5.411	N.D	N.D	4.8	13.7
Cu K_α	8.040	2.4	5.9	N.D	N.D
Au L_α	9.712	2.2	2.9	3.3	3.9

N.D: Not detected.

The Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, (20) which is expressed by Eq. (6):

$$R_L = \frac{1}{1 + bC_o} \tag{6}$$

where, C_o (mg/L) is the initial concentration of metal ion and b is the Langmuir constant (mL/mg). R_L values indicate whether the isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), and unfavorable ($R_L > 1$). As given in Table 4, the calculated R_L values are in the range of $0 < R_L < 1$, which indicates that the adsorption of Cu(II)

TABLE 4
R_L values based on the Langmuir equation

		R_L value	
Ion	Initial concentration (mg/L)	Untreated	Treated
Cu(II)	50	0.6834	0.3146
	100	0.5302	0.2869
	150	0.4017	0.1852
	200	0.2995	0.0563
Cr(VI)	50	0.8315	0.5994
	100	0.7485	0.5063
	150	0.6846	0.4397
	200	0.5954	0.3105

and Cr(VI) on untreated and treated *Shorea dasyphylla* bark are favorable.

Although a comparison of the adsorption characteristics of the different adsorbent tested under different conditions could be misleading, it is necessary to compare the maximum adsorption capacity value obtained from this study with values from other reported low-cost adsorbents. The adsorption capacity for Cu(II) and Cr(VI) using *Shorea dasyphylla* bark are comparable with other low-cost adsorbents as shown in Table 5. This result highlights the applicability of chemical treatment method used in this study.

Adsorption Kinetics

Kinetic study is important in determining the rate of adsorbate uptake at the solid-phase interface. Three kinetic models, namely pseudo-first order, pseudo-second order, and intraparticle diffusion were applied to evaluate adsorption dynamics and to describe the adsorption rate of Cu(II) and Cr(VI) onto untreated and treated bark.

The pseudo-first order equation (31) is described as Eq. (7):

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

where, q_e and q_t (mg/g) are the amount of Cu(II) or Cr(VI) adsorbed at equilibrium and at time t (min), respectively and k_1 (min^{-1}) is the rate constant of pseudo-first order adsorption. The straight line plots of log $(q_e - q_t)$ against t were used to determine the values for the rate constant, k_1 and correlation coefficient, R. The pseudo-second order equation (32) is expressed as Eq. (8):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where, k_2 (g/(mg · min)) is the rate constant of pseudo-second order adsorption. The straight-line plots of t/q_t against t were tested to obtain rate parameters and the results suggest the applicability of this kinetic model to fit the experimental data. The intraparticle diffusion rate (33) is given as Eq. (9):

$$q_t = k_{id} t^{0.5} \tag{9}$$

where, k_{id} (mg/(g · min$^{0.5}$)) is the intraparticle diffusion rate and k_i is the slope of the straight-line portions of plot of q_t against $t^{0.5}$.

The rate constant and correlation coefficient values for each model are shown in Table 6. Based on the correlation coefficients, the adsorption of Cu(II) and Cr(VI) are best described by the pseudo-second order equation. The pseudo-first order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases, whereas the pseudo-second order kinetic model assumes that the rate-limiting step may be the adsorption mechanism but not mass transport (34, 35). The rate constant of pseudo-second order adsorption (k_2) obtained for treated bark was found to be lower than that estimated for natural bark. This indicates that the adsorption of Cu(II) and Cr(VI) onto chemically treated bark was more rapid and favorable. This result also

TABLE 5
Comparison of adsorption capacities of Cu(II) and Cr(VI) on various agricultural wastes (selected papers)

Heavy metal	Adsorbent	Treatment agent(s)	q_{max} (mg/g)	Reference
Cu(II)	Groundnut shells	Natural form	4.46	(37)
	Groundnut shells	Reactive Orange 13	7.60	(37)
	Sago waste	Natural form	12.40	(38)
	Nipah palm shoot	Mercaptoacetic acid	66.71	(39)
	Lentil shells	Natural form	9.59	(40)
	Rice shells	Natural form	2.95	(40)
	Shorea dasyphylla bark	Hydrochloric acid and sodium hydroxide	184.66	This study
	Shorea dasyphylla bark	Natural form	75.18	This study
Cr(VI)	Groundnut husk carbon	Sulfuric acid and silver impregnation	11.40	(41)
	Groundnut husk carbon	Natural form	7.00	(41)
	Terminalia arjuna nuts	Zinc chloride	28.43	(42)
	Sugar cane bagasse	Natural form	13.40	(43)
	Maize cob	Natural form	13.80	(43)
	Sugar beet pulp	Natural form	17.20	(43)
	Shorea dasyphylla bark	Hydrochloric acid and sodium hydroxide	42.72	This study
	Shorea dasyphylla bark	Natural form	18.95	This study

TABLE 6
Kinetic parameters for Cu(II) and Cr(VI) adsorption onto *Shorea dasyphylla* bark

		Pseudo-first order		Pseudo-second order		Intra particle diffusion	
Ion	Bark	k_1 (min^{-1})	R	k_2 (g/(mg · min))	R	k_i (mg/(g · min$^{0.5}$))	R
Cu(II)	Untreated	4.25×10^{-2}	0.9973	2.53×10^{-3}	0.9998	7.74	0.9772
	Treated	3.77×10^{-2}	0.9852	1.99×10^{-3}	0.9995	4.29	0.9718
Cr(VI)	Untreated	7.92×10^{-2}	0.9978	5.82×10^{-3}	0.9991	8.12	0.9599
	Treated	6.15×10^{-2}	0.9888	4.81×10^{-3}	0.9993	6.93	0.9514

suggests that the rate of adsorption is influenced mainly by structural properties of the adsorbent such as surface area, porosity and surface morphology.

Adsorption Thermodynamic

Thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and free energy change (ΔG°) must be considered in order to determine the spontaneity of a process. In this study, the thermodynamic parameters of the adsorption process were obtained at various temperatures (300, 310, and 320 K) and were estimated using Eqs. (10–12). (36):

$$K_c = \frac{C_{Ad}}{C_e} \tag{10}$$

$$\Delta G^\circ = -RT \ln K_c \tag{11}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{12}$$

where, K_c is the equilibrium constant, C_{Ad} (mg/L) is the concentration of Cu(II) and Cr(VI) adsorbed onto the solid at equilibrium, C_e (mg/L) is the equilibrium concentration of Cu(II) and Cr(VI) in solution, R (8.314 J/(K · mol)) is the universal gas constant and T (K) is temperature. The values of ΔH° and ΔS° can be obtained from the slope and intercept of the Van't Hoff plot of ln K_c versus $1/T$. The negative value of ΔH° as shown in Table 7 indicates the exothermic nature of adsorption. The negative values of ΔG° for both Cu(II) and Cr(VI) indicate that the adsorption on untreated and treated bark is a spontaneous process. However, the ΔG° values decreased with increasing temperature, suggesting that adsorption of Cu(II) and Cr(VI) on bark became less favorable at higher temperature. The negative value of entropy change (ΔS°) reflects the increasing randomness at the solid-solution interface during metal ion adsorption.

Adsorption Mechanism

The contribution of the ion exchange mechanism to metal ion uptake and the relationship between initial metal concentration and pH, was investigated by measuring the initial and final solution pH. As shown in Table 8, the final solution pH decreased as the initial metal ion concentration increased. This was due to the replacement of H^+ ions on functional groups of the bark by Cu(II) and Cr(VI) ions in bulk solution. This indicates that metal ions prevailed over H^+ ions for the ion exchange mechanism during metal ion adsorption. From Table 8, it is obvious that the ΔpH values for Cu(II) were relatively higher than that of Cr(VI) after adsorption onto adsorbents. This phenomenon takes place because more H^+ ions are in solution during Cu(II) ion adsorption, leading to a significant decrease in pH. Therefore, it can be speculated that Cu(II) ions have a greater affinity for the H^+ binding sites than Cr(VI) ions.

TABLE 7
Thermodynamic parameters of Cu(II) and Cr(VI) adsorption by *Shorea dasyphylla* bark

		ΔG° (kJ/mol)		ΔS°(J/(K · mol))		ΔH° (kJ/mol)	
Bark	Temperature (K)	Cu(II)	Cr(VI)	Cu(II)	Cr(VI)	Cu(II)	Cr(VI)
Untreated	300	−8.44	−6.29	−5.96	−5.14	−0.98	−0.16
	310	−9.85	−7.52	−6.06	−5.62		
	320	−10.17	−8.51	−6.45	−5.83		
Treated	300	−2.46	−0.79	−1.05	−0.38	−4.72	−3.18
	310	−3.19	−1.07	−1.43	−0.62		
	320	−4.26	−1.88	−1.88	−0.77		

TABLE 8
Initial and final solution pH values

Adsorbent	Initial metal ion concentration (mg/L)	Initial pH	Final pH	ΔpH
Cu(II)				
Untreated	50	4.74	3.35	1.39
	150	4.77	3.04	1.73
	300	4.78	2.77	2.01
	500	4.80	2.53	2.27
Treated	50	4.75	3.20	1.55
	150	4.77	2.86	1.91
	300	4.79	2.73	2.06
	500	4.81	2.33	2.48
Cr(VI)				
Untreated	50	6.67	6.03	0.64
	150	6.68	5.83	0.85
	300	6.70	5.73	0.97
	500	6.72	5.62	1.10
Treated	50	6.65	5.93	0.72
	150	6.67	5.69	0.98
	300	6.69	5.55	1.14
	500	6.74	5.48	1.26

FTIR analysis was performed before and after chemical treatment, in order to identify functional groups present in untreated and treated bark. As depicted in Fig. 5, a broad band appeared at 3414 cm^{-1}, corresponding to the intermolecular H- bonded O-H and the extension vibration of N-H. Two discernible bands at wavenumbers 2919 and 2852 cm^{-1} are assigned to saturated C-H stretchings. The prominent band observed at 1637 cm^{-1} can be attributed to N-H bending, while bands located at 1543, 1513, and 1454 cm^{-1} are characteristic of amine deformation. O-H bending was represented by two absorption bands observed at 1424 and 1262 cm^{-1}. The presence of O-S-O groups is confirmed by the appearance of two absorption bands at 1378 and 1319 cm^{-1}. The absorption bands appeared at 1157, 1059, and 1034 cm^{-1} represent the C-O stretching vibration. FTIR spectrum for treated bark showed no shift in wavenumbers or appearance of new absorption bands, implying that all functional groups in bark are intact after chemical treatment.

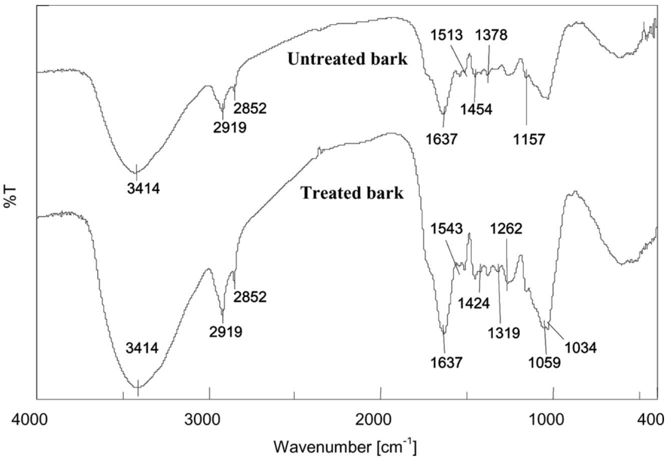


FIG. 5. Infrared spectra of untreated and treated *Shorea dasyphylla* bark.

After Cu(II) and Cr(VI) adsorption had taken place (Fig. 6), the absorption intensity of the S-O stretching vibration at 1378 cm^{-1} increased dramatically in the spectrum of treated bark. Cu(II) adsorption has caused greater increment in absorption intensity of S-O stretching vibration due to better extent in the amount of Cu(II) ions adsorbed on treated bark. The absorption band of intermolecular H-bonded O-H and extension vibration of N-H at 3414 cm^{-1} was shifted to 3433 cm^{-1}, while the absorption

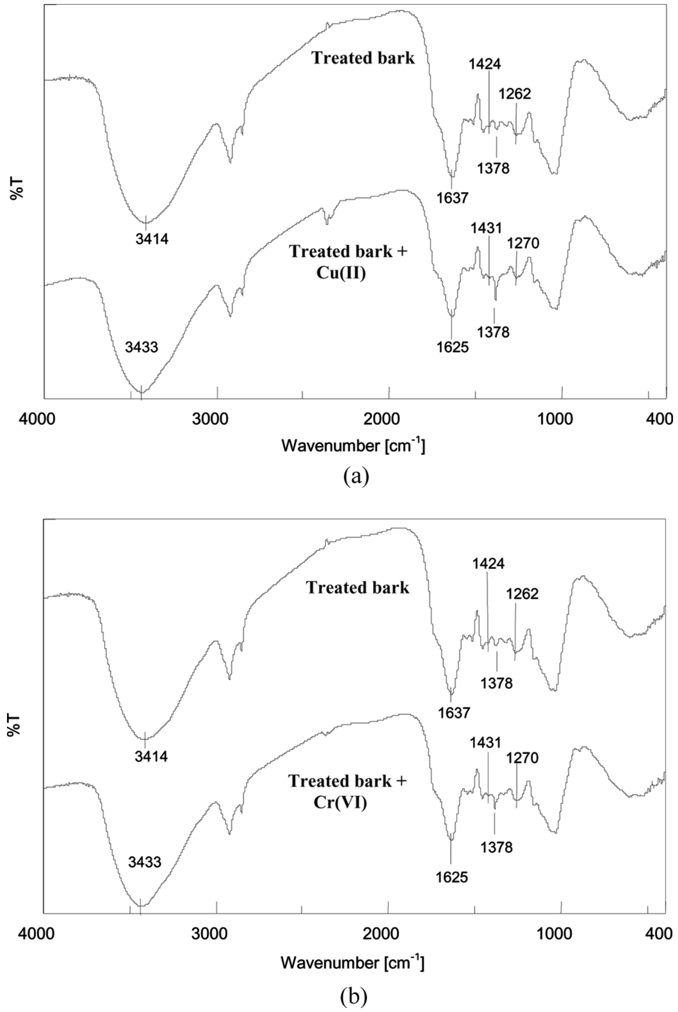


FIG. 6. Infrared spectra of treated bark before and after (a) Cu(II) and (b) Cr(VI) adsorption.

band of N-H bending at 1637 cm^{-1} was shifted to 1625 cm^{-1} after metal ion uptake. The interaction of metal ions with hydroxyl groups was proven by the shift in the wavenumbers of the O-H bending vibration. The absorption bands had shifted from 1262 cm^{-1} to 1270 cm^{-1} and from 1424 cm^{-1} to 1431 cm^{-1}, respectively. Presumably, the change in the absorption intensity and wavenumber of functional groups could be due to complexation between metal ions and adsorbent binding sites, through electron pair sharing between electron donor atom and metal ion. The FTIR results suggest that O-, S-, and N-containing groups are indeed the main adsorption sites in *Shorea dasyphylla* bark.

CONCLUSION

This study has shown that *Shorea dasyphylla* bark treated with HCl and NaOH can be effectively employed to adsorb Cu(II) and Cr(VI) from aqueous solution. Cu(II) and Cr(VI) adsorption was found to be highly pH-dependent and governed by some other experimental parameters such as the agitation period, the initial metal concentration, and temperature. Treated bark showed better adsorption capacity than its natural form, due to the greater surface area and morphology. The adsorption data fitted well with the Langmuir isotherm model, while adsorption kinetic data properly obeyed the pseudo-second order model. Thermodynamic studies indicated that the adsorption process was spontaneous and exothermic. EDX and FTIR analyses revealed that both ion-exchange and chemical interaction via electron sharing are the two main adsorption mechanisms involved in the adsorption of Cu(II) and Cr(VI) from aqueous solution onto untreated and treated *Shorea dasyphylla* bark.

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