

Adsorption of Cr(III), Ni(II), Zn(II), Co(II) Ions onto Phenolated Wood Resin

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ABSTRACT: In this study, phenolated wood resin was used as adsorbent for the removal of Cr(III), Ni(II), Zn(II), Co(II) ions by adsorption from aqueous solution. The adsorption of metal ions from solution was carried at different contact times, concentrations and pHs at room temperature (25°C). For individual metal ion, the amount of metal ions adsorbed per unit weight of phenolated wood resin at equilibrium time increased with increasing concentration and pH. Also, when the amounts of metal ions adsorbed are compared to each other, it was seen that this increase was order of Cr(III) > Ni(II) > Zn(II) > Co(II). This increase was order of Cr(III) > Ni(II) > Co(II) > Zn(II) for commercial phenol–formaldehyde resin. Kinetic studies showed that the adsorption process obeyed the intraparticle diffusion model. It was also determined that adsorption isotherm followed Langmuir and Freundlich models. Adsorption isotherm obtained for commercial phenol–formaldehyde resin was consistent with Freundlich model well. Adsorption capacities

from Langmuir isotherm for commercial phenol–formaldehyde resin were higher than those of phenolated wood resin, in the case of individual metal ions. Original adsorption isotherm demonstrated the monolayer coverage of the surface of phenolated wood resin. Adsorption kinetic followed the intraparticle diffusion model. The positive values of ΔG° determined using the equilibrium constants showed that the adsorption was not of spontaneous nature. It was seen that values of distribution coefficient (K_D) decreasing with metal ion concentration in solution at equilibrium (C_e) indicated that the occupation of active surface sites of adsorbent increased with metal ions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2838–2846, 2006

Key words: adsorption; heavy metal ions; adsorption isotherm; kinetics; resin; phenolated wood resin; commercial phenol formaldehyde resin

INTRODUCTION

Industrial wastewater streams containing a great deal of heavy metal, such as Zn, Ni, Cu, Cr, Co, Pb, etc., which are of atomic density and related with toxicity, would be seriously danger to environment and human health if they were discharged without suitable treatment.^{1,2} For this purpose, many methods such chemical oxidation, reverse osmosis, coagulation and flocculation, biological treatments, etc. have been developed for treating heavy metal-containing wastewater.³

Various synthetic ion exchange resins such as Amberlite IRC-64, Amberlite IRC-68, Amberlite CG-50, Duolite ES-468,⁴ and Amberlite IR-120⁵ have also been utilized for heavy metal removal from wastewater in resent. However, some synthetic resins, such as novolak resin (phenol–formaldehyde resin, for example: Amberlite XAD761), are hazardous to the environ-

ment because of emission of free formaldehyde remaining in novolak resin. For example, it has been indicated that the phenol–formaldehyde resin has been used for the removal of some organic materials in water treatment.⁶ Also, it has been reported that coir pith made from phenol–formaldehyde and urea–formaldehyde resins have been used for water adsorption characteristic by Viswanathan et al.⁷ Moreover, synthetic novolak resins (phenol–formaldehyde resin) have also been consumed for various fields such as plastic industry,⁸ wood-based panels, brake-linings,⁹ etc. so far. To escape from the hazardous of the emission of free formaldehyde remaining in novolak resin, therefore, recently various studies have been carried out on the production of phenol–formaldehyde-type resin without using formaldehyde.^{7,10,11}

In this study, phenol–formaldehyde-type resin was produced without using formaldehyde. It was made by condensation of phenol with wood powder in the presence of acidic catalyst, as will be described in the following section.

The aim of this study was to use phenolated wood resin, instead of synthetic resins, which are commonly

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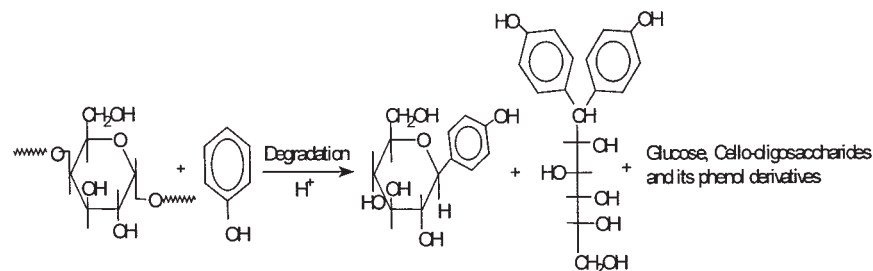


Figure 1 Scheme for the reaction mechanism of cellulose with phenol under acidic conditions.

used as adsorbent for water treatment (especially heavy metal removal). Moreover, the adsorption capacity of phenolated wood resin is to determine for the removal of Cr(III), Ni(II), Zn(II), and Co(II) ions, and the effects of treatment time, initial metal ion concentration, and pH on the adsorption is to investigate in detail.

EXPERIMENTAL

Materials

Wood meals (20–80 mesh) of sapwood portion of birch (*Betula maximowicziana* Regel) species were used after dried in a vacuum oven at 60°C for 24 h. 36.5% HCl aqueous solution was directly used as a catalyst. The other chemicals and solvents used were of extra pure or guaranteed reagent grade and used without further purification.

Metal ion stock solutions were prepared from an analytical-grade chloride salts, i.e., CoCl₂, NiCl₂, ZnCl₂, KCl, and CrCl₃·6H₂O. In the preparation of the aqueous solution of the metal ions, distilled water was used. To prevent the hydrolysis, species of metal ions pH values of aqueous solutions of metal ions were kept between two and six by dropping of diluted HCl and NaOH using a pH meter.

Methods

Preparation of phenolated wood resin

Wood meals (20 g), phenol (60 g), and 36.5% aqueous HCl (2.16 g) catalyst were mixed together in two-necked round-bottomed glass (1000 cm³). The glass was dipped into an oil bath, and liquefaction (phenolation) process was conducted at a temperature of 150°C for under 4 reflux hours.

After the liquefaction, black liquid obtained in the tube was diluted with about 250 cm³ of methanol and filtrated with a glass-fiber filter (Toyo GA-100) (1 μm particle-retainable). The methanol-insoluble part, thus collected, was dried in an oven at 105 ± 2(°C) for 24 h and weighed for the determination of the methanol-insoluble part, while methanol-soluble fraction was

neutralized with MgO. And then, the neutralized solution was once again filtered with the glass-fiber to remove the salt produced during the neutralization. Subsequently, methanol and free phenol were removed from the methanol-soluble fraction under reduced pressure at 50 and 180°C, respectively.

The phenolated wood resin obtained was ground into powder, having reacted phenol (as described in one of our earlier publications¹¹) of about 104%. Hypothetical chemical structure of phenolated wood powder is given in Figures 1 and 2. Figure 1 illustrates a complex reaction mechanism of phenol with cellulose, one components of wood.¹⁰ Figure 2 illustrates possible reaction pathway of some phenol derivative such as guaiacol, formaldehyde, and guaiacylglycerol-β-guaiacyl ether of lignin with phenol in acidic medium.¹⁰ Also, some properties of the phenolated wood resin obtained are given in Table I.

Adsorption experiments

Batch adsorption experiments were performed using 0.50 mg of phenolated wood resin with 50 mL of aqueous metal ion solutions in 150 mL-Erlenmeyer flasks, of which concentrations, pH, and temperature have already been known. The samples were shaken at 300 rpm in a shaking water bath (Clifton shaking water bath, England). After desired contact time, suspensions were filtered. The filtrate was analyzed for metal ions by using an atomic absorption spectrometer (GBC 902 AAS, Australia). Blank solutions containing no metal ions were used for each series of experiments. The amounts of metal ions adsorbed onto the resin were calculated from difference between initial and the final concentrations of aqueous solutions. For each adsorption process, the average of two replicates was reported.

RESULTS AND DISCUSSION

Effect of contact time on adsorption

The effect of contact time on the amount of all metal ions adsorbed per unit of adsorbent was investigated

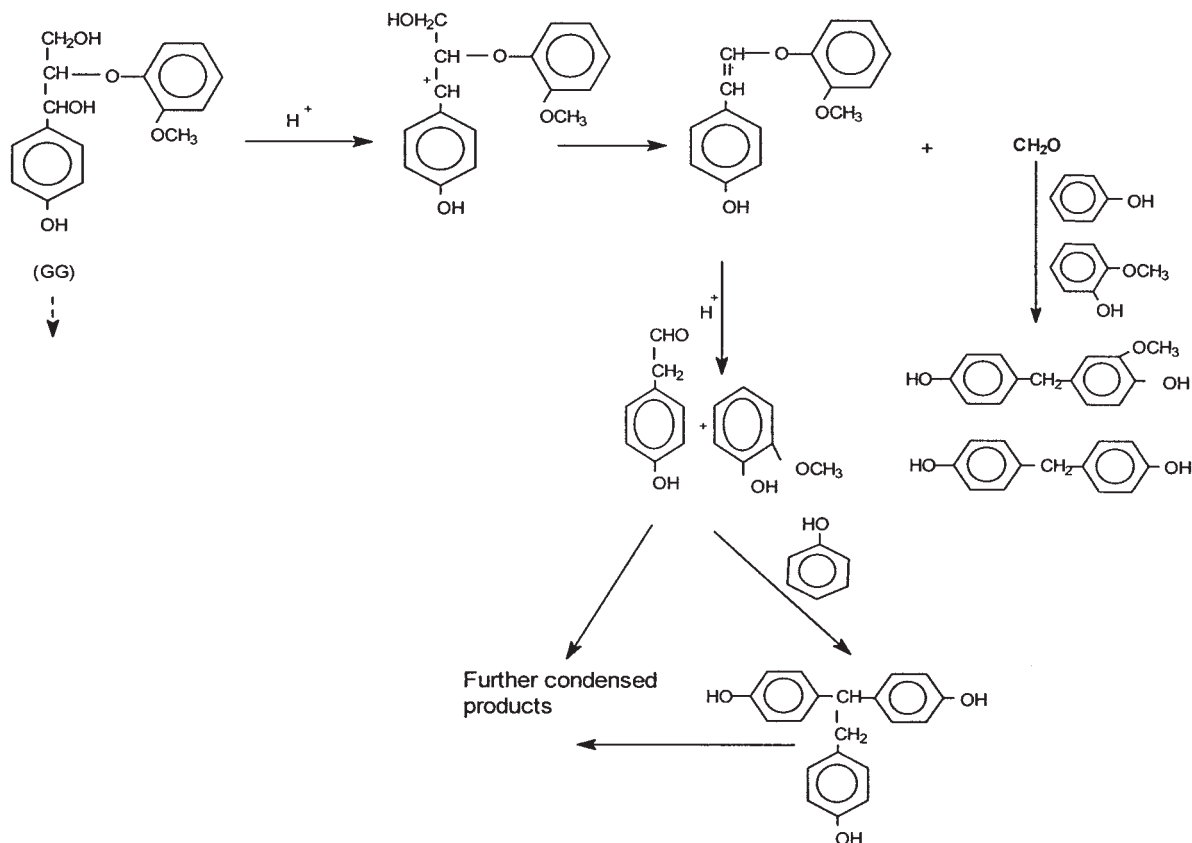


Figure 2 Scheme for the possible reaction pathway of guaiacylglycerol- β -guaiacyl ether (GG) with phenol in the presence of sulfuric acid as a catalyst.

for an initial concentration of 300 mg/L at pH 5 and 25°C. The amounts of all metal ions adsorbed per unit of adsorbent were tested for times of 20, 40, 60, 80, 100, 120, and 140 min. The amounts of all metal ions adsorbed per unit of adsorbent were increased with increasing contact time. For all metal ions, it was observed that a maximum adsorption had occurred at a contact time of 120 min. Therefore, the time of 120 min is fixed as the optimum contact time (i.e., equilibrium time). And, further experiments were carried out at a contact time of 120 min. Relationship between the amounts of metal ions adsorbed per unit of adsorbent and contact times is illustrated in Figure 3. As also shown in Figure 3, the maximum amount of metal ions adsorbed per unit of adsorbent at equilibrium time were 49.519, 46.114, 43.968, and 32.380 mg/g for Cr(III), Ni(II), Zn(II), and Co(II), respectively.

Effect of pH on adsorption

The adsorption of the metal ions onto an adsorbent varies generally with pH, because pH causes to change the radius of hydrolyzed cation and the charge of the adsorbent surface. Therefore, in this study, the adsorption of metal ions onto phenolated wood resin was studied as a function of pH. The initial pH values

TABLE I
Some Physical Properties of Phenolated Wood Resin

Color	Brown
Density (mg cm ⁻³)	0.86 ± 0.04
Particle size (mesh) ^a	108 ± 12 (100) ^b
Water regain (%)	65.10 ± 4.9
Cation exchange capacity (meg g ⁻¹) ^c	0.19
Functional group	H ⁺ (part weakly dissociated in — OH)
The regeneration degree for each cation (%)	
I ^d	
Cr(III)	9
Zn(II)	12
Ni(II)	14
Co(II)	17
II ^d	
Cr(III)	55
Zn(II)	64
Ni(II)	69
Co(II)	70

^a The value obtained from viscosimetric measurement, Einstein Equation for spherical particles)

^b The value obtained by molecular sieve

^c The value obtained by means of potentiometric titration with 0.1 M KOH)

^d I: The values determined for 600 mg dm⁻³ K(I)

^d II: The values determined for saturated K(I)

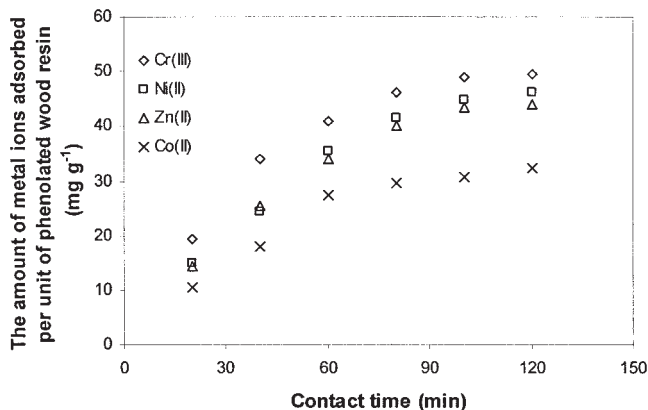


Figure 3 Effect of contact time for adsorption of metal ions onto phenolated wood resin (initial metal ion concentration 300 mg/L, initial pH 5.5, and temperature 25°C).

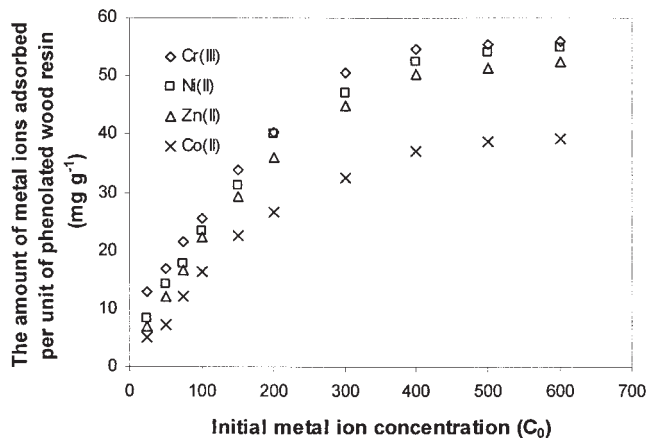


Figure 5 Maximum amounts of metal ions adsorbed onto phenolated wood resin as a function of initial metal ion concentration at a contact time of 120 min, pH 6, and 25°C.

of metal ion solutions were kept between two and six to prevent the formation of their various hydrolyzed metal ion species. The relationship between initial pH and the amounts of all metal ions adsorbed on phenolated wood resin for initial solution concentrations of 300 mg/L for at 25°C and a contact time of 120 min is illustrated in Figure 4. When initial pH values of all metal ion solutions are increased from 2.0 to 6.0, the amounts of metal ions adsorbed per unit adsorbent also increase. For example, the amounts of metal ions adsorbed per unit adsorbent increase from 5.32 to 50.50 mg/g for Cr(III) when the pH value increase from two to six. It can be seen that the same tendency has also been found for the other metal ions as shown in Figure 4. Herein, the pH 6 is an optimum value for the maximum adsorption of all metal ions. The amounts of metal ions adsorbed per unit adsorbent at pH 6 are 50.50, 47.00, 44.812, and 32.60 mg/g for Cr(III), Ni(II), Zn(II), and Co(II), respectively. The fact that a rise in the pH cause to the increase of the

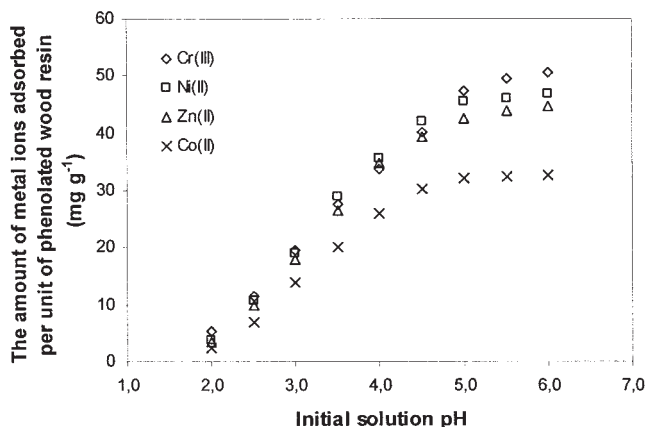


Figure 4 Effect of initial pH for adsorption of metal ions onto phenolated wood resin (initial metal ion concentration 300 mg/L and temperature 25°C).

adsorption of metal ions is attributed that hydroxyl groups (—OH) on the phenolated wood resin (see Figs. 1 and 2) has become more negative. Negatively charged adsorbent surface adsorbs more the metal cations.

Effect of metal ion concentration on adsorption

Ten different concentrations for all metal ions, i.e., concentrations of 25, 50, 75, 100, 150, 200, 300, 400, 500, and 600 mg metal dm⁻³, are selected to investigate the effect of initial metal ion concentration on the adsorption of metal ions onto phenolated wood resin, and the amounts of metal ions adsorbed at equilibrium at 25°C (room temperature) and pH 6 are graphed in Figure 5. As shown in Figure 5, with increasing initial metal ion concentration from 25 to 600 mg/L, the amount of metal ions adsorbed by adsorbent increases from 12.88 to 55.95 mg/g for Cr(III). However, the percentage removal of the Cr(III) ions was also decreased from 51.54 to 9.32 with increasing initial metal ion concentration from 25 to 600 mg/L. The similar tendencies are also observed for the adsorption of other metal ions. If the amounts adsorbed of metal ions at equilibrium time are compared between each other, while the highest removal is for Cr(III), it is seen that the lowest removal is for Co(II). The amount of metal ions adsorbed by phenolated wood resin, in the case of each concentration, increases in order of Cr(III) > Ni(II) > Zn(II) > Co(II).

Moreover, the amounts of metal ions adsorbed onto commercial phenol-formaldehyde resin are determined between initial metal ion concentrations of 100 and 300 mg/L at 25°C and pH 6 at a contact time of 120 min. The results are compared with values obtained for the phenolated wood resin under the same conditions. The amounts of metal ions adsorbed by

TABLE II
Isotherm Constants for the Adsorption of Metal onto Phenolated Wood Resin at pH 6 and 25°C

Freundlich isotherm			Langmuir isotherm				Metal cation
k_f (mg/g)	n (g/L)	r^2	Q_0 (mg g ⁻¹)	b (L/mg)	r^2	R_L^a	
4.095	2.315	0.977	66.66	10.40	0.987	0.242	Cr(III)
1.947	1.798	0.970	70.92	0.70	0.992	0.322	Ni(II)
1.398	1.646	0.966	70.92	0.58	0.992	0.363	Zn(II)
0.775	1.528	0.960	54.47	0.47	0.972	0.414	Co(II)

^a The values obtained for initial concentration of 300 mg/L.

commercial phenol–formaldehyde resin are found to be higher than those of phenolated wood resin. For example, the percentage amounts of metal ions adsorbed by commercial phenol–formaldehyde resin in comparison to the phenolated wood resin are higher by about 14–18, 33–34, 4–30, and 53–10,040 for Cr(III), Ni(II), Zn(II), Co(II), respectively. Also, the amount of metal ions adsorbed by phenolated wood resin have the following order: Cr(III) > Ni(II) > Zn(II) > Co(II), while those for commercial phenol formaldehyde resin are of the following range: Cr(III) > Ni(II) > Co(II) > Zn(II) for the concentrations studied. For both resins, the adsorption degree of Cr(III) was found to be the highest due to its greatest ionic charge value (z) compared to those of the other cations, but its replacement magnitude with K(I) was minimum among all the cations, as shown in the Table I.

Also, in the case of each concentration, the magnitude of experimental errors have been determined for the amounts of metal ions adsorbed at equilibrium at 25°C and pH 6, and it has found that standard deviations increase while adsorption equilibrium constants decrease with increasing initial metal ion concentrations. For instance, in the case of Cr(III) ion adsorption, standard deviations of the amount of adsorption for initial metal ion concentrations of 50 and 300 mg/L are ± 0.078 and ± 0.223 mg/g polymer for the phenolated wood resin, whereas those are ± 0.093 and ± 0.260 mg/g polymer for commercial phenol–formaldehyde resin. In the case of Zn(II) ion, while standard deviations of the amount of adsorption for initial metal ion concentrations of 50 and 300 mg/L are ± 0.202 and ± 0.719 mg/g polymer for the phenolated wood resin, whereas they are ± 0.228 and ± 0.817 mg/g polymer for commercial phenol–formaldehyde resin. The magnitudes of standard deviations of the amount of adsorption for Ni(II) and Co(II) ions between initial metal ion concentrations of 50 and 300 mg/L line between these values.

Analysis of adsorption isotherm

To determine the adsorption capacity, the experimental equilibrium data were fitted to the commonly used Langmuir and Freundlich equations. The isotherm re-

sults indicate that the adsorption of metal ions onto phenolated wood resin is consistent with the Freundlich and Langmuir isotherms. Freundlich adsorption isotherm can be expressed as follows:

$$\ln q_e = \ln k_f + 1/n \ln C_e \quad (1)$$

where q_e is the amount of metal ions adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of the metal ions in solution (mg/L). k_f and n are isotherm constants, which indicate capacity and intensity of the adsorption, respectively.

The correlation coefficients from the plots of $\ln q_e$ against $\ln C_e$ for all metal ions at 25°C are between 0.96 and 0.99 (see Table II), and the plots comply with Freundlich adsorption model. The values of k_f and n were calculated from the slope and intercept of the plot $\ln q_e$ versus $\ln C_e$. The values of k_f and n obtained are shown in Table II. As shown in Table II, the values of n range between 1.733 and 2.315 L/mg. If the value of n is in the range $1 < n < 10$, the adsorption is favorable.¹² On the other hand, the rearranged Langmuir isotherm is expressed as

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \quad (2)$$

where, Q_0 and b Langmuir constants, which are the adsorption capacity (mg g⁻¹) and energy of adsorption (L/mg), respectively. The correlation coefficients from the plots of C_e/q_e versus C_e for all metal ions at 25°C are between 0.96 and 0.99 (see Table II), and the plots are in harmony with Langmuir adsorption model. The values of Q_0 and b were determined from the slope and intercept of the plots of C_e/q_e versus C_e for all metal ions. The constant values obtained are shown in Table II. The values of Q_0 are found to be 66.66, 70.92, 70.92, and 54.47 mg/g for the Cr(III), Ni(II), Zn(II), and Co(II) under conditions studied, respectively. And, they were compared with the Q_0 value obtained for the adsorption of individual metal by some other synthetic resins, as presented in Table III. Also, from isotherm studies of the adsorption of all the metal ions on commercial phenol–formaldehyde resin, which is performed at 25°C and pH 6, it is seen that the adsorption process is in the agreement with

TABLE III
Kinetic Parameters for Metal Ions Adsorption onto Phenolated Wood Resin at pH 6 and 25°C for Initial Concentration of 300 mg/L

Metal	q_e^a	q_e^b	$k_2^c \times 10^4$	h^d	r_2^{2e}	q_e^f	k_1^g	r_1^{2h}	k_i^i	r_1^{2j}
Cr(III)	49.52	71.13	2.975	1.505	0.985	100	0.047	0.942	4.648	0.934
Ni(II)	46.11	84.70	1.285	0.992	0.961	90.99	0.039	0.956	5.113	0.967
Zn(II)	43.97	76.65	1.628	0.956	0.971	114.28	0.047	0.914	4.767	0.964
Co(II)	32.38	55.42	2.318	0.712	0.932	44.48	0.033	0.976	3.457	0.925

- ^a Equilibrium adsorption capacity obtained as experimental (mg g⁻¹).
- ^b Equilibrium sorption capacity obtained from pseudosecond-order equation (mg g⁻¹).
- ^c The rate constant of pseudosecond-order reaction (g/mg min).
- ^d The initial sorption rate from pseudosecond-order kinetics (mg/g min).
- ^e Correlation coefficient from pseudosecond-order equation.
- ^f Equilibrium adsorption capacity obtained from pseudofirst-order equation (mg g⁻¹).
- ^g The rate constant of pseudofirst-order reaction (l/min).
- ^h Correlation coefficient from pseudofirst-order equation.
- ⁱ Intraparticle diffusion rate constant (mg/g min^{1/2}).
- ^j Correlation coefficient from intraparticle diffusion equation.

Freundlich model, as well. Adsorption capacities obtained from Langmuir for commercial phenol-formaldehyde resin are given in Table III. As shown in Table III, adsorption capacities obtained for the phenolated wood resin are lower than those of commercial phenol-formaldehyde resin for all the metal ions studied.

Moreover, the original adsorption isotherm (isotherms drawn between the amounts of metal ions adsorbed per unit of adsorbent and metal ions concentration remaining in solution at equilibrium time) for individual metal is also presented in Figure 6. As shown in this figure, Isotherms obtained for individual metal is in consist with L-type isotherm model. This model shows that monolayer coverage occurs on the surface of phenolated wood resin, reflecting a relatively high affinity between the adsorbate and adsorbent.¹³

Furthermore, the essential characteristic of the Langmuir isotherm can be expressed by a dimension-

less separation factor called equilibrium parameter R_L .¹⁴

$$R_L = 1/1 + bC_0 \tag{3}$$

where, b is the Langmuir constant (L/mg), and C_0 is the initial metal ion concentration (mg/L).

Parameter R_L indicates the shape of isotherm as follows:

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

An R_L value between 0 and 1 indicates a favorable adsorption. Herein, the values of R_L between 0 and 1 indicate a favorable adsorption. For example, the R_L values obtained for initial concentration of 300 mg/L at pH 6 and 25°C are given in Table II.

Adsorption kinetics

Several models have been proposed to express the adsorption mechanism of solute molecules onto an adsorbent: (a) Pseudofirst-order-kinetic model, (b) Intraparticle diffusion model, and (c) Pseudosecond-order-kinetic model.

A pseudofirst-order-kinetic model of Lagergren¹⁵ is given as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

A pseudosecond-order-kinetic model of Ho is as follows¹⁶⁻¹⁸

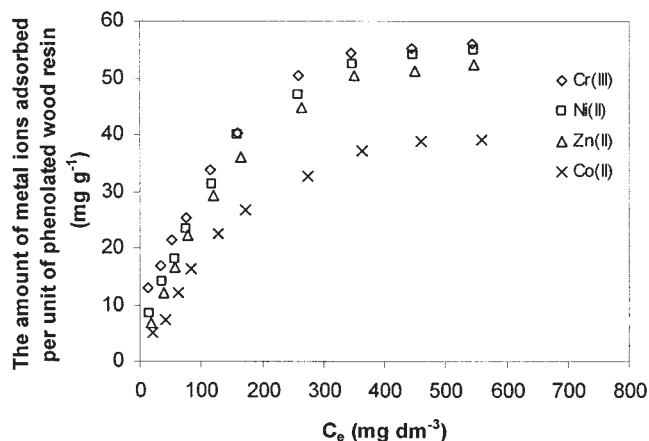


Figure 6 Adsorption isotherm of metal ions onto phenolated wood resin at pH 6 and 25°C.

TABLE IV
Comparison of Langmuir Equilibrium Adsorption Capacity (Q_0) of Phenolated Wood Resin and Commercial Phenol-Formaldehyde Resin with Those of Some Other Synthetic Resins for Metal Ions Adsorption

Adsorbent	Adsorption capacity Q_0	Metal ion	References
Commercial phenol-formaldehyde resin	1.88 (mmol/g)	Cr(III)	This study
	98 (mg/g)		
	2.129 (mmol/g)	Ni(II)	This study
	125 (mg/g)		
	1.987 (mmol/g)	Zn(II)	This study
Phenolated wood resin	130 (mg/g)		
	5.65 (mmol/g)	Co(II)	This study
	333 (mg/g)		
	1.281 (mmol/g)	Cr(III)	This study
	66.66 (mg/g)		
Amberlite IR-120 resin	1.208 (mmol/g)	Ni(II)	This study
	70.92 (mg/g)		
	1.085 (mmol/g)	Zn(II)	This study
	70.92 (mg/g)		
	0.925 (mmol/g)	Co(II)	This study
Duolite GT-73	54.47 (mg/g)		
	0.819 (mmol/g)	Ni(II)	(5)
	48.075 (mg/g)		
	1.315 (mmol/g)	Zn(II)	(5)
	86.00 (mg/g)		
Amberlite 200	0.97 (mmol/g)	Ni(II)	(20)
	56.939 (mg/g)		
	0.85 (mmol/g)	Zn(II)	
	55.59 (mg/g)		
	1.51 (mmol/g)	Ni(II)	(20)
Amberlite IR-718	88.637 (mg/g)		
	1.30 (mmol/g)	Zn(II)	
	85.02 (mg/g)		
	2.20 (mmol/g)	Ni(II)	(20)
	129.14 (mg/g)		
	2.36 (mmol/g)	Zn(II)	
	154.344 (mg/g)		

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

and an intraparticle diffusion model of Weber and Morris¹⁹ is shown as

$$q_t = k_i t^{1/2} \quad (6)$$

where, k_1 is rate constant for pseudofirst-order-model, k_2 is rate constant for pseudosecond-order-model, and k_i is intraparticle diffusion rate constant. q_e and q_t are the amount adsorbed of solute per unit adsorbent at equilibrium and any time, respectively. Herein, the initial adsorption rate is $h = k_2 q_e^2$.

The phenolated wood resin/metal adsorption system in the present study was investigated in terms of the above-mentioned kinetics models for understanding the adsorption kinetics.

First, the plots of $\log (q_e - q_t)$ versus t for the pseudofirst-order-model given in eq. (4) for the adsorption of metal ions onto the phenolated wood resin were drawn for all metal ions at pH 6 and 25°C. From linear regression analysis obtained, it is determined

that the values of r^2 are 0.942, 0.956, 0.914, and 0.976 for Cr(III), Ni(II), Zn(II), and Co(II) ions, respectively.

Second, the linear plots of t/q_t versus t for the pseudosecond-order-model in eq. (5) were obtained for all metal ions at pH 6 and 25°C. The values of r^2 obtained for the linear plots of t/q_t versus t are found to be 0.985, 0.961, 0.971, and 0.932 for Cr(III), Ni(II), Zn(II), and Co(II) ions, respectively. Although the correlation coefficients obtained for both the pseudofirst-order and the pseudosecond-order models have high values, the values of q_e from the pseudofirst- and second-order kinetics models are not in agreement with experimental data, q_e as shown in Table IV. Therefore, the adsorption does not follow the pseudofirst- and second-order kinetics. Herein, these plots obtained for the pseudofirst- and second-order model are not shown because they do not obey the pseudofirst- and second-order model.

And then, because of mass transfer effects, the plots of q_t versus $t^{1/2}$ for intraparticle diffusion model given in eq. (6) were obtained for all metal ions at pH 6 and 25°C. The plots for intraparticle diffusion model are demonstrated in Figure 7. The r^2 values from the

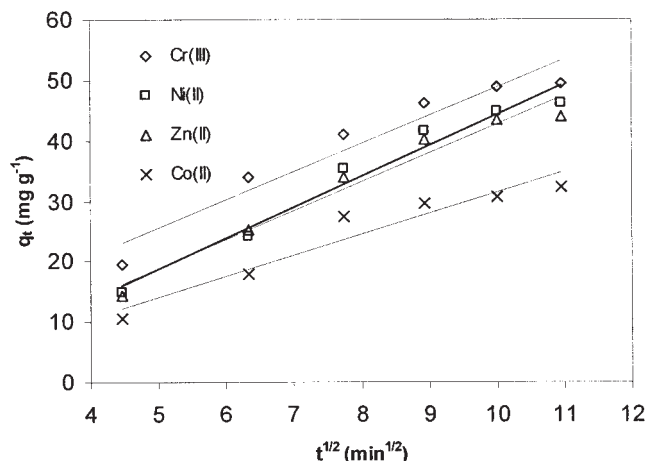


Figure 7 Intraparticle diffusion kinetics of individual metal ion for an initial concentration of 300 mg/L at pH 6 and 25°C.

figure are found to be 0.934, 0.968, 0.964, and 0.925 for Cr(III), Ni(II), Zn(II), and Co(II) ions, respectively. The intraparticle diffusion of all metal cations within the particles of the phenolated wood resin using as an adsorbent was found to be rate controlling in the adsorption process.

Study of equilibrium constant and distribution coefficient

The equilibrium constant of the adsorption of metal ions by phenolated wood resin (K_c) is calculated from the following equation²¹

$$K_c = C_{Ae} / C_{Se} \tag{7}$$

where, K_c is adsorption equilibrium constant, C_{Ae} is the equilibrium concentration of the metal ions on adsorbent (m/L), and C_{Se} is the equilibrium concentration of the metal ions in the solution (mg/L). The relationship between equilibrium constant (K_c) and the initial concentration of metal ions is shown in Figure 8. As shown in Figure 8, the value of equilibrium constant is higher at lower initial concentration, and, therefore, this process is in favor of lower initial concentration. It has been seen that the values of K_c are increased in sequence Cr(III) > Ni(II) > Zn(II) > Co(II) in the case of all the initial concentration ion. For example, the values of K_c are found to be 1.060–0.102, 0.50–0.10, 0.380–0.095, and 0.25–0.07 for Cr(III), Ni(II), Zn(II), and Co(II), respectively.

Moreover, standard Gibbs free energy (ΔG°) using equilibrium constant (K_c) for the adsorption of metal ions by phenolated wood resin is calculated from the following equation:

$$\Delta G^\circ = - RT \ln K_c \tag{8}$$

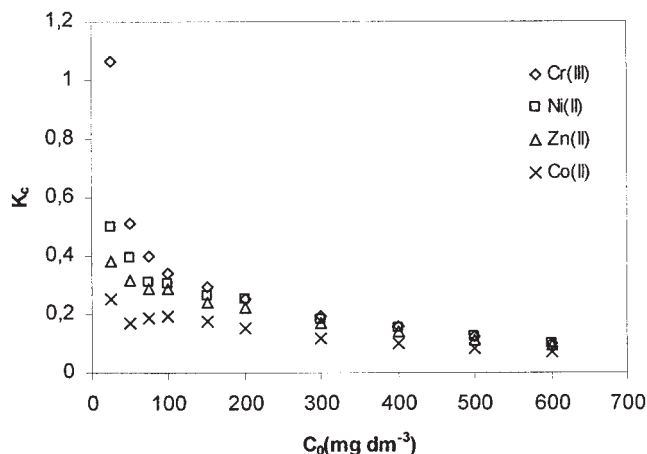


Figure 8 Equilibrium constant of individual metal ion for each concentration at pH 6 and 25°C.

where, R is the ideal gas constant and T is the absolute temperature. The values of ΔG° are given in Table V. As shown in the table, the positive values of ΔG° at different concentrations for all the metal ions indicate that the adsorptions do not have a process of spontaneous nature. Also, the ΔG° values were estimated for commercial phenol–formaldehyde resin, and they are shown in Table V. As shown in Table V, the ΔG° values for commercial phenol–formaldehyde resin are higher than those of phenolated wood resin. Furthermore, the variation of distribution ratio for metal ions is estimated from the following equation:^{22,23}

$$K_D = q_e / C_e \tag{9}$$

where, K_D is the distribution coefficient of metal cation (L/g). q_e and C_e are the amounts adsorbed on adsorbent and metal ions remaining in solution (in mg/g).

TABLE V
Standard Gibbs Free Energies for the Adsorption of Metal Ions onto Phenolated Wood Resin for Various concentrations at pH 6 and 25°C

Co (mg/L)	Standard Gibbs free energy + ΔG° (J/mol)				Resin
	Cr(III)	Ni(II)	Zn(II)	Co(II)	
50	1649.37	2295.43	2852.05	4398.24	PWR
	2154.41	3775.98	4135.47	13678.5	CPFA
100	2660.90	2950.54	3084.07	4103.10	PWR
	3166.47	3201.33	4024.71	7713.82	CPFA
200	3410.28	3427.07	3741.30	4631.50	PWR
	4024.13	3547.01	4078.01	7641.97	CPFA
300	4056.89	4236.98	4392.16	5267.68	PWR
	5111.68	6270.73	6588.24	10271.9	CPFA
400	4576.32	4683.06	4801.66	5640.52	PWR
500	5163.14	5225.65	5374.44	6129.93	PWR
600	5634.34	5691.43	5814.38	6585.82	PWR

PWR, phenolated wood resin; CPFA, Commercial phenol-formaldehyde resin.

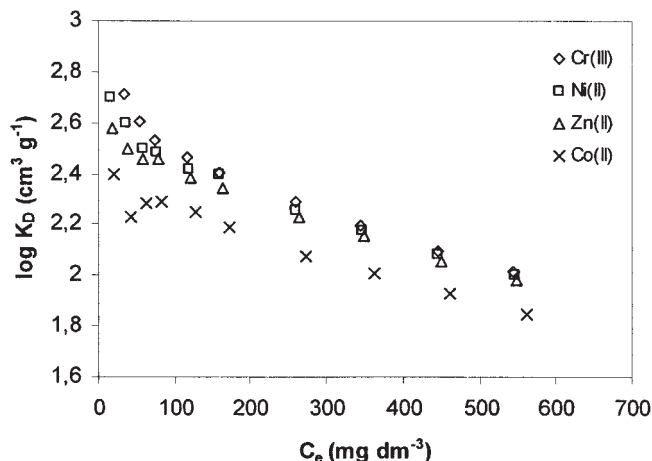


Figure 9 Distribution coefficient of individual metal ion as a function of equilibrium solution concentration at pH 6 and 25°C.

The relationship between K_D and C_e is given in Figure 9. As illustrated in this figure, it is seen that K_D decreases with metal ion concentration in the solution at equilibrium (C_e). This phenomenon indicates that the occupation of active surface sites of adsorbent increases with metal ions. The similar results have been reported earlier.^{22,23} The value of K_D for an effective adsorbent should be found between 10^{-2} and 10^{-1} (L/g).²² In this study, the values of K_D for all metal ions are between 10^{-2} and 10^{-1} (L/g).

CONCLUSIONS

In this study, it was determined that phenolated wood resin could be utilized as an effective and environmentally friendly adsorbent for the removal of several heavy metal ions from aqueous solution. The most effective pH was 6 for the maximum amounts of all the metal ions adsorbed onto both phenolated wood and commercial phenol-formaldehyde resins. The findings indicated that the highest amounts of metal ions adsorbed on the phenolated wood resin was found for Cr(III), followed by Ni(II), Zn(II), and Co(II), respectively, while those determined for commercial phenol-formaldehyde resin were in the order of

Cr(III) > Ni(II) > Co(II) > Zn(II) for all the concentrations and pHs. Furthermore, while adsorption isotherms followed the Langmuir and Freundlich models for phenolated wood resin, it was consistent with well Freundlich model for commercial phenol-formaldehyde resin. Adsorption kinetics followed the intraparticle diffusion model. The positive values of ΔG° determined using the equilibrium constants showed that the adsorption was not of spontaneous nature, and the ΔG° values obtained for phenolated wood resin were higher relative to commercial phenol-formaldehyde resin. The values of distribution coefficient (K_D) for all the metal ions were between 10^{-2} and 10^{-1} L/g, meaning an effective adsorbent.

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