

CHROMIUM (III) ADSORPTION FROM AQUEOUS SOLUTION BY *Rhizophora apiculata* TANNINS

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Received 3 May 2007; Accepted 12 June 2007

ABSTRACT

Adsorption of Cr^{3+} from aqueous solution by *Rhizophora apiculata* tannins was investigated in batch shaking experiments. Tannins extracted from *R. apiculata* mangrove barks was chemically modified with formaldehyde in the basic solution of sodium hydroxide. The performance of the produced adsorbent on the adsorption of Cr^{3+} was evaluated based on the effect of several parameters like initial pH, adsorbent dosage, initial Cr^{3+} concentration and contact time. Equilibrium adsorption data was analyzed by Langmuir, Freundlich, Sips and Dubinin-Raduskhevich (D-R) isotherms. The fitness of the isotherms to the experimental data was determined by non-linear regression analysis. Adsorption capacity calculated from Langmuir isotherm was found to be 10.14 mg Cr^{3+} /g of adsorbent at optimum adsorption pH of 4.5. Mean energy of adsorption with the value of 10.35 kJ/mol indicated that adsorption Cr^{3+} on *Rhizophora apiculata* tannins followed ion-exchange reaction. Kinetic study showed that the adsorption process followed the pseudo second-order kinetic model.

Keywords: *Rhizophora apiculata*, tannins, isotherms, kinetic, chromium.

INTRODUCTION

Industrial waste water discharged to the environment without proper treatment sometimes contains trace amount of heavy metal ions. Industries that produce aqueous waste contaminated with heavy metal ions always involve activities like metal plating, mining operation, tanneries, fertilizer and textiles industries [1,2]. Heavy metal ions are biological undegradable tend to accumulate in the environment had posed as major pollutant and threat to all living organisms.

Several conventional methods like precipitation, membrane filtration, oxidation/reduction, carbon filtration have been used to remove metallic pollutants from aqueous solutions [3,4]. These methods, however, are involving high operation cost and only work effectively in high concentration metallic solutions. At low concentration of heavy metal ions, lower than about 100 mg/l, these methods are less effective [3,5]. Recently, natural products or waste products from industries such as *Pinus pinaster* bark [5], maple sawdust [6] and Turkish brown coal [7] were studied for their potential in removing trace heavy metal ions from aqueous solutions. Biomaterials like tannins had showed high performance in removing heavy metal ions due to the present of many adjacent hydroxyl groups in their structures [7].

In Malaysia, tannins can be extracted from the barks of *Rhizophora apiculata* mangrove. The mangrove barks are the waste product of charcoal industry in Kuala Sepetang, Malaysia. In this study, extracted tannins

were pretreated with formaldehyde under basic catalyzed condition and its performance in removing Cr^{3+} from aqueous solution was evaluated.

EXPERIMENTAL SECTION

Materials and Methods

Tannins were extracted from the grounded barks of *R. apiculata* mangrove using water :acetone (70:30, v/v) and dried at 40 °C. To produce tannins-based adsorbent which is insoluble in aqueous solutions, the extracted tannins were dissolved in 0.225 M of NaOH and formaldehyde 37% (v/v) was added to the solution. The solution was well mixed and heated at 80 °C for 3 h. Tannins gel obtained after heating was grinded and washed with 0.05 M HNO_3 . Finally, the tannins gel was washed with distilled water and dried in the oven.

Adsorption study of Cr^{3+} from aqueous solution

Effect of pH

Solutions of Cr^{3+} with concentrations of 10.00 mg/L was prepared from the chromium(III)-nitrate-9-hydrate salt. The solutions were adjusted to different pH and added to 0.20 g of produced adsorbent. After shaking for 3 h, the solutions were filtered. The filtrates were then analyzed with atomic absorption spectrometer, AAS (Perkin Elmer – 3100) for the amount of Cr^{3+} being adsorbed.

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Effect of adsorbent dosage

Various amount of the produced adsorbent (0.10 – 2.00 g) was weight and added into 50 mL of Cr^{3+} solutions with fixed initial concentrations of 10.00 mg/L and pH of 4.5. The solutions were shaken at room temperature for 3 h and filtered. The filtrates were analyzed with AAS for the remaining amount of Cr^{3+} .

Effect of Cr^{3+} initial concentration

The produced adsorbent was weight at 0.50 g and added into Cr^{3+} solutions with various initial concentrations and adjusted pH value of 4.5. The solutions were then shaken for 3 h at room temperature and filtered. The remaining amount of Cr^{3+} in the filtrates was analyzed by AAS.

Effect of contact time

For kinetic study, 10 mg/L of Cr^{3+} solutions were prepared and the pH was adjusted to 4.5. To the prepared solutions, 0.50 g of produced adsorbent was added and shaken at room temperature for different periods. The solutions were then filtered and the filtrates were analyzed with AAS for the amount of Cr^{3+} being adsorbed.

RESULT AND DISCUSSION

Effect of pH

Adsorption of heavy metal ions is strongly affected by the pH of the aqueous solution. Fig 1 shows that more Cr^{3+} was adsorbed onto the produced adsorbent when the initial pH of the aqueous solution was increased from pH 2 – 8. At low pH, more protons are present in the solution; protons will compete with the anionic Cr^{3+} for the available adsorption sites and reduced the adsorption percentage [7,8]. At higher pH values, greater than five, excessive OH^- ions in the aqueous solution forms hydroxyl complexes of chromium, $\text{Cr}(\text{OH})_3$ [7,9]. Thus, to represent the removal

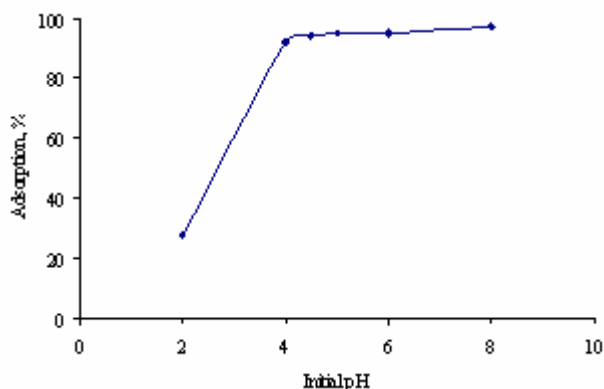


Fig 1. Effect of initial pH on adsorption of Cr^{3+} onto the produced adsorbent

of Cr^{3+} from the aqueous solution by the produced adsorbent is an adsorption process, pH 4.5 as the optimum adsorption pH was used for the following experiments.

Effect of adsorbent dosage

Tannins adsorb heavy metal ions through the interaction among the metallic ions and the polyhydroxyl groups on its structure. Fig 2 shows that, when more adsorbent was added into the solution with fixed concentration of Cr^{3+} at optimum adsorption pH of 4.5, adsorption percentage of Cr^{3+} increased. At fixed Cr^{3+} concentration, increasing the adsorbent doses provides greater surface area or adsorption site [6, 9], in this case more hydroxyl groups. Thus more Cr^{3+} can be adsorbed and reached equilibrium when 0.50 g of adsorbent was used.

Effect of initial concentration

The effect of initial concentration on adsorption percentage of Cr^{3+} by the produced adsorbent is shown in Fig 3. At optimum adsorption pH and fixed amount of adsorbent, increasing the initial concentration of Cr^{3+} will reduce the adsorption percentage as the availability of the adsorption is limited. Adsorption capacity, however, increased with the increasing of Cr^{3+} initial concentration until it reached a plateau which represented the maximum adsorption capacity of the produced adsorbent. The adsorption data at equilibrium was studied by various isotherm models like Langmuir, Freundlich, Sips and Dubinin-Raduskhevich (D-R) isotherms. Non-linear regression analysis was applied to investigate the fitness of each isotherm model to the experimental data, in which, higher value of correlation coefficient (r) and lower value of residue root mean square error (RMSE) indicate better fit [10]. The results are shown in Fig 4, 5 and Table 1.

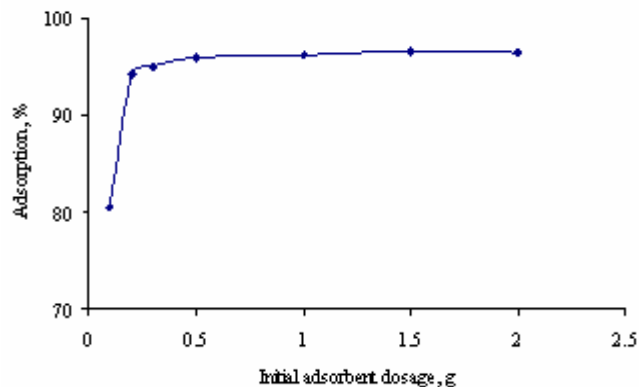


Fig 2. Effect of initial adsorbent dosages on adsorption of Cr^{3+} .

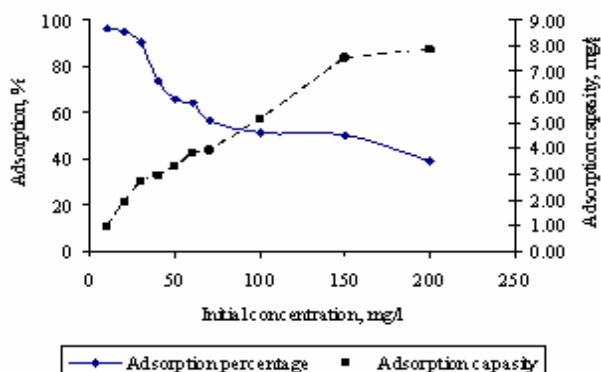


Fig 3. Effect of initial concentration of Cr^{3+} on the adsorption percentage and adsorption capacity.

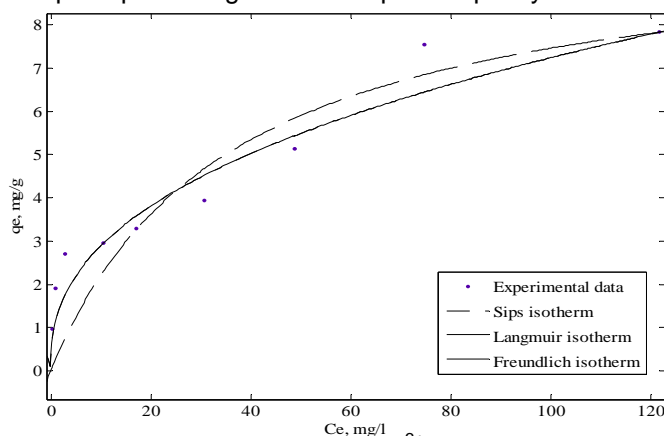


Fig 4. Adsorption isotherms of Cr^{3+} onto the produced adsorbent.

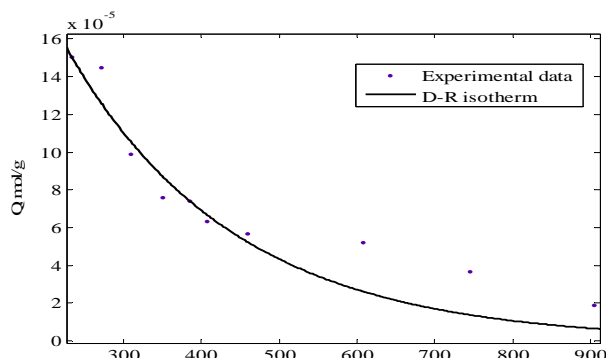


Fig 5. Dubinin-Raduskhevich (D-R) isotherm of adsorption of Cr^{3+} onto the produced adsorbent.

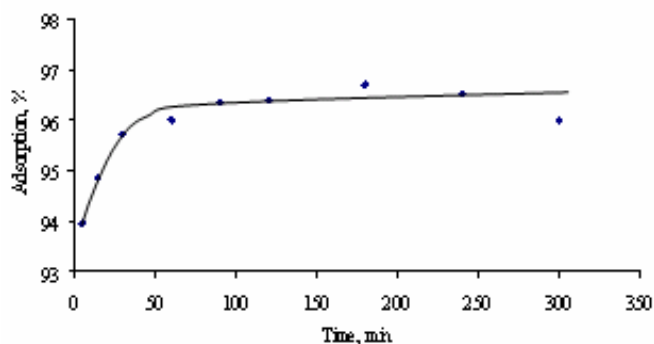


Fig 6. Effect of contact time on the removal of Cr^{3+} by the produce adsorbent.

Table 1. Langmuir, Freundlich, Sips and Dubinin-Raduskhevich (D-R) isotherms' parameters

	Langmuir	Freundlich	Sips	D-R
K_L	0.0279			
V_m	10.14			
K_f		1.1550		
$1/n$		0.3986		
b			0.031	
$1/n$			0.3986	
q_m			10.48	
Q_m				44.65×10^{-5}
K				0.0047
E				10.35
r	0.9582	0.9867	0.9784	0.9795
RMSE	0.7282	0.4141	0.5679	9.2190×10^{-6}

Langmuir isotherm

Langmuir isotherm applies to monolayer adsorption on adsorbent with homogeneous surface and neglects the interaction between adsorbed molecules [7]. This

model assumes that there is no steric hindrance between the adsorbed molecules and incoming ions, all the adsorption sites are alike and uniform in microscopic scale [11]. The Langmuir isotherm is written as:

$$q_e = \frac{V_m K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/l), V_m is the monolayer adsorption capacity (mg/g) and K_L is the equilibrium constant (l/mg). From the isotherm plot in Fig 4, the produced adsorbent has monolayer adsorption capacity of 10.14 mg Cr³⁺/g adsorbent with the value of K_L is 0.0279 l/mg.

Freundlich isotherm

Freundlich isotherm is an empirical isotherm model used for adsorption on heterogeneous surfaces [12]. The Freundlich model is formulated as:

$$q_e = K_f C_e^{1/n} \quad (2)$$

where K_f is the adsorption capacity (mg/g) and $1/n$ is the adsorption intensity, which is varies with the heterogeneity of the adsorbent. Non-linear regression analysis showed that Freundlich isotherm is better fitted to the experimental data with r value of 0.9867. The value of $1/n$ was found to be 0.3986, which is in between $0 < 1/n < 1$, indicated that the adsorption is favorable [13].

Sips isotherm

Sips or Langmuir-Freundlich isotherm is a combination of both Langmuir and Freundlich isotherms [14]. Sips isotherm is expressed as:

$$q_e = \frac{q_m (b C_e)^{1/n}}{1 + (b C_e)^{1/n}} \quad (3)$$

where q_m is the total binding sites, b is the median association constant and $1/n$ is the heterogeneity factor. From the study, it was found that the value of $1/n$ is 0.3986 ($\ll 1$). This indicated that the produced adsorbent has heterogeneous binding sites [13] and confirmed with Freundlich isotherm which assumes heterogeneous adsorption.

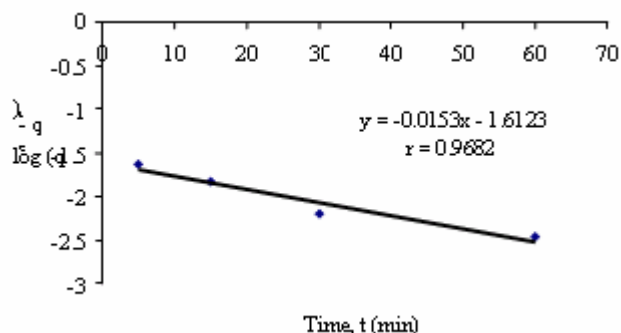


Fig 7. Pseudo first-order kinetic model.

Dubinin-Raduskhevich (D-R) isotherm

D-R isotherm describes adsorption on a single type of uniform pores. It is an analogue of Langmuir type but is a more general model as it does not assume homogeneous adsorption or constant sorption potential [2]. D-R isotherm is given as:

$$Q = Q_m \exp(-K\varepsilon^2) \quad (4)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (5)$$

where Q is the amount adsorbed at equilibrium (mol/g), Q_m is the maximum adsorption capacity (mol/g), K is the D-R constant (mol/kJ). ε is the Polanyi potential, R is the gas constant (kJ/mol K) and T is temperature in Kelvin.

The value of K is used to calculate mean energy of adsorption, E to estimate the type of adsorption process. E is calculated as below:

$$E = \frac{1}{\sqrt{2K}} \quad (6)$$

if the value of E is between 8 – 16 kJ/mol, the adsorption follows ion-exchange process [2]. For adsorption of Cr³⁺ onto the produced adsorbent, it was found that E has value of 10.35 kJ/mol, thus it follows the mechanism of ion-exchange.

Adsorption kinetic

Effect of shaking time on adsorption of Cr³⁺ onto the produced adsorbent is showed in Fig 6. A steep slope was obtained at the first 30 min, indicated that adsorption took place at high rate. After that, Cr³⁺ uptake rate by the produced adsorbent was slower and reached equilibrium at 90 min with the adsorption percentage of about 96 %. Experimental data was analyzed with pseudo first-order and pseudo second-order kinetic models.

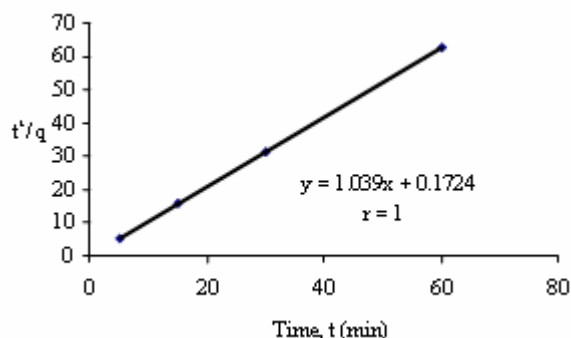


Fig 8. Pseudo second-order kinetic model.

The pseudo first-order kinetic model expressed by Lagergren [2, 8, 15] is given as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (7)$$

where q_e and q_t are the amount of metal ions adsorbed at equilibrium and time t respectively. K_1 is the adsorption rate constant (min^{-1}). Values of q_e and K_1 can be calculated from the linear plot in Fig. 7. It was found that q_e equal to 0.0244 mg/g and K_1 equal to 0.0352 /min.

The pseudo second-order kinetic model assumes that the rate-limiting step may be a chemical sorption involving sharing or exchange of electrons between the adsorbate and adsorbent [8, 15, 16]. This model is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where K_2 is the second-order kinetic rate constant (g/mg min). Fig 8 shows the linear plot of t/q_t against t , q_e was calculated as 0.9625 mg/g with the value of K_2 is 6.2613 g/mg min.

From the study, pseudo second-order kinetic model is best fitted to the experimental data with correlation coefficient, r of 1.000. The value of q_e calculated from pseudo second-order kinetic model was also in agreement with the experimental data which is 0.9630 mg/g. It can be concluded that adsorption of Cr^{3+} onto the produced adsorbent follows second-order kinetic reaction.

CONCLUSIONS

Adsorbent produced from *Rhizophora apiculata* tannins pretreated with formaldehyde in basic condition showed high performance in removing Cr^{3+} from aqueous solution. Initial pH of the Cr^{3+} solution strongly governed the adsorption percentage. At optimum adsorption pH of 4.5 and shaking time of 90 min, 96 % of Cr^{3+} was adsorbed. The non-linear regression analysis showed that the produced adsorbent has monolayer adsorption of 10.14 mg Cr^{3+} /g adsorbent. Mean energy of adsorption, E calculated from D-R isotherm showed that adsorption of Cr^{3+} onto the produced adsorbent is an ion-exchange process and it follows second-order kinetic reaction.

ACKNOWLEDGEMENTS

The authors would like to thank Universiti Sains Malaysia for the financial support (203/PKIMIA/671081).

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