

REMOVAL OF Cd(II) FROM AQUEOUS SOLUTION BY *BRUGUIERA SEXANGULA POIR* TANNIN-BASED ADSORBENT

HANGGARA SUDRAJAT^{1*}, NGUYEN DINH BANG² and PHAM XUAN TRUNG³

¹Faculty of Biology, Gadjah Mada University, Teknika Selatan, 55281 Jogjakarta, Indonesia.

²Department of Environmental Chemistry, Faculty of Chemistry, Hanoi University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam.

³Institute for Environmental Science and Technology, Hanoi University of Technology, Room 303, C10 Building, 1 Dai Co Viet Road, Hanoi, Vietnam.

*Corresponding author: Phone: +62 858 68077123; Fax: +62 274 546175, E-mail: angga_vanniveau@yahoo.co.id

Received: 9th June 2008; Revised: 26th June 2008; Accepted: 30th June 2008

Abstract: Tannins extracted from the mangrove barks of *Bruguiera sexangula Poir* species were modified into tannin-based adsorbent (TBA) by using formaldehyde in the basic solution of ammonia. The produced adsorbent showed high efficiency in removal of Cd²⁺ from the aqueous solution. Effect of adsorption parameters like initial adsorption pH, initial desorption pH and initial Cd²⁺ concentration were studied in batch experiments. The optimum adsorption pH of Cd²⁺ was at pH 7.0 with an adsorption percentage of 96.20%. Meanwhile, 82.68% of Cd²⁺ was desorbed from the loaded TBA at the initial pH of 4.0, which was the optimum desorption pH. Non-linear regression analysis was conducted to determine the fitness of Langmuir, Freundlich, Sips and Dubinin-Raduskhevich (D-R) isotherms to the experimental data at equilibrium. TBA showed high monolayer adsorption capacity of 17.41 mg g⁻¹. Mean energy of adsorption, *E* calculated from D-R isotherm showed that adsorption of Cd²⁺ on TBA followed ion-exchange mechanism.

Keywords: Adsorption, *Bruguiera sexangula Poir* tannin-based adsorbent, Cd²⁺ removal, desorption

INTRODUCTION

Recently, natural products or waste products from industries were studied for their potential in removing heavy metal ions from aqueous solutions [1-4]. Biomaterials like tannins had showed high performance in removing heavy metal ions such as cobalt, chromium and uranium due to the present of many adjacent phenolic hydroxyl groups in their structures [3]. Tannins in nature are able to react with heavy metal ions in aqueous solution; however, their application as adsorbent is restricted because of their solubility in water. Thus, tannins have to be modified into insoluble

tannins gel as an effective adsorbent for heavy metal ions. This is done through the reaction between tannins and formaldehyde. Insoluble tannin gel is considered highly applicable because it consists of only carbon, hydrogen and oxygen and its volume is easy to be reduced by drying and incinerating. In general, the residue after incineration will be the oxide of the adsorbed metal [2]. In this work, tannins were extracted from mangrove bark of *Bruguiera sexangula* Poir species, which is a by-product of charcoal industry in Vietnam. The extracted tannins then will be immobilized by polymerization using formaldehyde as a cross-linking agent to produce tannin-based adsorbent. The optimum adsorption and desorption pH and adsorption isotherms of this tannin-based adsorbent towards Cd^{2+} were characterized and evaluated.

MATERIALS AND METHODS

Tannins extraction

The bark wastes of *Bruguiera sexangula* Poir species were collected from a charcoal industry. The dried bark was grounded by using grinder which passed through a 20 mesh sieve. Tannins were extracted from mangrove bark of *Bruguiera sexangula* Poir species by using acidified acetone 50% (v/v) solution as solvent. The extraction was done for three consecutive days. During each 24 h, the solvent was replaced with fresh acidified acetone 50% (v/v). The extract was then concentrated by using rotary evaporator and the final product was dried in the oven at 40 °C.

Preparation of tannin-based adsorbent, TBA

Tannin-based adsorbent was prepared based on the optimum volume of the basic solution of ammonia. 1.000 g of tannins were added into 6.25 ml of 13.3 N aqueous ammonia and stirred for 5 minutes to dissolve it. The solution was then added with 8.15 ml of 37% (v/v) formaldehyde and stirred for 30 minutes to ensure uniform mixing. A precipitation was formed, which was filtered and added with 6.25 ml of deionized water. The solution was refluxed at 70 °C for 3 h with stirring. The heated solution was filtered and the obtained precipitate was added to 0.1 M of diluted nitric acid, followed by stirring for 30 minutes. The nitric acid solution was then filtered and the precipitate was washed with deionized water, and dried in the oven at 40 °C.

FTIR and TEM Characterization

The functional groups of the produced adsorbent were characterized using Fourier Transform Infrared Spectroscopy (FTIR). Infrared spectra were obtained on Shimadzu IRPrestidge-21/FTIR-8000 spectrophotometer by transmittance sampling technique. Samples were measured with spacer of 0.01 mm ~ 0.02 mm thickness on a KBR cell plate and then placed in the sample holder. Apodization was performed by Happ-Genzel method with number of scans: 45, resolution: 4.0 and wavelength range: 400 – 4000 cm^{-1} . The FTIR spectra was then analyzed to obtain data of functional groups.

Transmission Electron Microscope (TEM) was used to study the nanostructures morphology of the produced adsorbent using philips CM12 model (100 kV acceleration voltage). Ultramicrotome was used to produce the ultrathin film specimens using Leica-Reichert Supernova (Glass cutter) at room and below room temperature (cryogenically).

Determination of optimum pH for adsorption and desorption of Cd^{2+}

Cd^{2+} ions solutions with a concentration of 5.0 mg L^{-1} were prepared and the initial pH of the solutions were adjusted to pH 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0. 50.00 ml of each solution was added

to 0.1000 g of TBA and shaken for 2 h. After shaking, the solution was filtered and the filtrate was analyzed with atomic absorption spectrometer, AAS (Perkin Elmer – 3100) for the amount of Cd²⁺ being adsorbed.

In the desorption study, TBA with adsorbed Cd²⁺ was added to 50.00 ml of deionized water. The initial pH of the deionized water was adjusted to pH 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 respectively and shaken for 2 h. After shaking, the solutions were filtered and the filtrates were analyzed with AAS to determine the amount of Cd²⁺ being desorbed.

Determination of optimum adsorption capacity of Cd²⁺

50.00 ml of Cd²⁺ solutions with concentrations of 2.0, 5.0, 10.0, 15.0 and 20.0 mg L⁻¹ were prepared. The initial pH of the solutions were adjusted to pH 7.0 and added to 0.1000 g of TBA. The solutions were shaken for 2 h and filtered. The filtrates were then analyzed with AAS to determine the amount of Cd²⁺ being adsorbed and calculated by mass balance equation as below:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where q_e is the amount of Cd²⁺ adsorbed/gram of adsorbent (mg g⁻¹), C_i and C_e are concentration of Cd²⁺ at initial and equilibrium respectively (mg L⁻¹), V is volume of the solution and m is the amount of adsorbent.

RESULTS AND DISCUSSION

Characteristics of mangrove tannins

A study on the mangrove tannins by reversed-phase HPLC analysis has shown that the mangrove tannins constitute mainly of four flavanoid monomers namely catechin, epicatechin, epigallocatechin and epicatechin gallate [5]. Fig. 1(a) shows the FTIR spectra of the produced adsorbent, TBA. The characteristic broad band peak existed in the vicinity of 3413 cm⁻¹ arises from the water molecules hydrogen-bonded with –OH group, indicating that tannins are phenolic compounds with the –OH group attached to the aromatic rings. Peaks in the vicinity of 1650 - 1450 cm⁻¹ showed the presence of aromatic rings. The 1384 cm⁻¹ absorption band attributes to the O-H inplane deformation in polyphenols [3, 6]. Peaks appearing in 900 – 600 cm⁻¹ and weak peaks in 1200 – 1000 cm⁻¹ indicated the characteristic of the substituted benzene ring [7]. The resulting tannin-based adsorbent was able to adsorb metal element efficiently because of the polyphenolic hydroxyl group possessed by the gelled tannins become a functional group and adsorbs a metal element by hydrogen ion exchange reaction more effectively. In the gelled tannins, the degree of freedom of the molecular chain increases whereby the functional group of the molecular chain becomes a steric structure which is easily coordinated with a metal element so that the gelled insoluble tannins are excellent adsorbent for metal elements [8].

Fig. 2(a) and (b) shows the TEM image of tannin-based adsorbent and tannin-based adsorbent loaded with Cd²⁺. The dark lines represent the thickness of the individual layers or agglomerates of adjacent phenolic hydroxyl groups. It is clear that Fig. 2(a) shows homogeneous dispersion of individual layers in nanometer range. The structure exhibits the partially exfoliated and intercalated. However, Fig. 2(b) shows heterogeneous dispersion of layers, where large agglomerates can be seen. Small Cd particles are nevertheless aggregated.

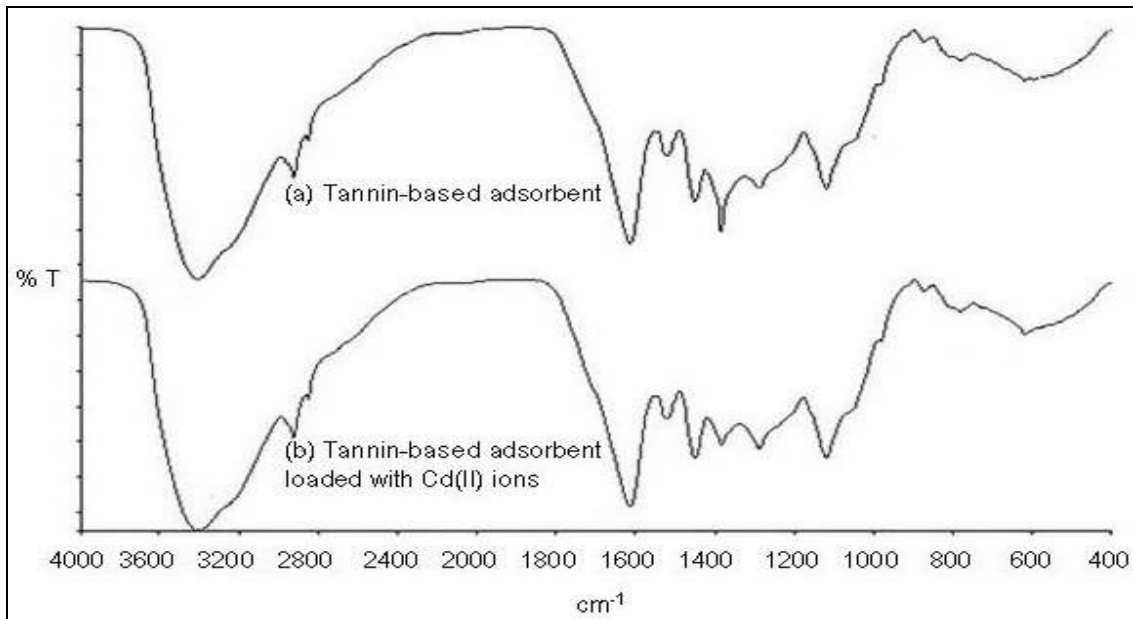


Fig. 1: FTIR spectra of (a) tannin-based adsorbent and (b) tannin-based adsorbent loaded with Cd²⁺.

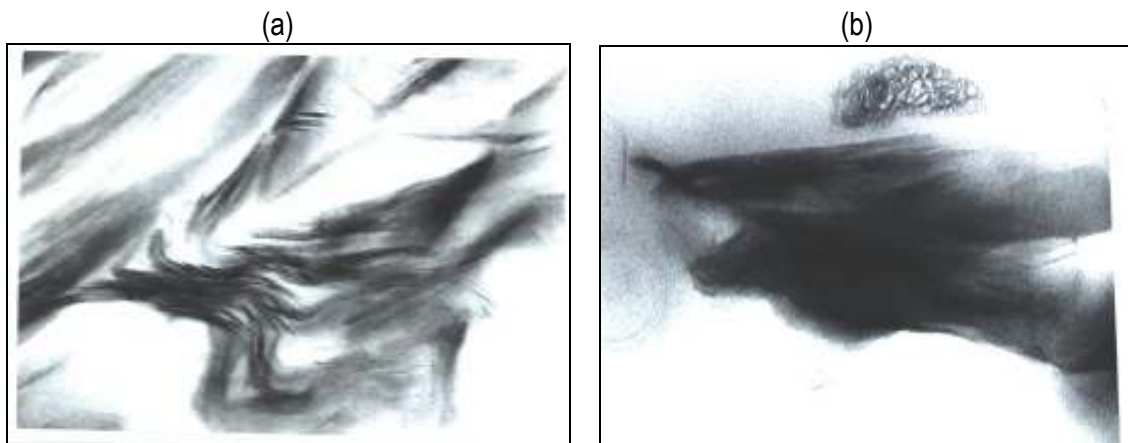


Fig. 2: TEM micrographs of (a) tannin-based adsorbent and (b) tannin-based adsorbent loaded with Cd²⁺.

Optimum adsorption and desorption pH of Cd²⁺

The effectiveness of the produced tannin-based adsorbent in the adsorption of Cd²⁺ was studied at pH ranged from 3.0 to 8.0 with the initial concentration of 5.0 mg L⁻¹ of Cd²⁺ solution. Fig. 3 shows that the adsorption of Cd²⁺ by 0.1000 g of TBA was more effective at pH 7.0 and 8.0 with highest adsorption percentage of 96.2%. Percentage of adsorption decreased when the solution had lower initial pH, where lowest adsorption percentage of 24.8% was recorded at pH 3.0. Significant increment in the adsorption percentage was noticed in the pH range of 4.0 and 7.0. The adsorption pattern of Cd²⁺ shows that adsorption was more effective at higher pH and the optimum adsorption pH of Cd²⁺ by the produced adsorbent was at pH 7.0 [9, 10]. This increase of Cd²⁺ adsorbed may be due to the fact that more phenolic hydroxyls could be ionized at higher pH range, resulting in stronger reaction activity with Cd²⁺. Moreover, at low pH, more

protons are present in the solution, protons will compete with the anionic Cd^{2+} for the available adsorption sites and reduced the adsorption percentage. Adsorption at higher pH (more than pH 8.0) was not encouraged due to the precipitation of cadmium hydroxide (excessive OH^- ions in the aqueous solution forms hydroxyl complexes of cadmium). Thus, to represent the removal of Cd^{2+} from the aqueous solution by the produced adsorbent is an adsorption process, pH 7.0 as the optimum adsorption pH was used for the following experiments.

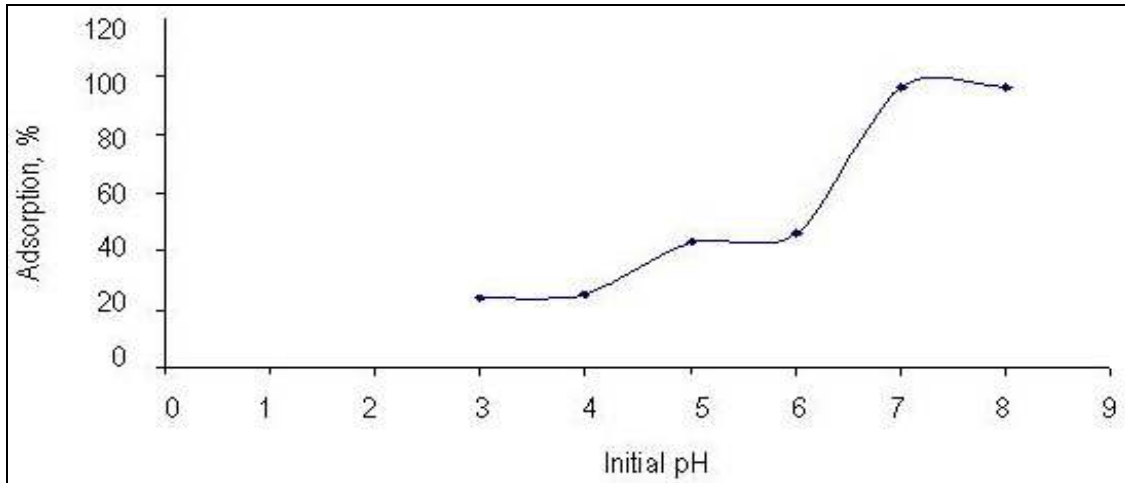


Fig. 3: Adsorption of Cd^{2+} onto TBA at pH ranged from 3.0 to 8.0.

Desorption of Cd^{2+} from the loaded TBA was studied at pH ranged from 3.0 to 8.0. Fig. 4 shows that the highest desorption percentage (82.68%) was achieved when the initial pH of the solution was 4.0. It is noticed from the graph that the desorption percentage decreases as the pH is shifted above or below this value. At pH 3.0, the desorption percentage was lower than at pH 4.0. We have yet not been understood exactly about this phenomenon. Sudden decrement in desorption percentage was noticed at pH 5.0 with a value of 6.91%. Low desorption percentage was recorded at pH 6.0, 7.0 and 8.0. At pH 7.0, the desorption percentage was 0.0%, indicating that at this pH TBA adsorbed Cd^{2+} effectively. The results showed that, desorption of Cd^{2+} from TBA was more effective at lower pH with optimum desorption pH of 4.0.

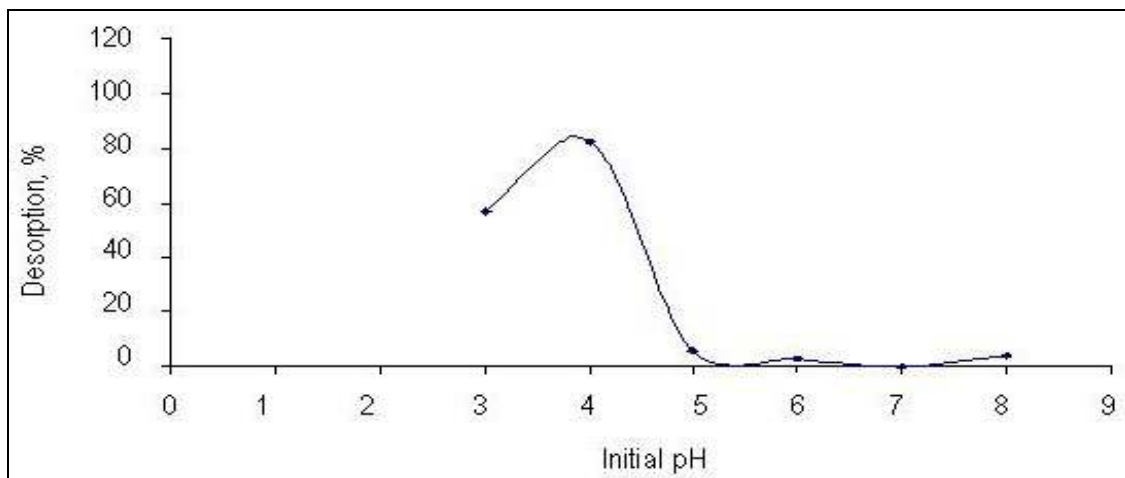
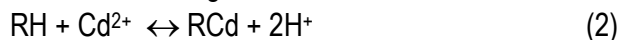


Fig. 4: Desorption of Cd^{2+} from loaded TBA at pH ranged from 3.0 to 8.0.

The performance of TBA on adsorption and desorption of Cd²⁺ was affected by the pH of the solution containing the ions. The adsorption and desorption data was well illustrated by the stoichiometric equation for ionic exchange between H⁺ and Cd²⁺ as shown in Eq. (2):



where, RH represents the produced adsorbent. Once the initial pH of the solution containing Cd²⁺ was low (acidic), the reaction shifted to the left of Eq. (2) and Cd²⁺ was desorbed from TBA. Meanwhile, when the solution was basic, the reaction shifted to the right of Eq. (2) and Cd²⁺ was adsorbed onto TBA. In Fig. 1(b), the weaker intensity of peak 1384 cm⁻¹ indicated that H⁺ was dissociated from the hydroxyl functional group when Cd²⁺ was adsorbed onto TBA. This confirms that adsorption of Cd²⁺ onto TBA is an ion-exchange process.

For different heavy metal ions, the optimum adsorption pH may be very different as the metals may possess different properties with regard to the acidity of the solution [10]. Thus, pH of the solution containing the ions is adjusted to the desired value to maximize the adsorption percentage. The adsorption rate of a heavy metal element adsorbed by a tannin-based adsorbent also varies with the pH of the solution containing the heavy metal ions. Adsorbent having adsorbed heavy metal ions is regenerated by contacting the adsorbent with dilute mineral acid to elute the heavy metal ions when the adsorbing ability of the tannin-based adsorbent is lowered [11].

Effect of initial concentration of Cd²⁺ on the adsorption capacity

Effect of initial concentration of Cd²⁺ on the adsorption capacity was studied. From Fig. 5, the adsorption percentage decreased with increasing initial concentration of Cd²⁺ at a constant adsorbent dosage. This was due to the limited adsorption sites, at higher concentration of Cd²⁺, all the active sites on the adsorbent were occupied. The adsorption equilibrium data was also studied by Langmuir, Freundlich, Sips and Dubinin-Raduskhevich (D-R) isotherms to evaluate the nature of adsorption of Cd²⁺ onto TBA as shown in Table 1, Fig. 6 and 7. Non-linear regression analysis was applied to determine the fitness of isotherms to the experimental data. The goodness-of-fit was measured by the values of correlation coefficient (r), and residue root mean square error (RMSE), where the smaller the value indicate the better curve fitting [12].

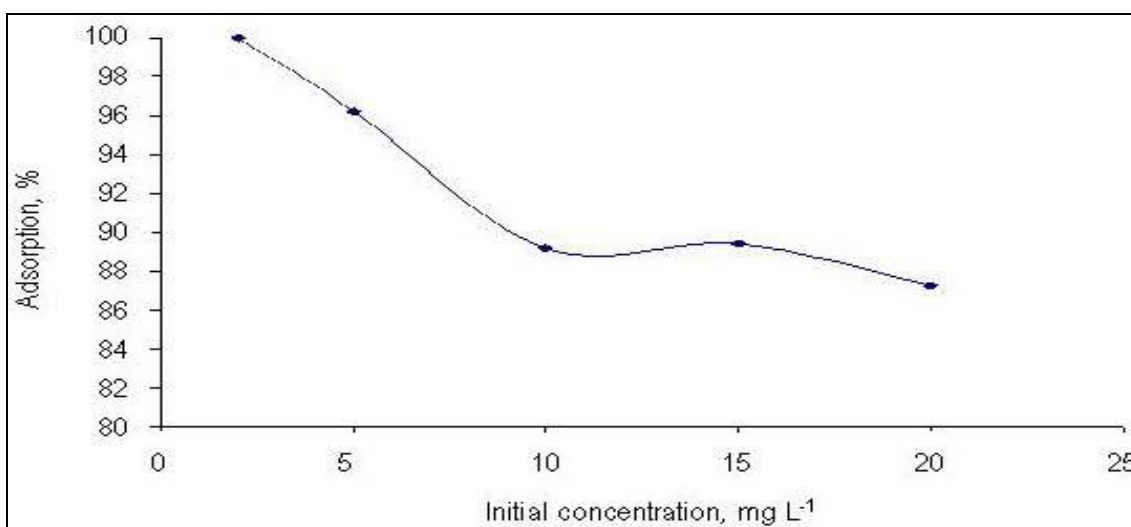


Fig. 5: Effect of initial concentration of Cd²⁺

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

Parameter	Langmuir	Freundlich	Sips	D-R
K_L	0.3944	-	-	-
V_m	17.41	-	-	-
K_f	-	5.182	-	-
$1/n$	-	0.5571	-	-
b	-	-	0.0919	-
$1/n$	-	-	0.5841	-
q_m	-	-	19.00	-
Q_m	-	-	-	0.0076
K	-	-	-	0.00617
E	-	-	-	9.00
r	0.9819	0.9886	0.9845	0.9913
RMSE	0.6842	0.5447	0.7772	2.92×10^{-5}

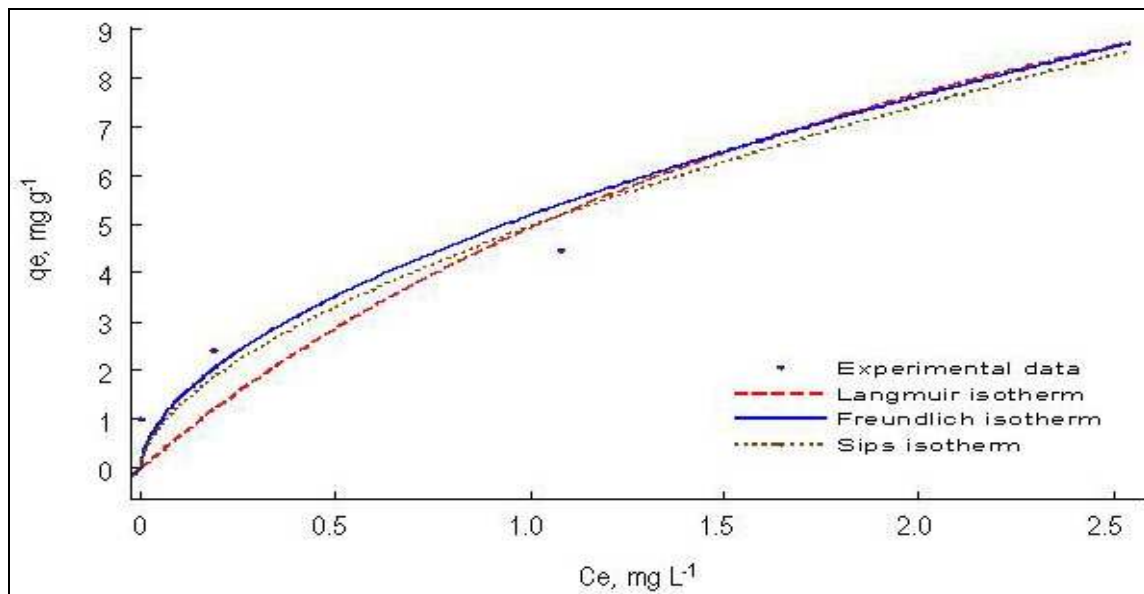


Fig. 6: Adsorption isotherms of Cd²⁺ onto TBA.

Langmuir isotherm

Langmuir isotherm describes monolayer adsorption on homogeneous surface of the adsorbent with negligible interaction between the adsorbed molecules [10]. The Langmuir isotherm is given by:

$$q_e = \frac{V_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where q_e is amount of Cd²⁺ adsorbed/gram of adsorbent (mg g⁻¹), C_e is equilibrium concentration of Cd²⁺, K_L is the sorption equilibrium constant and V_m corresponds to the monolayer adsorption capacity (mg g⁻¹). TBA showed high monolayer adsorption capacity of Cd²⁺ with the value of 17.41 mg/g. The Langmuir isotherm fitted to the experimental data with r value of 0.9819 and K_L equal to 0.3944 l/mg.

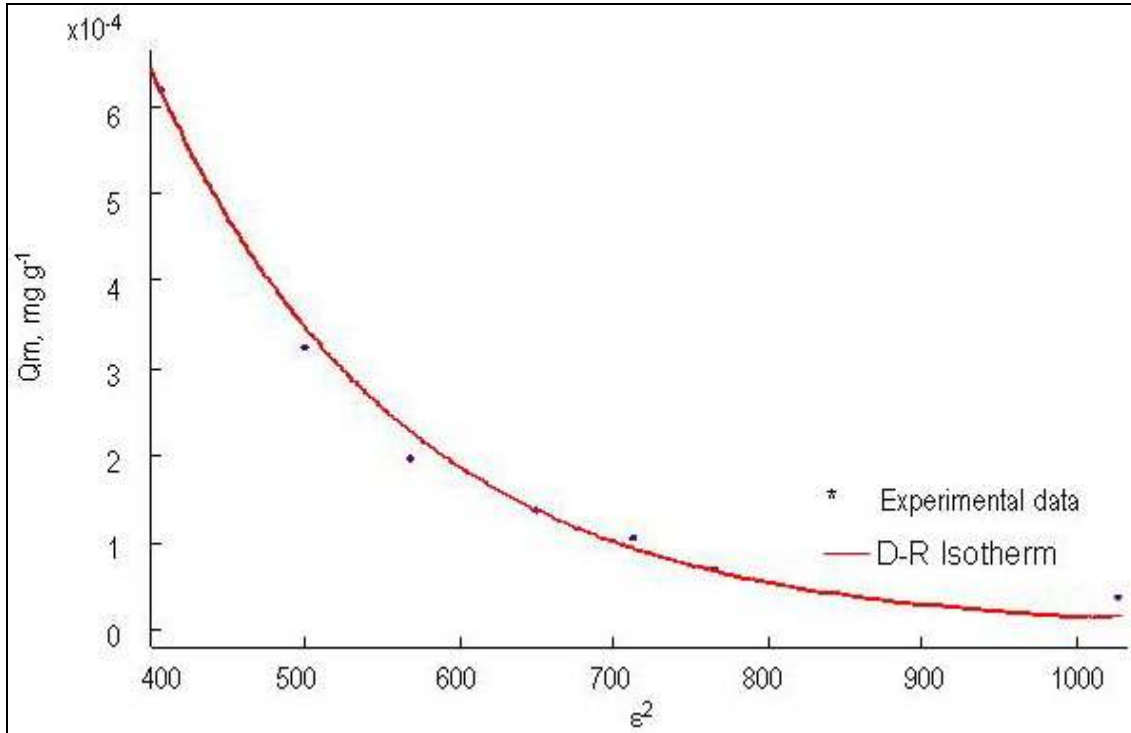


Fig. 7: Dubinin-Raduskevich (D-R) isotherm.

Freundlich isotherm

Freundlich isotherm describes monomolecular layer coverage of solute on the adsorbent [13]. It assumes adsorption on heterogeneous surface or surfaces supporting sites of varied affinities [4, 12]. The isotherm is given as:

$$q_e = K_f C_e^{1/n} \quad (4)$$

where K_f is the Freundlich constant which corresponds to the adsorption capacity was found to be 5.182 mg g⁻¹. Heterogeneity of the adsorbent was confirmed with the value of $1/n$ is in between 0 and 1 [4].

Sips isotherm

Sips isotherm [14] also known as Langmuir-Freundlich model is the combination of both previous models with equation:

$$q_e = \frac{q_m (bC_e)^{1/n}}{1 + (bC_e)^{1/n}} \quad (5)$$

where q_e is the total binding sites, b is the median association constant and $1/n$ indicates degree of heterogeneity. Non-linear regression analysis showed that Sips isotherm fitted to the

experimental data with r value of 0.9845. Value of $1/n$ which is 0.5841 ($\ll 1$) agreed with Freundlich isotherm that indicate heterogeneous adsorption of Cd^{2+} onto TBA.

D-R isotherm

Dubinin-Raduskhevich (D-R) isotherm does not assume homogeneous adsorption or constant sorption potential is a more general model compare to Langmuir isotherm [15]. The D-R isotherm is given as:

$$Q = Q_m \exp(-K\varepsilon^2) \quad (6)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

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^2/kJ^2) and ε is the Polanyi potential. The mean energy of adsorption, E is used to estimate the type of adsorption reaction and can be calculated from the equation:

$$E = \frac{1}{\sqrt{2K}} \quad (8)$$

from the isotherm, it was found that E has the value of 9.00 kJ/mol which is within the range of ion-exchange reaction, 8 – 16 kJ/mol [15].

CONCLUSIONS

Tannins extracted from mangrove bark of *Bruguiera sexangula* Poir species can be modified into insoluble tannins gel by using formaldehyde in the basic solution of ammonia. The produced insoluble tannins gel can act as an effective adsorbent for Cd^{2+} due to the present of many adjacent phenolic hydroxyl groups in their structures. The structure exhibits the partially exfoliated and intercalated. Adsorption and desorption of Cd^{2+} was strongly affected by the initial pH of the solution containing the ion. At high pH, adsorption of Cd^{2+} was dominant, in which the optimum adsorption pH of Cd^{2+} by the produced adsorbent was 7.0. At lower pH, the ability of the adsorbent to adsorb Cd^{2+} was reduced and Cd^{2+} was desorbed from the adsorbent at an optimum desorption pH of 4.0. The sorption equilibrium data was reasonably fitted to both Langmuir and Freundlich isotherms with adsorption capacity of 17.41 mg g^{-1} .

Acknowledgements: Financial support of this work by the Vietnam Research Fund (No. VRF-19-03-BT-0007) is gratefully acknowledged. The authors thank Prof. Ernst Anders for helpful discussion and their contributions to the work reviewed in this article

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