ABSTRACT

Tannins extracted from the mangrove barks of Rhizophora apiculata species were modified into tannins-based adsorbent (TBA) by using formaldehyde in the basic solution of ammonia. The produced adsorbent showed high efficiency in removal of Cu$^{2+}$ from the aqueous solution. Effect of adsorption parameters like initial adsorption pH, initial desorption pH and initial Cu$^{2+}$ concentration were studied in batch experiments. The optimum adsorption pH of Cu$^{2+}$ was at pH 7.0 with an adsorption percentage of 96.20%. Meanwhile, 82.68% of Cu$^{2+}$ 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-Raduskevich (D-R) isotherms to the experimental data at equilibrium. TBA showed high monolayer adsorption capacity of 17.41 mg of Cu$^{2+}$/gram of adsorbent. Mean energy of adsorption, $E$ calculated from D-R isotherm showed that adsorption of Cu$^{2+}$ on TBA followed ion-exchange mechanism.

Keywords: Rhizophora apiculata; mangrove; Tannins-based adsorbent; Adsorption; Desorption; Cu$^{2+}$.

INTRODUCTION

There has lately been a growing interest in biosorbents, especially tannins-based adsorbent for removing a low concentration of heavy metal ions from aqueous solutions [1 - 4]. The tannin compounds containing polyhydroxyphenyl groups have a high affinity for heavy metal ions such as cadmium, cobalt, chromium and uranium [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 Rhizophora apiculata species, which is a by-product of charcoal industry in Malaysia. The extracted tannins then will be immobilized by polymerization using formaldehyde as a cross-linking agent to produce tannins-based adsorbent. The optimum adsorption and desorption pH and adsorption isotherms of this tannins-based adsorbent towards Cu$^{2+}$ were characterized and evaluated.

EXPERIMENTAL SECTION

Materials and Methods
Tannins extraction
The bark wastes of Rhizophora apiculata 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 Rhizophora apiculata 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 tannins-based adsorbent, TBA
Tannins-based adsorbent was prepared based on the optimum volume of the basic solution of ammonia. 1.000 g of tannins was added into 6.25 ml of 13.3 N aqueous ammonia, and was 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.

**Determination of optimum pH for adsorption and desorption of Cu\(^{2+}\)**

Copper (II) ions solutions with a concentration of 5.0 ppm 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 was 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 Cu\(^{2+}\) being adsorbed.

In the desorption study, TBA with adsorbed Cu\(^{2+}\) 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 two hours. After shaking, the solutions were filtered and the filtrates were analyzed with AAS to determine the amount of Cu\(^{2+}\) being desorbed.

**Determination of optimum adsorption capacity of Cu\(^{2+}\)**

50.00 ml of Cu\(^{2+}\) solutions with concentrations of 2.0, 5.0, 10.0, 15.0 and 20.0 ppm 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 Cu\(^{2+}\) being adsorbed and calculated by mass balance equation as below: 

\[ q_e = \frac{(C_i - C_e)V}{m} \]  

where \(q_e\) is the amount of Cu\(^{2+}\)-adsorbed/gram of adsorbent (mg/g), \(C_i\) and \(C_e\) are concentration of Cu\(^{2+}\) at initial and equilibrium respectively (mg/l), \(V\) 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 tannins-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

| 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**           |                 |                 |                 | 9.0              |
| **r**           | 0.9819          | 0.9886          | 0.9845          | 0.9913          |
| **RMSE**        | 0.6842          | 0.5447          | 0.7772          | 2.92 x 10^{-5}  |

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.
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].

**Optimum adsorption and desorption pH of Cu\(^{2+}\)**

The effectiveness of the produced tannins-based adsorbent in the adsorption of Cu\(^{2+}\) was studied at pH ranged from 3.0 to 8.0 with the initial concentration of 5.0 ppm of Cu\(^{2+}\) solution. Fig. 2 shows that the adsorption of Cu\(^{2+}\) 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 Cu\(^{2+}\) shows that adsorption was more effective at higher pH and the optimum adsorption pH of Cu\(^{2+}\) by the produced adsorbent was at pH 7.0 [9, 10]. Adsorption at higher pH (more than pH 8.0) was not encouraged due to the precipitation of copper hydroxide.

Desorption of Cu\(^{2+}\) from the loaded TBA was studied at pH ranged from 3.0 to 8.0. Fig. 3 shows that the highest desorption percentage (82.68%) was achieved when the initial pH of the solution was 4.0. 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 Cu\(^{2+}\) effectively. The results showed that desorption of Cu\(^{2+}\) from TBA was more effective at lower pH with optimum desorption pH of 4.0.

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

\[
\text{RH} + \text{Cu}^{2+} \leftrightarrow \text{RCu} + 2\text{H}^+ \quad (2)
\]

where, RH represents the produced adsorbent. Once the initial pH of the solution containing Cu\(^{2+}\) was low (acidic), the reaction shifted to the left of Eq. (2) and Cu\(^{2+}\) was desorbed from TBA. Meanwhile, when the solution was basic, the reaction shifted to the right of Eq. (2) and Cu\(^{2+}\) 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 Cu\(^{2+}\) was adsorbed onto TBA. This confirms that adsorption of Cu\(^{2+}\) 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 tannins-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 tannins-based adsorbent is lowered [11].
**Optimum adsorption capacity of Cu$^{2+}$**

Effect of initial concentration of Cu$^{2+}$ on the adsorption capacity was studied. From Fig. 4, the adsorption percentage decreased with increasing initial concentration of Cu$^{2+}$ at a constant adsorbent dosage. This was due to the limited adsorption sites, at higher concentration of Cu$^{2+}$, all the active sites on the adsorbent were occupied. The adsorption equilibrium data was also studied by Langmuir, Freundlich, Sips and Dubinin-Radushkevich (D-R) isotherms to evaluate the nature of adsorption of Cu$^{2+}$ onto TBA as shown in Table 1, Fig. 5 and 6. 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].

**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:

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

(3)

where $q_e$ is amount of Cu$^{2+}$ adsorbed/gram of adsorbent (mg/g), $C_e$ is equilibrium concentration of Cu$^{2+}$, $K_L$ is the sorption equilibrium constant and $V_m$ corresponds to the monolayer adsorption capacity (mg/g). TBA showed high monolayer adsorption capacity of Cu$^{2+}$ 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.
Figure 6. Dubinin-Raduskhevich (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:

\[ q_e = K_f C_f^{1/n} \]  

(4)

where \( K_f \) is the Freundlich constant which corresponds to the adsorption capacity was found to be 5.182 mg/g. 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:

\[ q_e = q_m b C_e^{1/n} \left( 1 + b C_e^{1/n} \right)^{-1} \]  

(5)

where \( q_m \) 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 (<< 1) agreed with Freundlich isotherm that indicate heterogeneous adsorption of Cu\(^{2+}\) 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:

\[ Q = Q_m \exp(-KE^{-\varepsilon}) \]

\[ \varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \]

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 \( \varepsilon \) 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:

\[ E = \frac{1}{\sqrt{2K}} \]

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 Rhizophora apiculata 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 Cu\(^{2+}\). Adsorption and desorption of Cu\(^{2+}\) was strongly affected by the initial pH of the solution containing the ion. At high pH, adsorption of Cu\(^{2+}\) was dominant, in which the optimum adsorption pH of Cu\(^{2+}\) by the produced adsorbent was 7.0. At lower pH, the ability of the adsorbent to adsorb Cu\(^{2+}\) was reduced and Cu\(^{2+}\) 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 of Cu\(^{2+}\)/gram of tannins-based adsorbent.

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