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Utilization of *m*-Phenylenediamine-Furfural Resin for Removal of Cu(II) from Aqueous Solution-A Thermodynamic Study

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Abstract: *m*-Phenylenediamine was condensed with furfural in absence of catalyst at room temperature. The produced *m*-phenylenediamine-furfural resin was used for the removal of Cu(II) from aqueous solution. The pH for the optimum removal of Cu(II) was 6. The negative values of Gibbs free energy at low concentration of Cu(II) (20, 30 ppm) indicative of the spontaneous adsorption process, while, at higher Cu(II) concentration (40,50 ppm) the positive and weak values of ΔG° indicate that the process is feasible but non spontaneous. The values of ΔH° were positive indicating that the sorption process is endothermic. On the other hand, the values of activation energy (E_a) were inconsistent with the values of ΔH° both are positive and lie in the range of physisorption. The entropy ΔS° of the process was positive indicative of the randomness of the Cu(II) ions at the solid / liquid interface. The values of sticking probability S^* were less than one which indicate a preferable adsorption process and the mechanism is physisorption.

Keywords: *m*-Phenylenediamine-furfural resin, Thermodynamic parameters, Sticking probability.

Introduction

Industrial and mining wastewaters are important sources of pollution of heavy metals¹. Copper is used extensively by electrical industries, in fungicides and in anti - fouling paints. When copper is ingested at high concentrations it can become toxic to humans, causing cancer and promoting oxidation. The present method for removal of Cu is to precipitate copper hydroxide by liming process. But with this process, residual Cu remain a problem². Owing to their wide use, the efficient removal of toxic metal ions from wastewater is an important and widely studied research area where a number of technologies have been developed over the years³. The most important of these methods include filtration, chemical precipitation, ion exchange, adsorption, electrodeposition and membrane systems. All these

approaches have their inherent advantages and limitations. Although filtration and chemical precipitation are low - cost and effective in removing large quantities of metal ions quickly, neither is capable of removing trace levels of metal ions. Adsorption is also ineffective at very low concentration of metal ions. Ion exchange can be used to reduce metal concentrations to region of part per million. Chelating resins provide a dramatic improvement in ion selectivity relative to traditional ion exchange resins but still suffer from two distinct drawbacks: slow metal uptake kinetics and limited operating pH range. On the other hand, chelating polymer resins are found to be more selective by nature^{4,5} as compared to other conventional techniques⁶⁻¹² in the removal of metal ions. The objective of the present work is to evaluate the thermodynamic parameters like ΔH° , ΔG° , ΔS° and activation energy E_a for the adsorption of Cu(II) onto *m*-phenylenediamine-furfural resin and prediction the mechanism of the adsorption process.

Experimental

Preparation of m-phenylenediamine-furfural resin(phdm-fu)

The condensation of *m*-phenylenediamine and furfural was carried out in the absence of catalyst, according to the procedure for preparation of *m*-aminophenol-furfural resin¹³ as follows: A mixture of *m*-phenylenediamine (0.04 mol, 4.32 g), freshly distilled furfural (0.04 mol, 3.84 g) and water (1 mL) was stirred at room temperature for 15 minutes. The mixture was converted to a solid mass, washed with 100 mL of distilled water then crushed and purified by dissolving in dimethyl sulfoxide (DMSO) and precipitated by addition to distilled water. The solid resin was filtered and dried under reduced pressure at 40 °C for 24 h.

Metal solutions

Metal stock solutions containing Cu(II) with a concentration of 500 ppm was prepared by dissolving 1.9005 g of $\text{Cu}(\text{NO}_3)_2$ in 1 L of deionized water. This solution was used for further experimental solution preparation. Analytical grade reagents were used throughout this study. The pH values of Cu(II) solutions were measured by pH meter type Hana, 301 instruments. The residual copper in the sorption solutions was determined by atomic absorption spectrophotometer type (A Analyst 200 Perkin Elmer).

Thermodynamic study

The thermodynamic experiments were carried out at different temperatures (15, 25, 35 and 45 °C) by shaking the phdm-fu resin 1 g/L with 50 mL of Cu(II) 20, 30, 40 and 50 ppm solutions for 120 minutes at pH 6. The amount of Cu(II) adsorbed onto the resin, q_e mg/g was calculated using the following equation:

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

Where: V = Volume of equilibrated solution.

M = The weight of the resin used

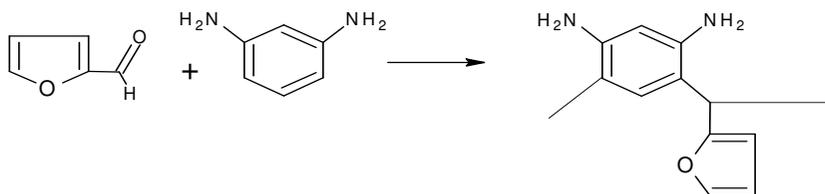
C_i = Initial concentration of Cu(II).

C_e = Equilibrium concentration of Cu(II).

Results and Discussion

Preparation and characterization of phdm-fu resin

The condensation of *m*-phenylenediamine with furfural was carried out without catalyst at room temperature for 15 minutes due to high reactivity of *m*-phenylenediamine.



Scheme 1.

The FTIR Spectrum of phdm-fu is shown in Figure 1, the figure shows an adsorption band at 3348 cm^{-1} belong to stretching vibration NH_2 group and absorption band of 3117 cm^{-1} for (C-H) stretching vibration of furan ring. The two adsorption bands at 1595 and 1626 cm^{-1} belong to the aromatic (C=C). The UV-Visible spectrum of Phdm-Fu resin was another support for the structure of Phdm-Fu resin, the absorption peak of 286 nm belong to $\pi\text{-}\pi^*$ transition for aromatic groups and that at 319 nm belong to $n\text{-}\pi^*$ transition for amine group. **Nitrogen analysis:** Calculated for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2$; N, 15.05 found 14.5%. The resin was soluble in DMSO, the intrinsic viscosity $[\eta]=5.1 \times 10^{-2}\text{ dL./g}$, softening point, 112-120, color, dark brown. The maximum pH of adsorption was 6.0 and the time required to attain the equilibrium was 120 minutes.

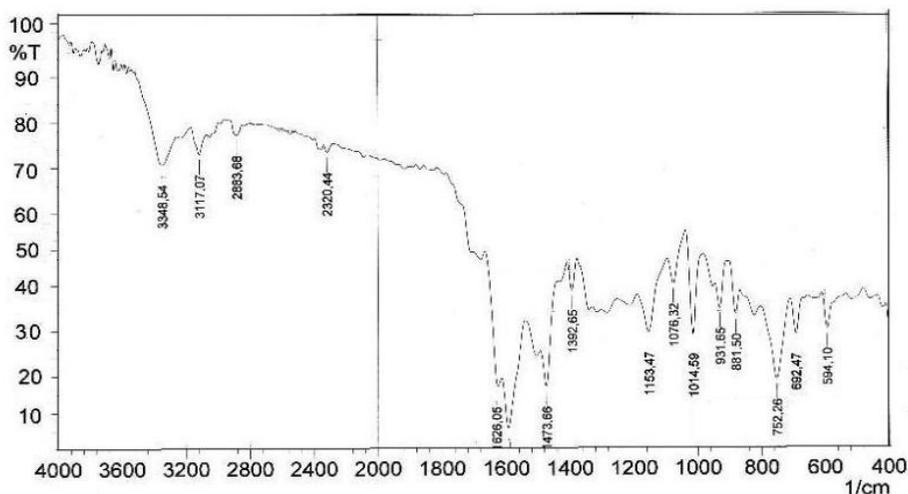


Figure 1. FTIR spectrum of phdm-fu.

Thermodynamic study

In order to determine the thermodynamic feasibility and the thermal effects of the sorption, the Gibbs free energy (ΔG^0), the entropy (ΔS^0) and the enthalpy (ΔH^0) were calculated using the following equation¹⁴⁻¹⁸.



$$K_0 = \frac{[\text{Cu}]_{\text{solid}}}{[\text{Cu}]_{\text{liquid}}} \quad (3)$$

$$\Delta G^0 = -RT \ln K_0 \quad (4)$$

$$\log K_0 = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (5)$$

Where, K_o is the equilibrium constant, $[Cu]_{solid}$ is the concentration of Cu, ppm, at the phdm-fu resin at equilibrium, $[Cu]_{liquid}$ is the liquid phase concentration of Cu, ppm, T is the absolute temperature (K) and R is the ideal gas constant. ΔS^0 and ΔH^0 can be obtained from the application of equation (5). The plot of $\log K_o$ as a function of $1/T$ (Figure 2) should give a liner relationship with slope of $\Delta H^0/2.303R$ and an intercept of $\Delta S^0/2.303R$. ΔG^0 is obtained at any temperature from equation (3). The plot of $\log K_o$ versus $1/T$ (Figure 2) gives effectively a liner relationship; the values of ΔS^0 , ΔH^0 and ΔG^0 are presented in Table 1. The positive and weak values of ΔG^0 indicates that the process is feasible but non spontaneous specially at higher concentration of Cu (40 and 50 ppm), but at lower concentration of Cu (20 and 30 ppm) the adsorption process was spontaneous. On the other hand, the values of ΔH^0 is positive, indicating that the sorption process is endothermic, the range of ΔH^0 values (Table 1), indicate that the mechanism of adsorption is physical and the positive values of ΔS^0 indicate that the adsorption lead to randomness at the solid/liquid interface.

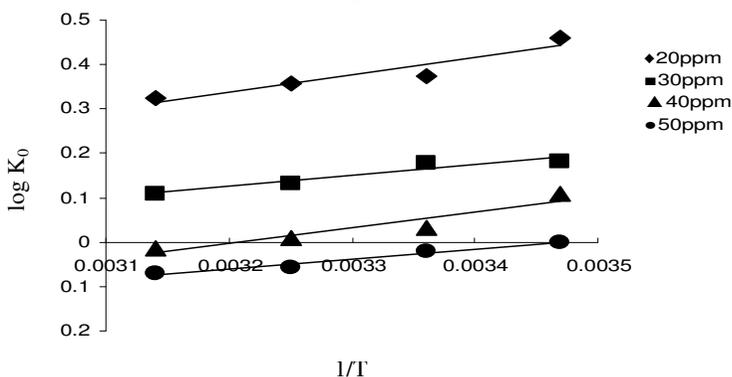


Figure 2. Plot of $\log K_o$ versus $1/T$ for the removal of Cu by phdm-fu resin at different temperature.

Table 1. Thermodynamic parameters for the removal of Cu by phdm-fu resin, 2 g/L.

Cu(II) Con. ppm	ΔH^0 kJ/mol ⁻¹	ΔS^0 J.mol ⁻¹ K ⁻¹	ΔG^0 kJ/mol ⁻¹				R ²
			15	25	35	45	
20	7.35	31.54	-1.79	-2.04	-2.2	-2.8	0.8886
30	4.67	18.32	-0.603	-0.75	-1.056	-1.129	0.9144
40	6.73	22.89	+0.074	+0.059	+0.195	+0.656	0.9043
50	4.30	13.5	+0.394	+0.322	+0.127	+0.004	0.9788

The other parameters which can be calculated from the experimental data are, the activation energy (Ea) and sticking probability (S^*), these two parameters can give further support for the involvement of physical adsorption mechanism in the removal of Cu(II) by phdm-fu resin. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows¹⁴⁻¹⁸.

$$\theta = 1 - \frac{C_e}{C_i} \quad \text{or} \quad \frac{C_e}{C_i} = 1 - \theta \tag{6}$$

$$S^* = (1 - \theta) e^{\frac{-E_a}{RT}} \tag{7}$$

$$\ln S^* = \ln(1-\theta) - \frac{Ea}{RT} \quad (8)$$

$$\ln(1-\theta) = \ln S^* + \frac{Ea}{RT} \quad (9)$$

The sticking probability (S^*), is a function of the adsorbent / adsorbate system under investigation, its value lies in the range $0 < S^* < 1$ for preferable process and is dependent on the temperature of the system^{19,20}. The plot of $\ln(1-\theta)$ against $1/T$, (Figure 3) should give a straight line with slope of Ea/R and an intercept of $\ln S^*$. The values of Ea were comparable with ΔH^0 which are also positive, (Table 2), indicate the endothermic nature of the adsorption process and the values lie in the range of physisorption.

The values of sticking probability for the adsorption of Cu(II) onto phdm-fu resin were less than one, (Table 2), indicates that the probability of Cu(II) ions to stick on surface of phdm-fu resin is high as $S^* \ll 1$ these values confirm that the sorption process is physisorption.

Table 2. Sticking probability and activation energy for the adsorption of Cu(II) onto phdm-fu resin.

Cu(II) conc. ppm	Ea kJ/mol ⁻¹	S^*	R^2
20	5.22	0.037	0.882
30	2.727	0.140	0.9138
40	3.54	0.117	-0.8937
50	2.06	0.23	0.9785

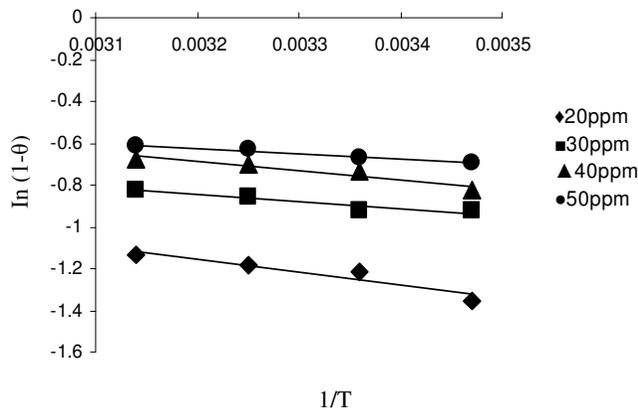


Figure 3. Plot of $\ln(1-\theta)$ versus $1/T$ for the removal of Cu by phdm-fu resin at different temperature.

Conclusion

This study confirm that the phdm-fu resin can remove Cu(II) ions from aqueous solution specially at low concentrations. The pH for optimum removal was 6. The values of ΔH^0 and E_a were positive and lie in the range of physical adsorption. Sticking probability values were less than one which indicates a preferable process and physisorption mechanism. The free energy values indicate that the process is spontaneous at low Cu(II) concentration and non spontaneous at high concentration but the process is feasible.

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