

# Equilibrium and Kinetic Studies on Adsorption of Copper from Aqueous Solution by Neem (*Azadirachta Indica*) Bark Powder

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## ABSTRACT

Adsorption of copper (II) from aqueous solution by neem bark powder (NBP) has been investigated in the present work. All the experiments were performed under batch mode technique. Copper (II) removal is maximum at the pH: 5, adsorbent dose: 0.9 g/50 ml, contact time: 90 min and initial copper (II) ion concentration: 62.5 mg/lit. The correlation coefficient values for the adsorption isotherms: Freundlich, Langmuir, Temkin and Dubinin-Radushkevich are 0.632, 0.719, 0.760 and 0.907 respectively and for kinetic models: pseudo-first order, pseudo-second order and intraparticle diffusion equations are 0.992, 0.994 and 0.991 respectively. Langmuir maximum adsorption capacity,  $q_{max}$ , Temkin heat of sorption, B, and the Dubinin-Radushkevich mean free energy, E, for NBP are 10.30 mg/g, 1.180 J/mol and 0.68 KJ/mol.

**Keywords :** Neem bark powder, Dubinin-Radushkevich, Langmuir, Adsorption

## I. INTRODUCTION

Copper has been known as one of the most common toxic heavy metal, which spreads to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the nonferrous metal industry, the printing and photographic industries and metalworking and finishing processes [1, 2]. Copper is a 3d block transition series element with three common oxidation states:  $Cu^0$  (metal),  $Cu^+$  (cuprous ion),  $Cu^{2+}$  (cupric ion). Among the three species cupric ion is the most toxic to the living organism. Major toxic and detrimental effect of copper includes damage to heart, kidney, liver, pancreas, brain, intestinal distress and anemia [3]. The World Health Organization (WHO) recommended a maximum permissible concentration of copper (II) in drinking water of 1.5 mg /lit [4] however in India acceptable limit is 3 mg/lit [5]. Therefore, the concentrations of copper (II) ions must be reduced to levels that satisfy environmental

regulations for various bodies of water before discharging into the water streams. Numerous processes are available for removing heavy metal ions from water and wastewater including chemical precipitation, ion-exchange, electrochemical deposition, solvent extraction, membrane filtration and adsorption. Among these, adsorption is one of the most economically favorable and technically simple method [6]. Activated carbon is known to be one of the best effective adsorbent for the removal of heavy metals [7, 8]. However, high cost of commercially available activated carbon and loss during the regeneration hamper its applicability in developing countries. Hence, there is a growing need for the discovery of alternative adsorbent to replace the costly activated carbon. Several researchers have tested different variety of adsorbents such as sawdust [9], fly ash [10], baggase [11], activated carbon-zeolite composite [12], zeolite A [13], fertilizer plant waste slurry [14], modified clay [15], biosorbents like cassava waste [16], Areca [17], Lentil shell [18], Pine cone

powder [19], Spent grain [20], crushed brick [21], alluvial soil of Bhagirathi river [22], Neem bark powder [23] etc. for the removal of copper ions from aqueous medium.

In the present study, adsorption of copper (II) ions from aqueous solution is investigated by a non-conventional finely ground neem bark powder (NBP). The main aim of this study is to examine the combined effect of different operating parameters like initial copper (II) concentration, adsorbent dose, pH and contact time on the removal of copper (II) ions from the aqueous solutions using neem bark powder. Adsorption kinetics and isotherms parameters were also evaluated and presented.

## II. METHODS AND MATERIAL

### A. Adsorbent collection and development

The brown colored neem (*A. indica*) bark used in the present work was collected from local wood shop. The collected *A. indica* bark was initially washed with deionised water to remove dirt particles and water soluble impurities. The washing process was continued till the wash water contains no colour. The washed *A. Indica* bark was then initially sun-dried for 10 days followed by drying in hot air oven at  $383 \pm 1$ K for 24 h. The dried bark was then cut into small pieces and powdered using local mixer grinder. The product was sieved to give a fraction of 150 mesh screen and finally stored in sterile, closed glass bottles until required. The developed powder is designated as NBP (neem bark powder).

### B. Reagents and chemicals

All the chemicals used were of analytical reagent grade procured from E. Merck Ltd., India and double distilled water was used throughout this study for the preparation of different solutions. Stock solution of copper (II) ions (100 ppm) was prepared by dissolving

0.3929 g copper sulphate penta hydrate in double distilled water and was suitably diluted as per the need. The range in concentrations of copper (II) ions prepared from standard solution varied between 25 and 100 mg/lit. Before addition of biosorbent, 0.1 M NaOH or 0.1 (M) HCl solutions were used for fixing the pH of each copper solution to the desired pH.

### C. Biosorbent characterization

The physico-chemical properties of NBP were obtained from previous studies [24]. Atomic absorption spectrophotometer (Model No. GBC HG3000) is used for estimation of residual copper (II) ions. For stirring purpose, magnetic stirrer (TARSONS, Spinot digital model MC02, CAT No. 6040, S. No. 173) issued. The Fourier transform infrared (FTIR) spectra and scanning electron microscopy (SEM) of NBP were also obtained from previous study on copper adsorption by NBP [23].

### D. Batch adsorption experiments

The influence of initial copper concentrations (25-100 mg/lit), NBP dosage (0.05-0.9 g/50 ml), pH (2.0-8.0) and contact time (5-90 min) was investigated for the biosorption of copper onto NBP. The experiments were optimized at the desired metal concentration, biosorbent dose, pH, and contact time using 50 mL of copper (II) test solution in 250 mL Erlenmeyer flask. All the experiments were conducted at a constant temperature 33°C. The solution pH was adjusted with 0.1 M HCl and 0.1 M NaOH. Samples were collected from the flasks at predetermined time intervals for analyzing the residual copper (II) concentration in the solutions. The amount of copper (II) ions adsorbed onto NBP was obtained by using the following mass balance equation:

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

Where  $q_e$  (mg/g) is the sorption capacity;  $C_i$  and  $C_e$  are the copper (II) ion concentrations (mg/lit) in the initial solution and after biosorption, respectively;  $V$  is

the volume of adsorbate in liter and  $m$  is the amount of the dry biosorbent (g). The percentage removal of copper (II) ions was calculated from the following expression:

$$\text{Removal}(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

All the experiments were performed in triplicate and the average values were recorded.

### III. RESULTS AND DISCUSSION

#### A. Characterization of adsorbent

The physico-chemical properties of neem bark powder (NBP) are as follows- Ash content :12.70 %, Bulk density ( $\text{g}/\text{cm}^3$ ): 0.563,  $\text{pH}_{\text{zpc}}$ : 6.80, Surface area ( $\text{m}^2/\text{g}$ ): 328.1, Volatile matter (%): 87.28, C (%): 43.23, H (%): 4.39, N (%): 0.93.

Previous work on the FTIR spectrum of NBP showed the presence of -OH stretching, methylene C-H asymmetric stretching, Carboxylate group, P-O-C stretching, C-O stretching and C-Cl stretching vibration [23].

The above results suggested that copper ions may interact with -O-H, carboxylate group and phosphate group present on the NBP surface.

Furthermore SEM micrograph indicated the porous, coarse and rough morphology of the prepared NBP biosorbent [23] thus making it possible for the adsorption of copper (II) on different parts of the adsorbent.

#### B. Adsorption isotherms

To examine the relationship between the adsorbate concentration in the aqueous phase and that on the adsorbent surface at a given condition at equilibrium various isotherm models were employed for fitting the data. In the present study, Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) models were used to describe the equilibrium data.

#### Freundlich adsorption isotherm:

The Freundlich isotherm is an empirical model that considers non-ideal adsorption on heterogeneous surfaces. The linearized form of the isotherm can be represented as [25]:

$$\log q_{\text{eq}} = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where,  $q_{\text{eq}}$  is equilibrium adsorption capacity ( $\text{mg}/\text{g}$ ),  $K_F$  ( $\text{mg}/\text{g}$ ) and  $n$  ( $\text{L}/\text{g}$ ) are the Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. Where,  $K_F$  and  $1/n$  can be calculated from the linear plot of  $\log q_{\text{eq}}$  versus  $\log C_e$  (Fig. not shown). The evaluated constants are given in Table 1.

#### The Langmuir isotherm model:

The Langmuir isotherm model assumes that adsorption takes place at specific homogeneous sites on the surface of the adsorbent by monolayer formation without interaction between adsorbed molecules. The linear form of the equation can be expressed as [26]:

$$\frac{1}{q_{\text{eq}}} = \frac{1}{q_{\text{max}} K_L C_e} + \frac{1}{q_{\text{max}}} \quad (4)$$

Where  $C_e$  ( $\text{mg}/\text{L}$ ) is the equilibrium concentration of copper (II),  $q_{\text{eq}}$  ( $\text{mg}/\text{g}$ ) is the amount of copper adsorbed per unit mass of biosorbent,  $q_{\text{max}}$  ( $\text{mg}/\text{g}$ ) is the monolayer biosorption capacity of the biosorbent, and  $k_L$  ( $\text{L}/\text{mg}$ ) is the Langmuir equilibrium constant related to energy of adsorption, respectively. Where  $q_{\text{max}}$  and  $k_L$  can be determined from the linear plot of  $1/q_{\text{eq}}$  vs  $1/C_e$  (Fig. not shown). The shape of the Langmuir isotherm can be used to predict whether a sorption system is favorable or unfavorable in a batch adsorption process. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant referred to as the separation

factor ( $R_L$ ) that can be calculated by the following equation [27].

$$R_L = \frac{1}{1 + K_L C_i} \quad (5)$$

where  $C_i$  (mg/lit) is the initial concentration of adsorbate and  $K_L$  (L/mg) is the Langmuir equilibrium constant already described above. The  $R_L$  parameter provides important insights about the nature of adsorption. The value of  $R_L$  indicated the type of Langmuir isotherm to be either irreversible ( $R_L=0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L=1$ ) or unfavourable ( $R_L > 1$ ). Furthermore, when  $K_L > 0$ , adsorption is also favorable [28]. The evaluated constants for the isotherm model are given in Table 1.

#### The Temkin isotherm model:

The Temkin isotherm [29] takes into account the adsorbent-adsorbate interactions and is based on the assumption that the free energy of sorption is a function of the surface coverage. The linear form of the Temkin isotherm is represented as:

$$q_e = B \ln A + B \ln C_e \quad (6)$$

Where  $RT/b_T = B$  (J mol/mol), which is the Temkin constant related to the heat of adsorption whereas  $A$  (L/g) is the equilibrium binding constant (L/min) corresponding to the maximum binding energy.  $T$  (K) is the absolute solution temperature and  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>). A plot of  $q_e$  versus  $\ln C_e$  enables the determination of constants  $A$  and  $B$ .

#### The Dubinin-Radushkevich isotherm model:

In order to get information about the energy needed for adsorption and mechanisms the Dubinin-Radushkevich isotherm model [30] is used. This model does not assume a homogeneous surface or a constant sorption potential. The linear form of D-R isotherm equation is represented as:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (7)$$

Where  $q_m$  is the theoretical adsorption capacity (mol/g),  $\beta$  (mol<sup>2</sup>/J<sup>2</sup>) is a constant related to the average energy of adsorption per mole of the adsorbate as it is transferred to the surface of the solid from infinity in the solution, and  $\epsilon$  is the polanyi potential, which is expressed as:

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (8)$$

where,  $C_e$  (mg/L) is the equilibrium concentration of adsorbate in solution,  $R$  (J mol<sup>-1</sup> K<sup>-1</sup>) is the universal gas constant and  $T$  (K) is the absolute temperature. The D-R constants  $q_m$  and  $\beta$  were calculated from the linear plots of  $\ln q_e$  versus  $\epsilon^2$ . The mean sorption energy  $E$  (kJ/mol) of adsorption can be calculated from the following relationship [22]

$$E = \frac{1}{\sqrt{2\beta}} \quad (9)$$

The mean adsorption energy ( $E$ ) calculated from the D-R isotherm provides information about the adsorption mechanism. If the magnitude of  $E$  is between 8 and 16 kJ/mol, the sorption process is supposed to proceed via chemisorption, while for values of  $E < 8$  kJ/mol, the sorption process is of physical nature [22].

#### C. Error analysis

In this study four different error functions of non-linear regression basin [sum of the square of the errors (SSE), sum of the absolute errors (SAE) and chi-square ( $\chi^2$ )] were employed to find out the best-fit isotherm model to the experimental equilibrium data.

SSE is given as:

$$SSE = \sum_{i=1}^n (q_{e,estm} - q_{e,exp})_i^2 \quad (10)$$

Here,  $q_{e,estm}$  and  $q_{e,exp}$  are, respectively, the estimated and the experimental value of the equilibrium adsorbate solid concentration in the solid phase (mg/g), and  $n$  is the number of the data point.

SAE is given as:

$$SAE = \sum_{i=1}^n |q_{e,estm} - q_{e,exp}| \quad (11)$$

Chi-square ( $\chi^2$ ) is given as:

$$\chi^2 = \sum_{i=1}^n \left[ \frac{(q_{e,exp} - q_{e,estm})^2}{q_{e,estm}} \right]_i \quad (12)$$

The respective values are given in the Table 1.

**Table 1:** Adsorption isotherm constants for adsorption of copper (II) onto NBP

Adsorption isotherms	Parameters		$R^2$	$\chi^2$	SSE	SAE
Langmuir isotherm	$q_{max}$ (mg/g)	10.30	0.719	1.346	4.987	3.369
	$K_L$ (L/mg)	0.089				
Freundlich isotherm	$K_F$ (mg/g) (L/mg) <sup>1/n</sup>	1.380	0.632	0.809	1.752	2.034
	$n$	2.32				
Temkin isotherm	$B$ (J/mol)	1.180	0.760	0.568	1.285	1.728
	$A$	2.83				
D–R isotherm	$q_m$ (mg/g)	5.15	0.907	0.25	0.768	1.37
	$\beta$ (mol <sup>2</sup> /kJ <sup>2</sup> )	1.074				
	$E$ (kJ/mol)	0.68				

As shown in Table 1, the Dubinin–Radushkevich isotherm showed good fit to the experimental equilibrium adsorption data than the Langmuir, Freundlich, and Temkin isotherm equation for copper (II) sorption according to the values of  $R^2$ ,  $\chi^2$ , SSE, and SAE. It was also seen from Table 1 that the Langmuir maximum adsorption capacity ( $q_{max}$ ) is 10.30 mg/g and the equilibrium constant  $K_L$  is 0.089 L/mg. The separation factor ( $R_L$ ) values are 0.310, 0.152 and 0.101 while initial Copper (II) concentrations are 25, 62.5 and 100 mg/lit, respectively. All the  $R_L$  values were found to be less than one and greater than zero indicating the favourable sorption of copper (II) onto NBP. The Freundlich constant  $K_F$  indicates the sorption capacity of the sorbent and the value of  $K_F$  is 1.380 mg/g. Furthermore, the value of 'n' at equilibrium was 2.32. The value of  $n$  between 1 and 10 represents a favourable adsorption [31]. From D–R isotherm, the value of the adsorption energy was found to be 0.68 kJ/mol. The estimated value of  $E$  for

the present study was found in the range expected for physical adsorption (Table 1). Thus, the sorption of Copper (II) on the surface of NBP was physisorption in nature. The effectiveness of NBP as an adsorbent for copper adsorption was also compared with other reported adsorbents. The maximum adsorption capacity obtained in this study is comparable with other adsorbents as shown in Table 2.

**Table 2:** A comparisons of maximum adsorption capacities for copper ions by different adsorbents

Adsorbent	$q_{max}$ (mg/g)	pH	T (K)	Reference
Sphagnum peat moss	12.60	5	298	[29]
Neurospora crassa	12.30	5	298	[32]
Modified carrot residue	8.74	5.2	293	[33]

Puracite C-104 ion-exchange resin	7.92	4.5	298	[34]
Modified oak sawdust	3.60	4	313	[35]
Potato peels	0.38	6	303	[36]
Periwinkle shell carbon	0.07	8	NA	[37]
Powdered limestone	0.29	7	298	[38]
A. Spinosus	0.206	N A	NA	[39]
ASBR	0.63	6	313	[22]
Sawdust	1.79	-	-	[40]
Neem bark powder (NBP)	10.33	5	313	This study

#### D. Adsorption Kinetics Modelling

In order to analyze the rate of adsorption and possible adsorption mechanism of copper onto NBP, The Lagergren first order [41], pseudo-second-order [42] and Intraparticle diffusion [43] models were applied to adsorption data.

##### The pseudo-first-order kinetic model:

The Lagergren first order rate equation is represented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (13)$$

Where  $q_e$  and  $q_t$  are the amounts of copper adsorbed (mg/g) at equilibrium and at time  $t$ , respectively and  $k_1$  is the Lagergren rate constant of first order adsorption ( $\text{min}^{-1}$ ). Values of  $q_e$  and  $k_1$  at different concentrations were calculated from the slope and

intercept of the plots of  $\log(q_e - q_t)$  versus  $t$  (Fig. not shown). The respective values are given in the Table 3.

##### The pseudo-second-order kinetic model:

The pseudo-second-order kinetic model which is based on the assumption that chemisorption is the rate-determining step can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

where  $k_2$  is the rate constant of second order adsorption (g/mg/min). Values of  $k_2$  and  $q_e$  were calculated from the plots of  $t/q_t$  versus  $t$  (Fig. not shown). The respective constant values are given in Table 3.

##### The intraparticle diffusion model:

The kinetic results were analyzed by the Weber and Morris intraparticle diffusion model to elucidate the diffusion mechanism. The model is expressed as:

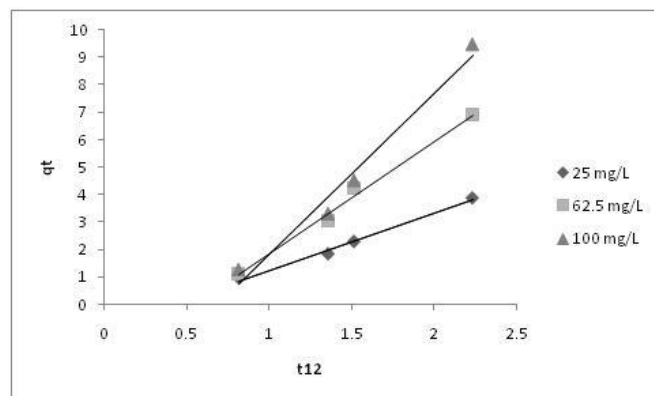
$$q_t = K_d t^{1/2} + I \quad (15)$$

Where  $I$  is the intercept and  $K_d$  is the intra-particle diffusion rate constant. The intercept of the plot reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step. Fig. 1 presents intra-particle plot for copper (II) onto NBP. The calculated diffusion coefficient  $K_d$  values are listed in Table 3. The  $K_d$  value was higher at the higher concentrations. Intraparticle diffusion is the sole rate-limiting step if the regression of  $q_t$  versus  $t^{1/2}$  is linear and passes through the origin. In fact, the linear plots at each concentration did not pass through the origin. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the sorption. This indicated the existence of some boundary layer effect and further showed that intraparticle diffusion was not the only rate-limiting step.

**Table 3:** Kinetic parameters for adsorption of copper (II) onto NBP

Kinetic model	parameters	Concentration of copper (II) solution		
		25 mg/L	62.5 mg/L	100 mg/L
	$q_{e,exp}$ (mg/g)	1.281	3.315	4.527
Pseudo-first-order	$k_1$ (min <sup>-1</sup> )	0.020	0.043	0.055
	$q_{e,cal}$ (mg/g)	0.488	2.648	4.446
	$R^2$	0.965	0.992	0.988
Pseudo-second-order	$k_2$ (g/mg <sup>-1</sup> min <sup>-1</sup> )	0.139	0.022	0.012
	$q_{e,cal}$ (mg/g)	1.329	3.745	5.347
	$R^2$	0.994	0.994	0.991
Intraparticle diffusion	$K_d$ (mg/g.min <sup>1/2</sup> )	2.068	4.115	5.878
	I	0.811	2.265	4.027
	$R^2$	0.991	0.991	0.974

It is clear from the Table 3 that the pseudo- second-order kinetic model showed excellent linearity with high correlation coefficient ( $R^2 > 0.99$ ) at all the studied concentrations in comparison to the other kinetic models. In addition the calculated  $q_e$  values also agree with the experimental data in the case of pseudo-second-order kinetic model. Therefore it could be concluded that the rate-limiting step of copper (II) adsorption onto NBP may be chemisorption. It is also evident from Table 3 that the values of the rate constant  $k_2$  decrease with increasing initial copper (II) concentrations. This is due to the lower competition for the surface active sites at lower concentration but at higher concentration the competition for the surface active sites will be high and consequently lower sorption rates are obtained.



**Figure 1:** Intraparticle diffusion model for adsorption of copper onto NBP (experimental conditions: adsorbent dose: 0.9 g/ 50 mL, pH: 5.0, Temperature: 313K).

#### IV. CONCLUSION

In this study, neem bark powder (NBP) was tested and evaluated as a possible adsorbent for removal of copper from aqueous solution using batch sorption mode. The maximum removal was found at pH 6.0. Equilibrium data fitted very well in the Dubinin-Radushkevich isotherm model, indicating that adsorption of copper onto NBP seems to be physisorption. The adsorption kinetics followed pseudo-second-order kinetic model with a good correlation. Intra-particle diffusion was not the sole rate controlling factor.

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