ISSN 2229-5518

Modeling of Copper Ions Adsorption on chemically modified Bio-waste material

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Abstract –Biowaste materials obtained from *Azadirachta indica* plant have shown potential towards adsorption of heavy metals like copper. In this work, Cu (+2) ion was adsorbed from synthetically made copper salt solution on chemically activated Neem sawdust (*Azadirachta indica*). Effect of Initial concentration of copper ions on percent removal and adsorption capacity was studied at four concentrations viz. 25, 50, 75 and 100 mg L^{-1} at constant adsorbent loading of 4 g L^{-1} and stirring speed of 150 rpm. The high value of adsorption capacity of 21.875 mg Cu (+2) per gram of adsorbent was obtained at 100 mg L^{-1} at 301K. Three different equilibrium isotherms namely Freundlich, Langmuir and Temkin were fitted and the best models representing the experimental results were founded as Langmuir and Temkin models with regression coefficients as 93 and 92% , respectively where Langmuir model represents monolayer adsorption of copper ions and Temkin model confirms the physical adsorption by the heat of adsorption b=288.04 J. mol^{-1}. The Kinetics of the adsorption process was best described by pseudo first order.

Index Terms— Wastewater. Copper. Adsorption. Isotherm. Kinetics.

1 Introduction

Industrialization and technological advancements have increased our standards of living, but at the same time, causing threats to our environment [1, 2]. Pollution pertaining to air, water and land has become a great matter of concern. Discharge of organic and inorganic impurities in surface water creates the water pollution and that causes harmful effects to humans as well as the environment [3]. Heavy metals are one of the pollutants creating detrimental effects when discharged in wastewater like chromium, lead, nickel, cadmium, zinc and copper [4, 5]. Among these metals Cu is commonly found in the wastes of mining and smelting, brass manufacture, electroplating industries and petroleum refining and causing toxic effects as it is non-biodegradable and accumulate in human body and the ecosystem in trace amounts[6, 7].

Short term exposure of Cu in water may create gastrointestinal pain, whereas long term exposure may damage liver or kidney. According to US EPA drinking water guidelines MCLG (Maximum Contaminant Level Goal) level should be 1.3 mg L^{-1}.

In previous years different conventional technologies have been applied to reduce the Cu (+2) from wastewater based on chemical and physical methods, such as chemical precipitation, ion exchange and electrolytic recovery. The disadvantages involved with these methods are addition of new chemicals, high amount of sludge formation and pH sensitivity, whereas electrolytic recovery faces corrosion problem to the electrodes [8]. Other methods like membrane filtration, electro-dialysis and photo-catalysis has disadvantages of membrane fouling, high operational cost, high energy consumption with photo-catalysis has been a long time and limited application method. So, to overcome these factors, innovative low cost & effective technology is required and to achieve this target, low cost adsorbent was aimed in the present work by using chemically activated Neem (Azadirachta indica) sawdust as an adsorbent.

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2 REAGENTS AND MATERIALS

All chemicals used in the preparation of synthetic copper solution and detection of copper ions were of Lab reagent grade and purchased from Merck and Rankem, India. Copper content in the residual solution was detected by colorimetric method (Neocuproine reagent) by using UV Visible Spectrophotometer (Varian, Model Cary 50 Bio) where absorbance of the solution was measured at 600 nm. Equipments used for physical characterization of the bio-adsorbents were muffle furnace (Ambassador), oven (Lab Tech. Instruments), Digital balance and Sieve Shaker (PSI Sales Pvt. Ltd).

2.1 Adsorbent Preparation

Neem (*Azadirachta indica*) sawdust was acquired from the local market, washed with water thoroughly to remove water soluble impurities and sun dried for 2-3 days. Afterwards it was placed in the oven at 353K till constant weight of the sample was achieved. Later on, it was activated chemically by treating it with 1N H_2SO_4 at 423K for a day, and then neutralized with sodium bicarbonate [9]. Finally, it was washed with Demineralized water till 7 pH was attained; further chemically activated adsorbent was dried, sieved to 90-125 (µm) and stored in airtight bags. Characteristics of adsorbent prepared by this method are shown in Table 1.

2.2 Adsorption Study

To study the adsorption isotherms and kinetics of adsorption of copper metal ions on chemically activated Neem sawdust, a stock solution of Cu^{+2} (100 mg L^{-1}) was prepared by dissolving 0.251 g of $CuSO_4.5H_2O$ in 1000 ml distilled water. Subsequent concentrations were made by diluting the stock solution in distilled water and a series of copper concentrations were made from 2 to 10 mg L^{-1} with one blank for calibration purpose and respective absorbance was determined by UV-spectrophotometer.

To find out the potential of adsorption of copper ions on Neem sawdust, a batch study was performed, synthetic solution (100 ml) of known copper concentrations (C_o=25 to 100 mg L^{-1}) was taken in an Erlenmeyer flask, 0.4 g L^{-1} of adsorbent was added to this solution and kept stirring at 150 rpm. Reduction in Cu (+2) metal ions with respect to time was noted to study the adsorption Isotherm. Equilibrium and Kinetics pertaining to biosorption were studied by fitting different models and various kinetic parameters were reported at a constant temperature of 301K.

Loading capacity of copper metal ions (mg copper per g of adsorbent) and Percentage Removal of Copper or adsorption efficiency is calculated by following expressions [10]

$$q = [(C_o - C\ ) * V] / M$$

$$PR(\%) = [(C_o - C) / C_o] * 100$$

Where, q = Amount of metal ion adsorbed per gram of biomass, mg g^{-1}

C_o and C = Initial and Equilibrium Copper ion concentrations, mg L^{-1}

V = Volume of solution, L

M = Weight of Biosorbent, g

PR = Percent Removal

Table 1: Adsorbent Characteristics

Parameters	Values
Yield of adsorbent (%)	81
Density (g ml^{-1})	0.21
Moisture content (%)	12
Ash content (%)	80
Mesh size (µm)	90-125

3 RESULT AND DISCUSSION

3.1 Effect of contact time

Removal of copper from aqueous solution was studied as a function of contact time by varying the initial concentration from 25 to 100 mg L^{-1} at a constant temperature of 301K and the constant stirring speed of 150 rpm at a constant adsorbent dosing of 0.4 g L^{-1}. The effect of contact time on percent removal of copper is shown in the Fig.1. From the figure it was observed that 62% of copper was removed in first 10 minutes for initial copper concentration of 25 mg L^{-1} and time to decrease the same percent increased up to 30 minutes when we go gradually to higher initial concentration of 100 mg L^{-1}, thereafter, the adsorption rate become practically very slow or starts decreasing. The difference in the degree of adsorption may be due to the fact that in the beginning all the sites on the surface of the adsorbent were vacant and the solute concentration gradient was relatively high [1].

3.2 Effect of Initial Cu (+2) Concentration

Fig. 1 shows the effect of initial concentrations of copper on percent removal (PR %) of Cu (II) metal ions. A batch adsorption experiment was conducted at initial copper concentrations of 25, 50, 75 and 100 mg L^{-1} by keeping constant temperature of 301K. It was observed that Percent Removal of copper decreased as we increase the initial copper concentration, i.e. 100, 92.3, 88.88 and 87.5% respectively as shown in Fig. 3.

Whereas in Fig. 2 the effect of initial concentrations of copper metal ions on adsorbent loading q (mg Cu (II) adsorbed/g adsorbent) showed a different trend and according to this adsorbed amount increased from 6.25, 11.53, 16.67 and 21.87 mg g^{-1} for 25, 50, 75 and 100 mg L^{-1} of initial Copper concentration respectively. This behavior of Copper adsorbate ions and adsorbent may be explained because of the fact that the high initial concentration of copper ions provides the high driving force to prevail over different mass transfer resistances of the copper ions from the liquid phase to the solid phase.

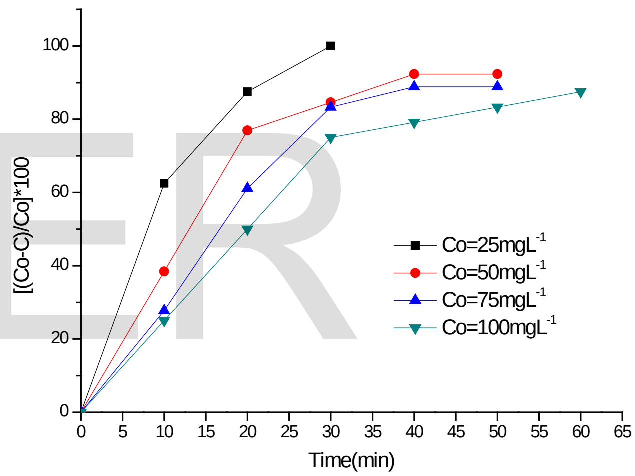

Fig.1: Percent Removal of Copper metal ions at different Initial concentrations of Copper (C_o)

3.3 Adsorption Isotherms

Adsorption Equilibria of copper ion removal by chemically activated adsorbent made from *Azadirachta indica* was studied by modeling three adsorption isotherms namely Freundlich, Langmuir and Temkin Isotherm.

Freundlich Isotherm model equation is nonlinear and extensively used from old times and it represents the heterogeneity of adsorption sites and can be applied to multilayer adsorption. The Freundlich equation is expressed in linear form as [11]

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f$$

Where q_e is equilibrium adsorption capacity (mg g^{-1}) at an equilibrium concentration of C_e (mg L^{-1}) and K_f (mg g^{-1}) and

1/n represents adsorption capacity and adsorption intensity respectively. A large value of n (or lower values of 1/n) implies the strong interaction between copper metal ions and adsorbent. The ideal value of n should lie between 1 and 10 [11].

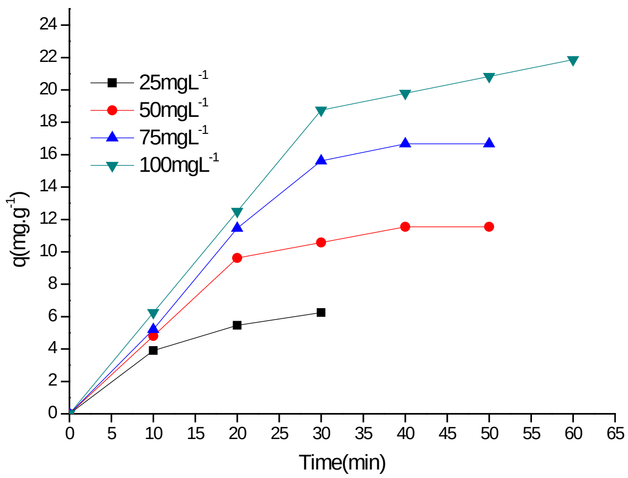

Fig. 2: Effect of Initial Copper Concentration on adsorption capacity at 301K

The Langmuir adsorption equation assumes that maximum adsorption is related to a saturated monolayer of solute molecules on the adsorbent surface and ensures that no lateral interaction between the adsorbed molecules takes place [12]. Non-linear form of Langmuir model can be written as

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e}$$

Where q_m (mg g^{-1}) and K_l (L mg^{-1}) are the Langmuir constants that corresponds to the maximum adsorption capacity and energy of adsorption respectively. A plot of 1/qe vs. 1/Ce gives the measure of these constants [11, 13].

Temkin Isotherm assumes that the declination in the heat of adsorption as a function of temperature is linear one rather than logarithmic, as also implied in the Freundlich equation [11].

A linear form of the Temkin equation can be expressed as [12]:

$$q_e = \frac{RT}{b} \ln a + \frac{RT}{b} \ln C_e$$

Where b is Temkin constant related to heat of sorption (J mol^{-1}) and a is the Temkin Isotherm constant (L g^{-1}).

To test the validity of all three models, uptake capacity q_e (mg g^{-1}) was predicted by Freundlich, Langmuir and Temkin models and plotted with experimental values on same graph showing q_e vs. equilibrium concentration C_e (mg L^{-1}) shown in Fig. 4. Isotherms explained in above equations were modeled by using Excel 2007 Solver Tool. Parameters of Freundlich model, Langmuir model and Temkin model are summarized in Table 2.

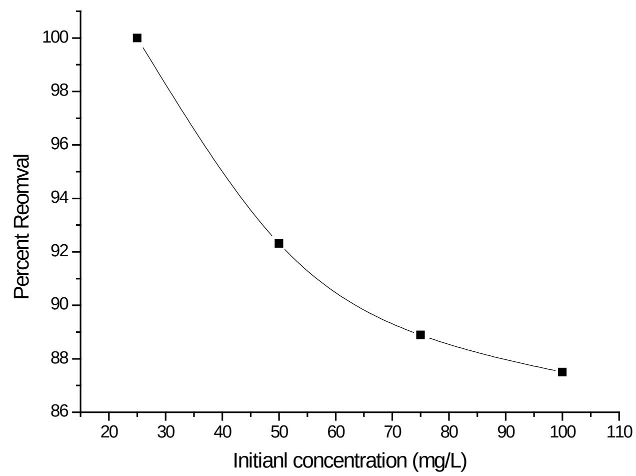

Fig.3: Percent removal of Copper shown at different initial Cu (II) concentrations

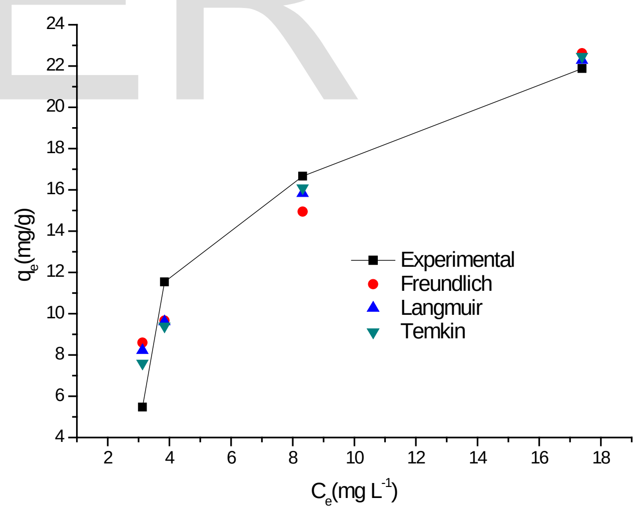

Fig. 4: Adsorption Isotherms at 301K and 4 gm L^{-1} of adsorbent dose.

A value of the regression coefficient (R^2) for Freundlich, Langmuir and Temkin model was found as 0.887, 0.919 and 0.933 respectively. Thus, it is concluded that the best models resembling the experimental data for the removal of copper on Neem sawdust are Temkin and Langmuir model.

Indirect interaction between adsorbate/adsorbate molecules on adsorption Equilibria was taken in account by Temkin and Pyzhev. The reason explained by them was reduction in heat of adsorption of the molecules in the layer

Table 2: Linear regression data for Langmuir and Freundlich isotherms for copper adsorption

	Freundlich			Langmuir			Temkin		
Estimated Parameters	K_f (L mg^{-1})	1/n	R^2	q_{max} (mg g^{-1})	k_l (L mg^{-1})	R^2	a (L g^{-1})	b (J mol^{-1})	R^2
Values	4.526	0.563	0.89	35.58	0.0962	0.92	0.769	288.04	0.93

with coverage linearly [12]. After fitting the model, Temkin constant "b" pertaining to the heat of adsorption and Temkin isotherm constant "a" was found to be 288.04 J mol^{-1} and 0.769 L g^{-1} respectively at absolute temperature of 301 K, where the value of Temkin constant b represents the physical adsorption. The high value of the regression coefficient for Langmuir isotherm indicates the monolayer adsorption of molecules. The q_{max} value and k_l value obtained after model fitting was found to be 35.58 (mg g^{-1}) and 0.0962 (L mg^{-1}) respectively.

3.4 Adsorption Kinetics

A kinetic study plays a vital role to an adsorption process because it determines the uptake of adsorbate and finds the mechanism of adsorption and rate controlling step. A number of kinetic models are used to explain the mechanism of adsorption processes. In the present work, pseudo first order, second order and the intra-particle diffusion kinetic models are tested in the adsorption process.

A pseudo first order equation can be written in a linear form as [14]:

$$\ln(q_e - q_t) = \ln(q_e) - k_t t$$

Where q_e is equilibrium copper uptake and q_t is adsorbate loading at time t expressed in mg g^{-1}. k_t is the pseudo first order time constant having units of $time^{-1}$.Values of k_t were calculated by a plot between ln (q_e-q_t) verses time at different initial Cu (+2) concentration as shown in Fig.5

The linear form of the pseudo second order model is written according to the following equation [12]:

$$\frac{t}{q_t} = \left[\frac{1}{2} K' q_e{}^2\right] + \frac{t}{q_e}$$

Where q_e is the mass of metal adsorbed at equilibrium (mg g^{-1}), q_t the mass of metal adsorbed at time t (min) and K' is the pseudo-second-order rate constant of adsorption (mg g^{-1} min). Values of K' and q_e were evaluated by using linear form of pseudo-second order equation by calculating intercept and slope at different initial Copper concentrations (25-100 mg L^{-1}) respectively shown in Fig. 6.

Where q_e is the mass of metal adsorbed at equilibrium (mg g^{-1}), q_t the mass of metal adsorbed at time t (min) and K' is the pseudo-second-order rate constant of adsorption (mg g^{-1} min). Values of K' and q_e were evaluated by using linear form of pseudo-second order equation by calculating intercept and slope at different initial Copper concentrations (25-100 mg L^{-1})

To recognize the diffusion mechanism, the kinetic results were

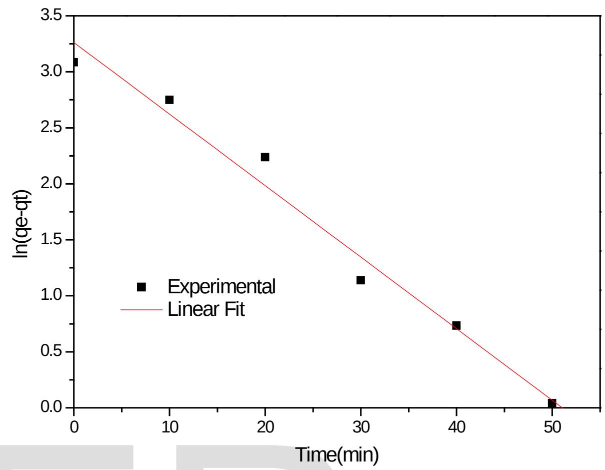

Fig.5: Pseudo first order Kinetics

analyzed by means of the intra-particle diffusion model to explain the diffusion mechanism, which is represented as [6]

$$q = k_d t^{0.5}$$

Where q (mg g^{-1}) is the quantity adsorbed at time t ($min^{0.5}$) and K_d is the intra-particle rate constant (mg g^{-1} $min^{0.5}$). This model suggests that, if the intra-particle diffusion is the only rate determining step, then the plots of q against $t^{0.5}$should be linear and pass through the origin (Fig. 7). The slope of the linear part was used to derive the intra-particle rate constant, K_d.

Different values of K and correlation coefficients R^2 for all three models at all four concentrations are summarized in Table 3. After observing these values, it is clear that Pseudo first order kinetics is having regression coefficients > 95% at almost all concentrations and hence represents the best fit among three.

4. CONCLUSION

Aim of batch adsorption study shown here was to analyze the potential of *Azadirachta indica* as an adsorbent and to explore its capability against removal of heavy metal like copper and model its experimental values with three isotherms. By analyzing data, it is concluded that chemically activated adsorbent obtained from Neem sawdust have the potential to reduce the Copper metal ions from the wastewater at all four tested concentrations viz. 25, 50, 75 and 100 mg L^{-1}.

ISSN 2229-5518

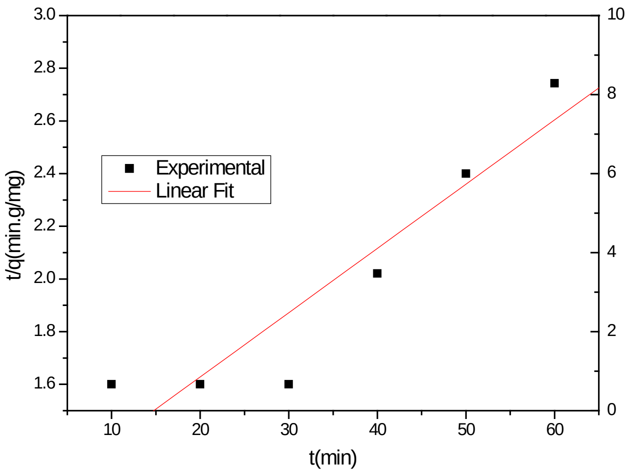

Fig.6: Pseudo Second Order Kinetics

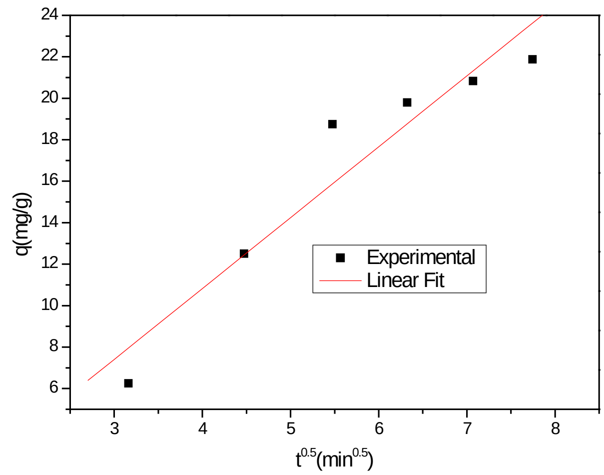

Fig.7: Intra Particle Diffusion

Experimental value		Pseudo-First-order			Pseudo-second-order			Intra-particle Diffusion	
Concentration (mg L^{-1})	q_{exp} (mg g^{-1})	q_e (mg g^{-1})	K_t (min^{-1})	R^2	q_e (mg g^{-1})	$K^/$ (mg $g^{-1}min^{-1}$)	R^2	k_d (mg $g^{-1}min^{-0.5}$)	R^2
25	6.25	6.37	0.104	0.99	8.92	0.035926	0.99	1.021	0.99
50	11.53	12.76	0.087	0.98	20.40	0.006656	0.90	2.081	0.90
75	16.66	22.22	0.091	0.91	62.50	0.000815	0.55	3.744	0.96
100	21.87	26.10	0.063	0.98	41.66	0.001313	0.88	3.418	0.91

Table 3: Pseudo-first-order, Pseudo-second-order and Intra-particle Diffusion kinetic model constant

It was observed from the equilibrium data that as we go on increasing the initial copper concentration from 25 to 100 mg L^{-1}, percent removal goes on decreasing from 100 to 87.5%, whereas uptake capacity goes on increasing from 6.25 to 21.875 mg Cu (II)/g of adsorbent. The high value of sorption capacity and high percent removal of adsorbate confirms the effectiveness of this work at very low cost on normal temperature of 301K. The best model among the three isotherms was explained by Langmuir isotherms (R^2= 0.92) and Temkin (R^2= 0.93), where the Langmuir model showing monolayer adsorption of Cu (+2) ions on the surface and Temkin confirms the physical adsorption. Kinetic data shown here can be used to scale up and design a wastewater plant.

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