Research Article

Adsorption dynamics of Copper (II) Ion from aqueous solution onto H_2SO_4 Activated carbon prepared from the wood of *Adina cordifolia* Hook

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Abstract

This work deals with the study of adsorption of Cu(II) ion from aqueous solution onto activated Carbon prepared from the wood of Adina Cordifolia Hook activated with Conc.H_2SO_4 (ACHC) under various experimental conditions. Batch mode adsorption experiments were conducted. The characteristics of the ACHC were determined by SEM, XRD, FTIR, BET analysis and pH_{ZPC}. The maximum removal efficiency of Cu(II) ion was70.50% at pH 5. Under the chosen conditions, Experimental data obtained were fitted with linearised forms of Legergren and Ho kinetic models. The Sum of Error Squares Percentage (SSE%) for first order and second order kinetics were3.10& 0.55 respectively. Thus this adsorption followed second order kinetics. The equilibrium adsorption data were analyzed with four isotherm models. Order of best fitting isotherm models were found to be Freundlich>Tempkin>Langmuir >Dubinin Raduskevich. The results in this study indicated that ACHC could be employed as an adsorbent for the removal of Cu(II) ion from an aqueous solution.

Keywords: Adsorption; *Adina Cordifolia* Hook activated carbon (ACHC); Cu(II)ion removal; Kinetics models; Isotherm studies.

1. Introduction

Water pollution caused by toxic heavy metals is a global problem [1]. The removal of heavy metals from the environment is a constantly critical issue because it directly affects public health. Usually, heavy metals can be successfully removed from solution by processes such as chemical precipitation, ion exchange [2,3], cementation [4], coagulation and flocculation [5], complexation, bio sorption [6] and membrane processes [7]. Most of these, however, become inefficient when metal ions are present in trace concentrations [5]. The application of membrane processes, including reverse osmosis and electro dialysis is generally expensive [8]. By contrast, the adsorption technique is simple, effective, and inexpensive, making it a promising alternative to costly removal methods. Recent research regarding adsorption has focused on enhancing the adsorbent's adsorption rate, capacity and selectivity for target metals [9–11], under the premise of lowering cost.

Activated carbon (AC) is a cost-effective adsorbent and has been recognized as an effective technology for the removal of trace heavy metals [12]. Several studies have revealed that AC can be used for heavy metal uptake [9,11,13]. However, the low capacity of simple AC limits its application. Thus, numerous materials, including sulfuric acid [9] and anionic surfactants [11], have been used to increase the loading capacity of AC. The introduction of certain functional groups is the reason for this improvement.

The present work is an attempt in that direction to find an alternate, cheap, green adsorbent. With that objective in mind, we conducted experiments to investigate the potential use of *Adina cordifolia* Hook activated carbon (ACHC) for removal of Cu(II) ions from aqueous solution.

Table: 1.0 Nomenclature

Nomenclature	
C_i	Liquid phase initial concentrations of the adsorbate (mg/L)
C_t	Liquid phase concentrations of the adsorbate at time "t" (mg/L)
C_e	Liquid phase concentrations of the adsorbate at equilibrium (mg/L)
V	Volume of the adsorbate solutions in liter (L)
W	Mass of the adsorbent (g)
q_e	Quantity adsorbed at equilibrium (mg/g)
q_t	Quantity adsorbed at time "t" (mg/g)
T	Time in minutes
Q_e	Amount of solute adsorbed per unit weight of adsorbent (mg/g)
C_e	Equilibrium concentration of solute in the bulk solution (mg/L)
Q_0	Langmuir adsorption efficiency
B	Langmuiradsorption energy
R_L	Langmuirseparation factor
C_0	Initial concentration of the adsorbate
K_f and n	Freundlich constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively
B_1	Tempkin constant related to heat of sorption (J/mol)
K_T	Tempkin equilibrium binding constant
q_D	D-R isothermtheoretical saturation capacity (mg/g)
B	D-R isothermconstant related to the mean free energy
	D-R isotherm polanyi potential
E	D-R isothermmean free energy of adsorption
R	Gas Constant
T	Temperature (K)
k_1	Rate constant of adsorption (l/min)
k_2	Second-order constants
h	Initial adsorption rate (mg/g min)
N	Number of data points

2. Materials and Methods

2.1 Materials:

All the chemicals used for these experiments are of analytical grade. Activated Carbon was prepared from *Adina cordifolia* Hook. $CuSO_4.5H_2O$, complexing reagent used as potassium ferrocyanide purchased from Merck company.

2.2 Preparation of Stock solution:

Stock solution Cu(II) ion solution of 1000 mg/L was prepared by dissolving 0.3929 g of $CuSO_4.5H_2O$ crystals in 1000 mL. While making up 1 ml of HCl was added to avoid the hydrolysis of cupric ions. From this, 100 ppm solution was prepared. 2, 3, 4, 5, 6, 7 and 8 ml of solution are taken in different boiling tubes, to each solution 2 ml of 5% potassium ferrocyanide complexing agent was added to form Reddish brown colour. This solution was diluted to exactly 20 ml using distilled water and the absorbance measured at 620 nm.

2.3 Preparation of Adsorbent:

The activated carbon was prepared from the wood of *Adina cordifolia* Hook. The wood were cut into smaller pieces and soaked in concentrated H_2SO_4 at 1:1 ratio (weight of raw material/volume of acid) for 24 hours and activated at 160°C for 5 hours. The activated carbon was repeatedly washed with distilled water until the pH of the wash water became the pH of the distilled water (nearly 7). The carbon obtained was dried at 110°C for nearly 2 hours to remove the moisture. The above prepared carbon was named ACHC. The prepared carbon were kept in a desiccator for further use.

2.4 *Physico - chemical characteristics of Adsorbent:*

The activated carbon prepared from *Adina cordifolia* Hook was designated as *Adina cordifolia* Hook Carbon (ACHC). The various characteristics of the ACHC determined were collected in the Table: 2.0

Table: 2.0 Physico - chemical characteristics of ACHC

S.No.	Properties	Values
1.	Surface area (BET), m^2/g	356.45
2.	Bulk density, g/mL	0.3841
3.	Particle size (mm)	0.106 -0.212
4.	Moisture content (%)	4,23
5.	pH_{zpc}	6.78
6.	Pore volume, cm^3/g	0.388
7.	Fixed Carbon, %	73.35
8.	Pore size (Pore width), nm	2.363

2.5 Batch Adsorption procedure:

Batch adsorption studies were carried out in 250 mL iodine flasks with 50 mL of the working Cu(II) ion solution of different concentrations ranging from 20 mg/L to 60 mg/L. Known amount of adsorbent was added to the solution. The flasks were agitated at a constant speed of 180 rpm. Samples were collected from the flasks at predetermined time intervals for analyzing the residual Cu(II) ion concentration in the solution. The amount of Cu(II) ions adsorbed in milligram per gram of adsorbent was determined by using the following mass balance equation:

$$q_e = (C_i - C_e)V/W$$

Where C_i and C_e are Cu(II) ion concentrations (mg/L) before and after adsorption, respectively, V is the volume of adsorbate in litre and m is the weight of the adsorbent in grams. The percentage of removal of Cu(II) ions was calculated using the following equation:

$$Removal (\%) = (C_i - C_e)/C_i \times 100$$

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3. Results and Discussion

3.1 Effect of Contact time and initial concentration:

The effect of contact time on percentage removal of Cu(II) ion for different initial concentration have been shown in figure 1. Adsorption of Cu(II) ion from the solution increases with the time and finally attains equilibrium at 80,100 and 120 minutes for the initial concentrations 20,40 and 60 mg/L respectively. The percentage of removal increased with the increase in contact time and decreased with the increase of initial concentration of the Cu(II) ion. However the amount of metal ion adsorbed on the adsorbent increased with the increase of initial concentration of the Cu(II) ion solution [14]. which is depicted in figure 1 and given in table 4
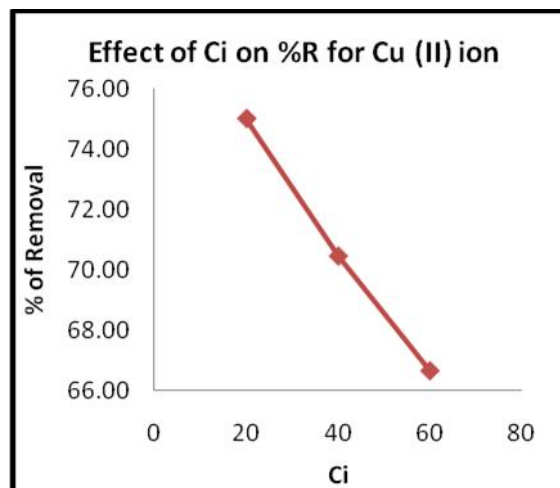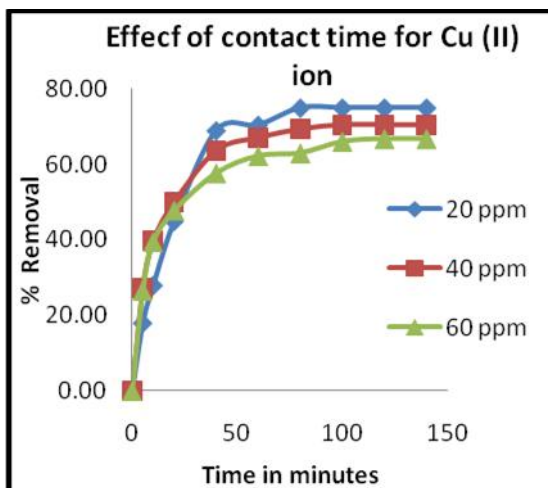
**Figure: 1 Effect of Contact time and Ci onto qe of metal ion adsorbed**

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Table: 4 Percentage of removal of metal ion and amount of metal ion adsorbed

C_i (mg/L)	% of Removal of metal ion at equilibrium	Adsorbed amount of Cu(II)ion at equilibrium (mg/g)
20	75.00	15.00
40	70.45	28.18
60	66.67	40.00

3.2 Effect of pH:

The pH of the adsorbate solutions has been identified as the most important parameter governing sorption of metal ion on different adsorbents. Cu (II) removal by ACHC increases with increase in pH and attains a maximum in the pH range 5.0 to 6.0. Afterwards it was found to decrease. Both adsorption and precipitation processes would have been occurred at pH >6. The decrease in the percentage of removal above the pH 6 might probably be due to the precipitate blocking the adsorbent sites leading to a reduced uptake by adsorption. The influence of pH on Cu(II) removal can be explained on the basis of an electrostatic interaction mode. pH_{zpc} of the ACHC is 6.78.As the pH decreases below the pH_{zpc} of the adsorbent, the surface of the carbon exhibits increasing positive characteristics. Since the species to be adsorbed,

Cu^{2+}, was also positive, the adsorption is not favoured. Besides this, H^+ ions present at a higher concentration in the reaction mixture compete with Cu^{2+} ions for the adsorption sites resulting in the reduced uptake of Cu(II). On the contrary, as pH increases the adsorbent surface becomes more and more negatively charged and therefore the adsorption of positively charged Cu^{2+} and $Cu(OH)^+$ species is more favourable. The mechanism of adsorption of Cu(II) may also be explained based on ion exchange model. A pure carbon surface is considered to be nonpolar, but in actual practice some carbon-oxygen complexes (C_xO, CO_x and C_xO_2) are usually present, which render the surface slightly polar. Since there is no satisfactory method for determining the polar character of the surface quantitatively, the above statement is relative[15].
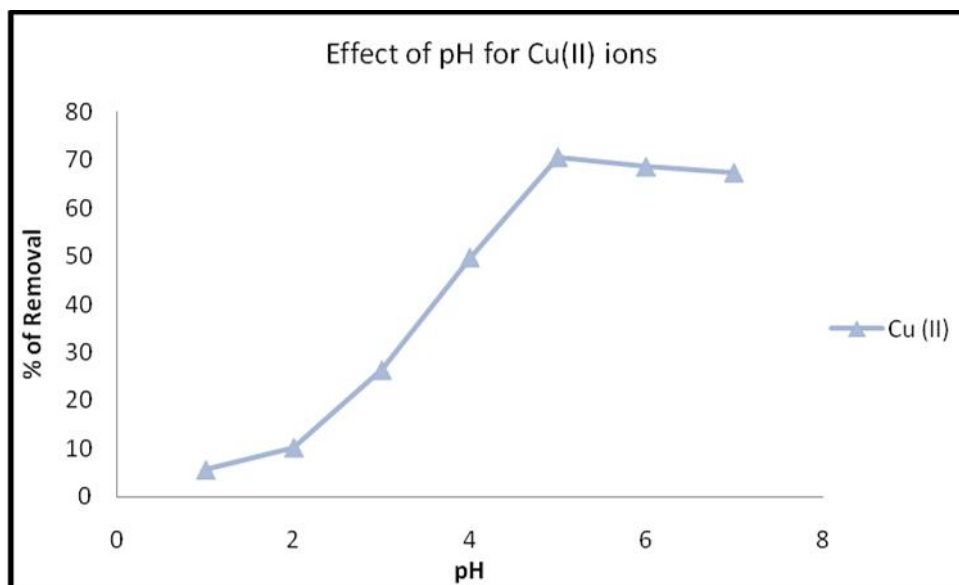
Figure: 2 Effect of pH for Cu(II) ion onto ACHC

3.3 Effect of Temperature:

It is well known that temperature plays an important role in the adsorption process. The metal ions removal increase rapidly from 305K, 315K and 325K this result suggests that the experimental temperature had a greater effect on the adsorption process implying that

the surface coverage increased at higher temperatures. This may be attributed to the increased penetration of metal ions inside micro pores or the creation of new active sites at higher temperatures. This indicates the endothermic nature of the controlled adsorption process. Similar result has been reported in the literature.

Table: 3 Data processing Tools

S. No.	Parameters		Formulae
1.	**Kinetic Models & SSE %**	Pseudo First order kinetics (Legergren equation)	$\log(q_e-q_t) = \log q_e - k_1/2.303 \times t$
		Pseudo Second order kinetics (Ho equation) The initial adsorption rate h	$t/q_t = 1/k_2 . q_e^2 + 1/q_e\, t$ $h = k_2 q_e^2$
		Sumoferror squares	SSE (%)= $[(q_e)_{exp}-(q_e)_{cal}]^2 / N$
2.	**Isotherms**	Langmuir Separation factor	$C_e/Q_e = 1/Q_0 b + C_e/Q_0$ $R_L = 1/(1+ bC_0)$
		Freundlich	$\log Q_e = \log K_f + 1/n \log C_e$
		Tempkin	$q_e = B_1 \ln K_T + B_1 \ln C_e$
		Dubinin – Raduskevich, Polanyi potential Mean free energy of adsorption	$\ln q_e = \ln q_D - B\,^2$ $= RT \ln(1+1/C_e)$ $E = 1/(2B)^{1/2}$

4.0 Adsorption Kinetics:

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. Plots of different kinetic models applied were given in the Figure: 3 and the kinetic parameters calculated were given in the Table 5. Between the first order and second order, second order kinetic model

seems to best describe the above adsorption system as its R^2 values were very close to unity. Moreover, difference between qe (cal) and qe (exp) values of second order is small when compared to first order kinetic model. Statistically it is tested with the tool Sum of error squares (SSE%) [16].The qe and SSE % values were given in the Table: 5 from which it was concluded that second order kinetic model was more appropriate rather than first order kinetic model.
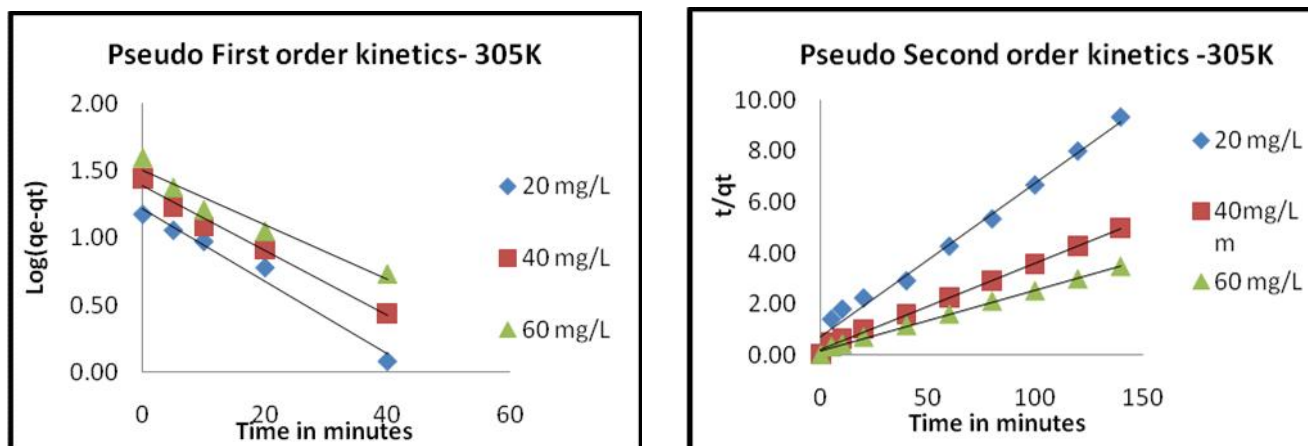

Figure: 3 Pseudo first and second order kinetics

Table: 5 Kinetic parameters for Cu(II) ions onto ACHC

Ci mg/L	Rate constants		$q_{e(cal)}$ mg/g		$q_{e(exp)}$ mg/g		q_e		R^2		(SSE %)	
	k_1 (10^{-2}) (min^{-1})	k_2 (10^{-3}) $(gmg^{-1} min^{-1})$	First Order	Second order	First order	Second Order	First order	Second Order	First order	Second order	First order	Second Order
20	0.0626	0.5000	16.63	15.00	16.67	15.00	1.63	1.67	0.9700	0.9890		
40	0.0553	0.5100	24.32	28.18	30.30	28.18	3.836	2.12	0.9800	0.9990	3.10	0.55
60	0.0461	0.3600	31.70	40.00	41.67	40.00	8.30	1.67	0.9500	0.9990		

5.0 Adsorption Isotherm Studies:

The existence of equilibrium between the liquid and solid phase is well described by adsorption isotherms. Equilibrium data collected at different temperatures were fitted in Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich adsorption isotherm models [17]. These isotherms are depicted in Figure: 4. The R^2 values of these isotherm plots reveal that Freundlich isotherm well describes the present system that is the possibility of multilayer adsorption. R^2 value of Dubinin-Raduskevich isotherm is very low. In Dubinin-Raduskevich isotherm, the very low value of the constant 'B' related to the mean free energy of adsorption per mole of the adsorbate and the adsorption is physical in nature. Results of various isotherms are presented in Table: 6.
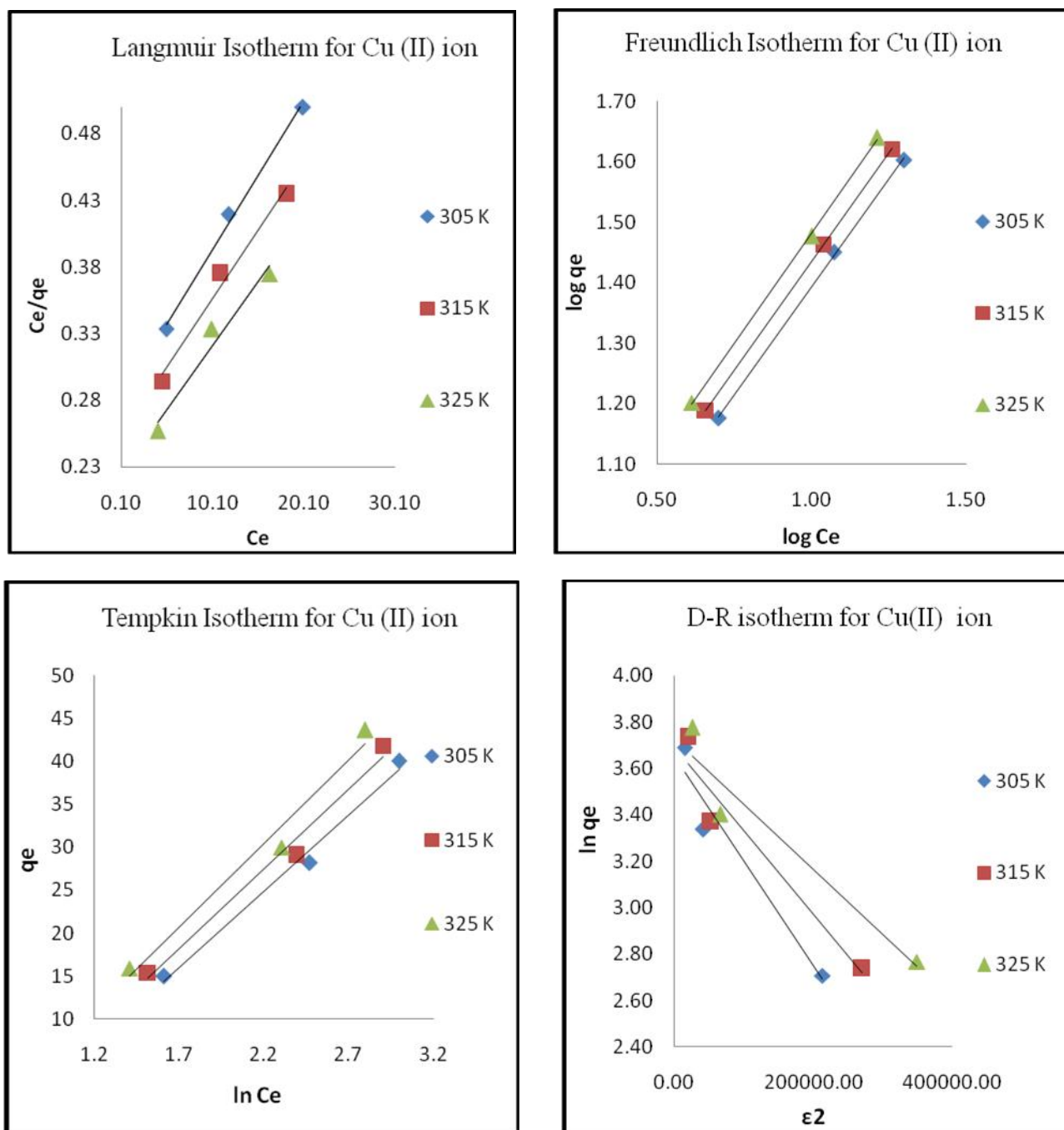

Figure: 4 Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich for the adsorption of Cu(II) ion onto ACHC

Table: 6 Results of various isotherms plots for the adsorption of Cu(II) ion onto ACHC

Isotherm Models	Temp (K)	Parameters and their results			
Langmuir		Q_0 (mg/g)	B	R_L	R^2
	305	90.10	0.0390	0.5500	0.9900
	315	98.00	0.0390	0.3500	0.9800
	325	104.20	0.0430	0.2800	0.9600
Freundlich		K_f (mg/g^{-1})	N		R^2
	305	4.80	1.40		0.9900
	315	5.10	1.39		1.0000
	325	5.70	1.37		0.9900
Tempkin		B1 (J/mol)	KT (L/g)		R^2
	305	446.60	0.9825		0.9900
	315	438.80	1.0679		0.9800
	325	428.20	1.0547		0.9800
Dubinin Raduskevich		q_D (mg/g)	E (kJ/mol)	B × 10^{-4} (mol^2/J^2)	R^2
	305	38.4	0.3535	0.0013	0.9600
	315	40.0	0.3535	0.0025	0.9400
	325	41.2	0.4082	0.0038	0.9300

6.0 Analysis of Isotherm:

6.1 Langmuir isotherm:

In the present study Q_0 value ranges from 90.10 to 104.20, as the temperature increases the monolayer adsorption capacity also found to increase. This kind of results were obtained in various similar studies [18]. The separation factor R_L values were in between 0 to 1 which indicates the favourable adsorption. R^2 values of isotherm ranged in between 0.9600 to 0.9900.

6.2 Frendlich isotherm:

The values of n were between 1 and 10 which indicates cooperative adsorption [19]. The R^2 values were close to unity which revealed the good fitting into frendlich isotherm.

6.3 Temkin Isotherm:

B_1-Temkin constant is related to the heat of adsorption. This B_1 value increased from 446.60 to 428.20 as the temperature of adsorption increased. The Temkin parameter K_T values give an idea about nature of adsorption [20]. In our present study the K_T values ranged from 0.9825 to 1.0547 which indicates that adsorption is physical nature. The R^2 value was low compared to Frendlich isotherm.

6.4 Dubinin-Raduskevich:

The activation energy E value ranges from 0.3535 to 0.4082 and B value from 0.0013 to 0.0038 indicates

the physisorption. The R^2 value was very low when compared to other three isotherms.

In general the fitting data in isotherm equation were in the following order: Frendlich>Temkin> Langmuir >Dubinin-Raduskevich.

7. 0 Conclusion

The present investigation shows that ACHC is an effective adsorbent for the removal of Cu(II) ion from aqueous solutions. From the kinetic studies, it is observed that adsorption of Cu(II) ion is very rapid in the initial stage and decreases while approaching equilibrium. The equilibrium time increases with initial concentration. The percentage removal of Cu(II) ion increases with the increase in adsorbent dosage and decreases with increase in initial concentration. Experimental results are in good agreement with Freundlich isotherm when compared to other three isotherm models. Adsorption of Cu(II) ion obeys pseudo-second order equation with good correlation.

8.0 References

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