

Characterization of Tur Dal (*Cajanus cajan*) Husk Carbon and its Kinetics and Isotherm study for Removing Cu (II) ions

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Abstract: The present study was carried out with the aim to characterise the various physicochemical properties of Tur dal (*Cajanus cajan*) husk based metal adsorbent carbon and to model its metal adsorption behavior in removing copper ion(II) from aqueous solution using kinetics (pseudo-first and pseudo second order) and isotherm (Langmuir, Freundlich and Temkin) models for selecting appropriate operating conditions for the full scale batch process. The metal adsorbent carbon (Ad₁) was obtained from Tur dal husk simply by their carbonization at 500^oC in air tight container for 1 hr. The obtained adsorbent was characterized for various physicochemical parameters using standard methods of analysis and instruments (Surface Area Analyser, CHNS Elemental Analyzer, Fourier Transformed Infra-red). The batch equilibrium and kinetics study was carried out by shaking the various concentration (10-50 ppm) of 50 ml Cu solution (6.0 pH) each with 0.25 g of adsorbent (0.15-0.25mm particle size) at 60 ^oC, agitated at 150 rpm for different contact time (10-300 minutes). The equilibrium time was observed to be 120 minutes for all initial concentrations studied. The experimental kinetic data obtained at different initial concentrations found to be fitted well to the pseudo-second-order kinetic model (R²=0.999). The analysis of equilibrium data confirmed fitting of all the isotherms in order Langmuir > Freundlich > Temkin and concluded Langmuir isotherm (R²=0.987) to be preferred model for the studied metal removal process with maximum adsorption capacity of 3.74 mg/g.

Keywords: Tur dal husk, metal adsorbent, copper, adsorption kinetics, adsorption isotherm

I. Introduction

The aquatic systems are being polluted by means of various sources. One of the important cause of water pollution is the introduction of heavy metals from the discharge of industries like batteries, mining, fertilizer, pesticides, tanneries, refining ores paper industries etc. [1, 2]. The presence of heavy metals like Lead (Pb), Chromium (Cr), Mercury (Hg), Arsenic (As), Ferrous (Fe), Selenium (Se), Zinc (Zn), Copper (Cu), Cobalt (Co), Nickel (Ni), Cadmium (Cd) etc. in water greater than their prescribed limit proving to be poisonous and matter of concern due their serious threat to the all the form of aquatic life, animals as well as human being [3]. Table 1 is showing the different health hazard to human being due to the various heavy metals.

Table 1: Health Hazard to Human by Various Heavy Metals

Metal Contaminant	Health Hazard
Pb	Carcinogen, loss of appetite, anemia, muscle and joint pains, diminishing IQ, cause, sterility, kidney problem and high blood pressure
Cr	Carcinogen, producing lung tumors, allergic dermatitis
Hg	Corrosive to skin, eyes and muscle membrane, dermatitis, anorexia, kidney damage and severe muscle pain
As	Carcinogenic, producing liver tumors, skin and gastrointestinal effects
Zn	Causes short term illness called "metal fume fever" and restlessness
Cu	Long term exposure causes irritation of nose, mouth, eyes, headache, stomachache, dizziness, diarrhea
Ni	Causes chronic bronchitis, reduced lung function, cancer of lungs and nasal sinus
Cd	Carcinogenic, cause lung fibrosis, dyspnea and weight loss

(Source: Sud et al., 2008) [4]

The industrial waste therefore needs to be treated to bring down their heavy metals content to the prescribed limits before their discharge in any aquatic receiving bodies. Every country has its own norms for discharging such industrial waste containing heavy metals in aquatic stream to control pollution and danger to aquatic life. Table 2 is showing the permissible maximum limits of heavy metals for discharge in inland surface water, public sewers and in marine coastal area as per Indian Environment (Protection) Rules, 1986.

Table 2: Permissible Maximum Limits of Heavy Metals for Discharge

Heavy Metal	Permissible Maximum Limits of Heavy Metals in mg/L for Discharge		
	Inland Surface Water	Public Sewers	Marine Coastal Areas
Arsenic (as As)	0.2	0.2	0.2
Mercury (As Hg)	0.01	0.01	0.01
Lead (as Pb)	0.1	1.0	2.0
Cadmium (as Cd)	2.0	1.0	2.0
Hexavalent chromium (as Cr +6)	0.1	2.0	1.0
Total chromium (as Cr)	2.0	2.0	2.0
Copper (as Cu)	3.0	3.0	3.0
Zinc (as Zn)	5.0	15	15
Selenium (as Se)	0.05	0.05	0.05
Nickel (as Ni)	3.0	3.0	5.0
Manganese (as Mn)	2.0	2.0	2.0
Iron (as Fe)	3.0	3.0	3.0

(Source: Environment (Protection) Rules, 1986) [5]

Chemical precipitation, Ion Exchangers, Coagulation–Flocculation, Flotation, Membrane Filtration, Electrochemical Treatment and Reverse osmosis methods and processes are available for removing heavy metals, but not much accepted because of several limitations [6]. Table 3 is showing the disadvantages associated with different methods of metal removal from waste water.

Table 3: Limitations with Various Methods of Metal Removal from Waste Water

Process	Disadvantage
Chemical precipitation	Large amount of sludge containing metals, Sludge disposal cost, High maintenance costs
Ion exchange	High initial capital cost, High maintenance cost
Coagulation–flocculation	Chemical consumption, Increased sludge volume generation
Flotation	High initial capital cost, High maintenance and operation costs
Membrane filtration	High initial capital cost, High maintenance and operation costs, Membrane fouling, Limited flow-rates
Electrochemical treatment	High initial capital cost Production of H ₂ (with some processes), Filtration process for flocks

(Source: O’Connell, 2008) [7]

In this context adsorption process has been proved to be useful because of the benefits like removing wide variety of target pollutants, high capacity, easy to operate with low operation cost, short operation time, fast kinetics, simplicity of design, possibly selectivity depending on adsorbent and effectiveness [8]. The most important feature of adsorption technique, where the other processes proving inefficient is its suitability for the removal of heavy metals even if metal ions are present in low concentration [9]. In removing metals by adsorption process there require adsorbent i.e. material having capability of binding metal ions by van der Waals or electrostatic forces. Biosorbent is believed to be one of the better solution for adsorption. In biosorption the removal of heavy metals from an aqueous solution is carried out by binding to living or non-living biomass [10-13]. However practical limitation is observed with the systems employing living microorganisms for adsorption. In most cases growth of microorganism is stopped when significant amount of metal ions are adsorbed by microorganisms or when the concentrations of metal ions are too high. In case of dead cells of agricultural wastes, the positive changes occur in the cell structure after death by heating to facilitate adsorption. The other reasons for preferring agro wastes and food industry byproducts are easy and ready availability in huge quantity, economical and effective [14-16]. Agro and food waste carries a variety of functional groups (hydroxyl, carboxyl, phosphoryl, amido, amino, acetamido, phenolic, esters, alcoholic, carbonyl, ether, sulphhydryl etc.) which facilitate the removal of heavy metal ions by forming complex with them. These functional groups to agro and food waste are contributed due to the presence of water, protein, starches, cellulose, hemicelluloses, pectin, lignin, simple sugar, fat, waxes, alcohol, colour pigments, low molecular weight hydrocarbons and other compounds [17, 18]. The adsorption of metal takes place on the surface of biomass of agro and food waste. Therefore if the surface area of these biomasses is increased by their conversion into carbon, it will drastically boost the metal removal capability.

Already many agro and food waste in its raw and carbon form have been proved effective in removing heavy metals. These include cassava waste [19, 20], waste tea leave [21, 22], tea waste [23, 24], coffee waste [25], mustard oil cake [26], coir pith [27], banana and orange peels [28], potato peels [29], wheat shell [30], rice husk [31, 32], peanut shells [33-37], coca shell [38], almond shell [39], soybean shell [40], coconut shell [41], mango seed shell [42], cashew nut shells [43], walnut shell [44], hazelnut shell [45, 46], pistachio shell and apricot stone [47-49], carrot residue [50], coconut fiber [51], sugar beet pulp [52], sugar cane bagasse [53, 54], olive cake [55], barley straw [56], grape stalks wastes [57], tamarind seed, tamarind hull, walnut waste, apple waste, maize cob, pumpkin waste, corncob, Jack fruit peels, saw dust, soya cake, palm sheath etc. [58]. The

trials of new approaches to the existing proved agro and food waste to enhance their performance and new waste source is still taken up by the scientists and technologists seriously in search of collecting all possible data for metal adsorption and discovering most superior adsorbent.

The pulse processing industries in India is generating huge amount of low cost byproducts and waste in the form of husk. Presently the use of this husk is only for the cattle feed and possessing very less value. However as this byproduct is biomass and naturally carries potential for removing heavy metals (due to presence of various functional groups). The metal adsorption potential of these byproduct and waste is still not fully tapped. Keeping in view the availability of huge amount of husk with potential of adsorption, development of metal adsorbent from the pulse processing waste may prove ideal for its value added utilization. One of the major pulse processed in India is Tur (Cajanus cajan) creating large amount of waste in the form of husk. Few researchers already studied the adsorption potential of raw husk obtained from pulse processing [59-68] and found suitable for metal adsorption application. Ahalya, et al. (2007) carried out preliminary investigation for the adsorption activity of Cajanus cajan husks in their raw form to remove Cr (VI) and Fe (III) and found appropriate for metal adsorption process [69]. The metal adsorption potential of Cajanus cajan husks in their carbon form however is still not deliberated and need extensive study for the better application of these husks for metal removal purpose.

The present investigation was carried out with the aim to characterize the carbon obtained from Cajanus cajan husks by thermal process and to study the kinetics and isotherm of the adsorption for removing copper (II) ions from aqueous solution by prepared carbon.

II. Materials And Methods

The Cajanus cajan husk waste was received from local pulse processing industry in Jalgaon. All the chemicals used for analysis purpose were of analytical grade and of standard brand. A copper (II) ion stock solution of 1000 ppm was prepared by dissolving appropriate amount of copper sulfate in double distilled water and diluted to required concentration at the time of batch study.

2.1 Preparation of Carbon from Tur Dal Husk

The metal adsorbent carbon from the Cajanus cajan husk was developed by slight alteration in method by El-Ashtoukhy et al., 2008 and by procedure described by Parate and Talib, 2014 [70, 71]. The method of preparation of adsorbent is given in Fig. 1.

2.2 Characterization of Adsorbent Carbon

The prepared carbon Ad_1 was characterized for various physical and chemical parameters using standard methods of analysis and instruments given in Table 4.

2.3 Equilibrium, Kinetics and Isotherm Study

The equilibrium of the adsorption and the kinetics are the two important physiochemical aspects for the assessment of the adsorption process as an unit operation. An equilibrium study gives the capacity of the adsorbent and the adsorption isotherms gives the equilibrium relationships between adsorbent and adsorbate (ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium). In order to optimize the design of an adsorption system, it is important to establish the most appropriate correlation for the equilibrium curves. The potential rate controlling steps in sorption and the mechanism of sorption can be investigated by using Kinetic models which is helpful for selecting optimum operating conditions for the full scale batch process.

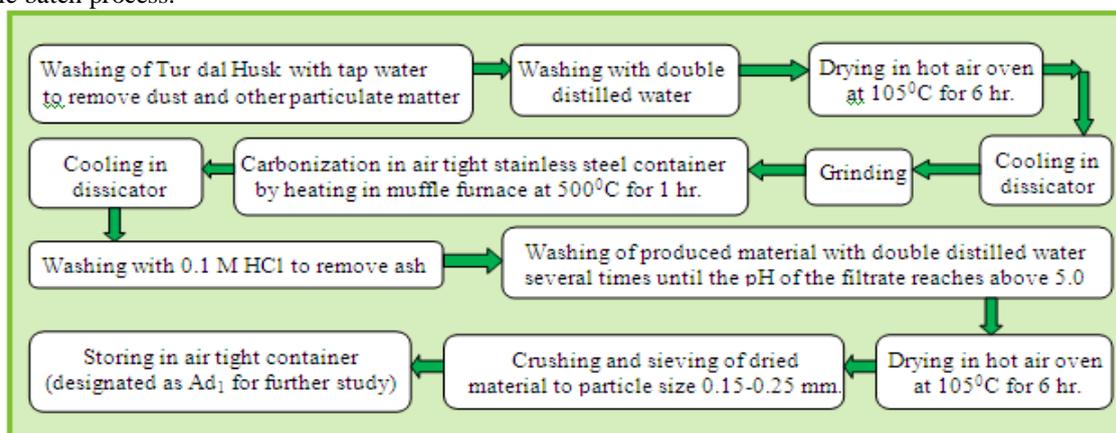


Figure 1: Method of preparation of adsorbent carbon from Cajanus cajan husk

Table 4: Methods and Instruments Used for Physico-Chemical Characterization of Ad₁

Parameter	Method of Analysis and Equipment
Specific surface area (m ² /g)	Analysed from Department of Chemistry, Bangalore Institute of Technology, Bangalore, India by nitrogen sorption measurement method in a NOVA-1000 QUANTACHROME instrument (version 3.70), at 77.4 K.
Total pore volume (cc/g)	
Average pore diameter (°A)	
Functional Group	Fourier Transformed Infra-red (FTIR), SHIMADZU 8400
Elemental C, H, N, S & O Analysis	Analysed from Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology (IIT), Mumbai, India using CHNS Elemental Analyzer (Make: Thermo finnigan, Italy, Model: FLASH EA 1112 series) and O by difference
Acid soluble content (%) (Mass basis)	Bureau of Indian Standards, 1989 [72]
Volatile matter content (%) (Dry basis)	International Organization for Standardization, 1981 [73]
Fixed carbon content (%) (Dry basis)	American Society for Testing and Materials, 1997 [74]
Sulphated ash (%) (Dry basis)	Food and agriculture organization/ World Health Organization, 2010 [75]
Alcohol soluble substances (%) (Dry basis)	
Iodine number (mg/g) (Mass basis)	Bureau of Indian Standards, 1995 [76]
Zero Point Charge	Arlette et al., 2012 [77]

The batch kinetic and isotherm study of adsorption of Copper (Cu II) ion from its solution by adsorbent Ad₁ was carried out by performing batch equilibrium test by shaking the various concentration of Cu solution (10-50 ppm) each with Ad₁ for different contact time 10-300 minutes as per maintaining the adsorption condition given in Table 5. All the experiments were carried out by mixing 50 ml of Cu solution (maintained at pH 6) and 0.25 g of Ad₁ (fix particle size 0.15- 0.25mm) in 100 ml capped conical flasks, agitated in orbital shaking incubator (REMI) at 150 rpm maintaining 60 °C temperature for various time periods (10-300 min.). At the end of each contact time the suspension was filtered through Whatman No. 42 filter paper. The filtrate was then diluted to desired dilution with double distilled water to analyse residual Cu concentration using Atomic Absorption Spectrophotometer (ELICO Ltd., Model: SL 176).

Table 5: Batch Adsorption Condition for Kinetic and Isotherm Study

Batch Adsorption Parameter	Batch Adsorption Condition
Concentration of Cu ion solution	10, 20, 30, 40 and 50 ppm
pH of each solution	6.0
Volume of each Cu ion solution	50 ml
Particle size of Ad ₁	0.15- 0.25mm
Adsorbent dose of Ad ₁ added in each Cu ion solution	0.25 g
Agitation speed	150 rpm
Temperature	60 °C
Time	10 min., 20 min., 40 min., 60 min., 90 min., 120 min., 150 min. 180min., 210 min., 240 min., 270 min., 300 min

The % Removal of Cu was calculated as per equation 1 [78]:

% Removal =

$$\left\{ \frac{\text{Initial concentration of Cu ions solution} - \text{Equilibrium concentration of Cu ions solution}}{\text{Initial concentration of Cu ions solution}} \right\} \times 100 \quad (1)$$

The effect of initial concentration of Cu solution and contact time on % removal of Cu ion by Ad₁ was studied by plotting % removal of Cu ion against contact time for each initial concentration of Cu solution.

The adsorption capacity q_t (milligram per gram) at time t was determined by the following equation 2:

$$q_t = V \frac{C_i - C_t}{W} \quad (2)$$

Where V is the volume of the solution in liter, W is the mass of the adsorbate in gram, C_i is initial concentration of Cu ions solution at time 0 and C_t is the concentration of Cu ions solution at the end of time t in mg/L [79].

The kinetic data obtained at different initial concentrations were analyzed using pseudo-first and pseudo second order models. The first order rate equation of Lagergren was used in the present study, and is represented as equation 3:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Where k_1 (1/min), is the first-order reaction rate constant, q_e (milligram per gram) is the amount of solute adsorbed on the surface at equilibrium and q_t (milligram per gram) is the amount of solute adsorbed at any time t . The value of k_1 and q_e was calculated as slope and y-intercept respectively of the line from the plot of $\log(q_e - q_t)$ against t . A straight line of $\log(q_e - q_t)$ versus t indicates the application of the first-order kinetic model.

In many cases the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes. Therefore, the pseudo-second-order kinetic model is used to study the adsorption kinetic of the system as per equation 4:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e} \right) t \quad (4)$$

Where k_2 (g/mg min) is the second-order rate constant. The q_e and k_2 was calculated from the slope and intercept of the plots t/q_t versus t . If a plot of t/q_t versus t give the linear relationship indicates the applicability of second order kinetic. The good application of pseudo-second-order kinetic model to equilibrium data is an indication of chemisorptions being the rate controlling step.

In order to determine the adsorption potential of the biosorbent, the study of sorption isotherm is essential. The most widely used isotherm equation for modeling equilibrium is the Langmuir and Freundlich. In the design of adsorption system in present study the Langmuir and Freundlich models were therefore tested in order to establish the most appropriate correlations for the equilibrium data. Langmuir equation, based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface, these binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules [80]. Thus Langmuir model represents the monolayer adsorption on to a homogeneous surface with a finite number of active sites [81]. The following linear form (equation 5) of the Langmuir isotherm was used in the present study:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (5)$$

Where C_e (milligram per liter) is the equilibrium concentration of the adsorbate, q_e (milligram per gram) is the amount of adsorbate per unit mass of adsorbent, Q^0 and b are Langmuir constants. Here Q^0 and b was calculated from the slope and intercept of the liner plots C_e/q_e versus C_e . The linearity of plot shows the applicability of the Langmuir isotherm. The essential characteristics of the Langmuir isotherm is expressed in terms of a separation factor R_L (dimensionless constant) and is given in the following equation (6):

$$R_L = \frac{1}{1 + bC_i} \quad (6)$$

Where b (L/mg) is Langmuir constant and C_i (milligram per liter) is the initial concentration. The separation factor R_L indicates the whether the adsorption is favourable or not, as per the following criteria given below:

R_L Value	Adsorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Freundlich model signify the multilayer adsorption on to a heterogeneous surface with a infinite number of active sites. The linear form of Freundlich isotherm applied in the study is given in equation 7:

$$\log q_e = \log K_F + \left(\frac{1}{n} \right) \log C_e \quad (7)$$

Where n and K_F are the Freundlich isotherm constants. The values of $1/n$ and K_F can be calculated from the slope and intercept of the plot $\log q_e$ verses $\log C_e$. The value of $1/n$ less than 1 represents favorable adsorption condition [82].

Temkin isotherm contains a factor that takes into account the adsorbent–adsorbate interactions. To test the fitness of the experiment data, the following equation (8) of Temkin isotherm model was also used in the study [83].

$$q_e = B \log kt + B \log C_e \tag{8}$$

Where q_e is the amount adsorbed at equilibrium (milligram per gram) and C_e is the equilibrium concentration of metal ions in solution (milligram per liter), $B = RT/b$ (represents heat of adsorption), T is the absolute temperature in Kelvin and R is the universal gas constant and $1/b$ indicates the adsorption potential of the adsorbent while kt (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy. The determination of isotherm constants kt and B was done using the plot of q_e versus $\log C_e$.

The best equilibrium model was decided on the basis of linear square regression correlation coefficient R^2 . The value of R^2 was taken as a measure of the goodness-of-fit for kinetics/isotherm's models. In case of kinetics model the deviation in experimental q_e and calculated q_e was also used to judge the most suitable model [84].

III. Results And Discussions

Table 6 represents physicochemical characteristics of prepared adsorbent. The Specific surface area of adsorbent was found be 129.29 m²/g indicating potential of adsorbent for metal removal. The porous adsorbent had pores of diameter 35.99 °A with pore volume 0.1163 cc/g. The elemental analysis of adsorbent reveled the carbon, hydrogen, nitrogen and oxygen as 74.55%, 2.67%, 1.31% and 21.47 respectively with no traces of sulfur. The adsorbent found to contain 1.37 % acid soluble matter, 0.45 % alcohol soluble substances, 28.36% volatile matter and 3.58 % sulphated ash. The fixed carbon content of adsorbent was 61.94% confirming carbonaceous nature of adsorbent required for metal removal. The Iodine number of adsorbent (25.5 mg/g) was also rough indication of its adsorption capability. The adsorbent found to posses zero point charge at pH 5.7 suggesting its effective application for metal removal from aqueous solution having pH around and beyond 5.7.

Table 6: Result of Physicochemical Characterization of Adsorbent

Parameter	Result
Specific surface area (m ² /g)	129.29
Total pore volume (cc/g)	0.1163
Average pore diameter (°A)	35.99
% Element (C, H, N, S, O)	
C %	74.55
H %	2.67
N %	1.31
S %	0.0
O %	21.47
Acid soluble content (%) (Mass basis)	1.37
Volatile matter content (%) (Dry basis)	28.36
Fixed carbon content (%) (Dry basis)	61.94
Sulphated ash (%) (Dry basis)	3.58
Alcohol soluble substances (%) (Dry basis)	0.45
Iodine number (mg/g) (Mass basis)	25.5
Zero Point Charge	5.7

Fig. 2 and 3 is showing FTIR spectra (X axis: Wave number in cm⁻¹ and Y axis: % Transmission of wave) of Ad₁ before and after copper adsorption. The spectra of adsorbents were measured within range of 500–4000 cm⁻¹. The FTIR of the adsorbent exhibited a number of peaks for various functional groups, indicating the complex nature of Ad₁. The FTIR results specified that Ad₁ contains many functional groups (Alkanes, Alkenes, Alcohol & Phenol, Amines, Carboxylic Acid and its Derivative (Amide), Phosphine, Aldehydes, Aryl Ketone, Organic Halogen) capable of adsorbing copper ions. Table 7 is comparison of the various functional group observed at different wave number on Ad₁ before and after adsorption. The functional group aldehydes (C=O) was absent on Ad₁ before adsorption (Cu) but appeared after adsorption at wave number 1739 (stretch). Alkene (C=C) bend at wave number 814 before adsorption was found to be shifted to 876 (C-H & =CH₂) after adsorption. Alcohol & phenol functional group (O-H) stretch (at wave number 3208) and bend (at wave number 667) was not detected before adsorption but was observed after adsorption. Phosphine functional group (P-H) stretch observed at wave number 2310 before adsorption was shifted to 2360 after adsorption. Also phosphine functional group stretch watched at wave number 2379 was disappeared after adsorption. The organic halogen stretch found at 576 (C-Halogen) before adsorption was shifted to 514 after adsorption. The changes observed in the spectrum (before and after adsorption) in the form of shifting and disappearing of functional groups peak and appearing of new functional group peak indicates the possible involvement of those functional groups on the surface of Ad₁ in the metal adsorption process [85, 86].

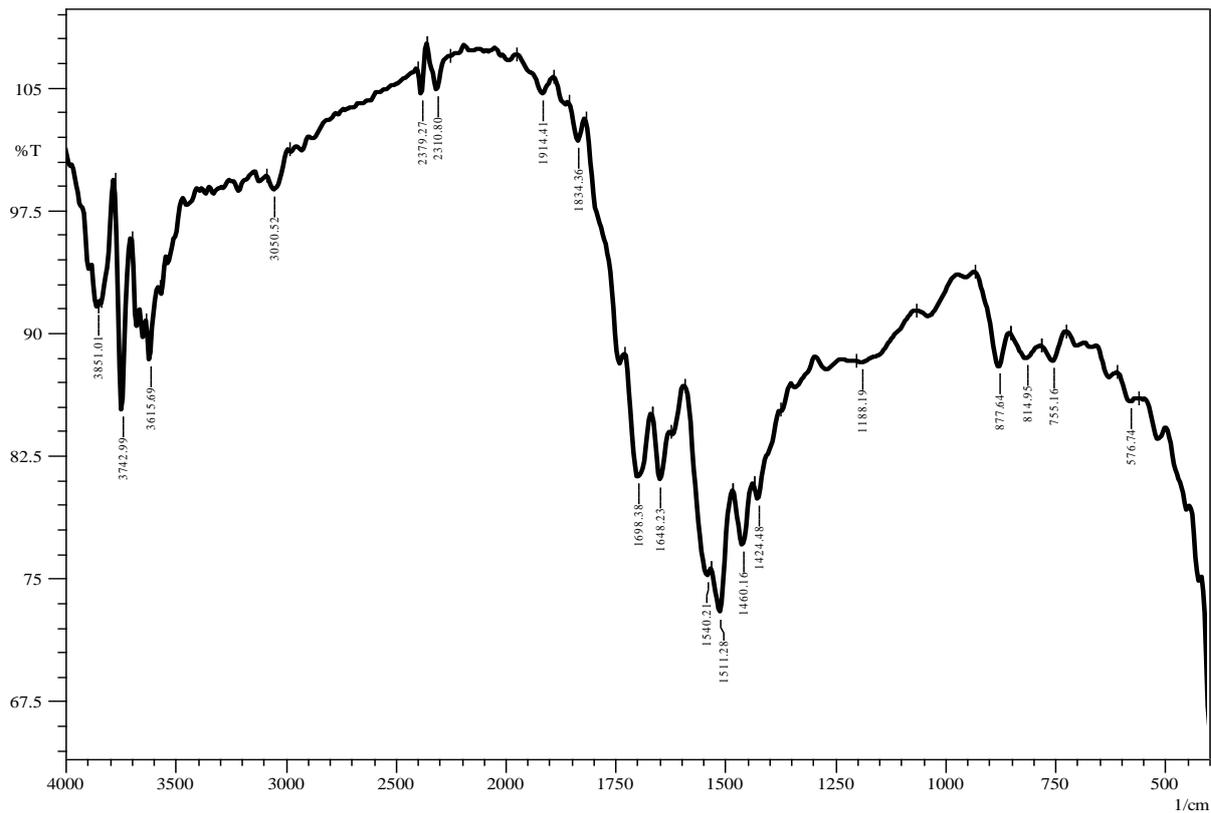


Figure 2: FTRI of Ad₁ before adsorption

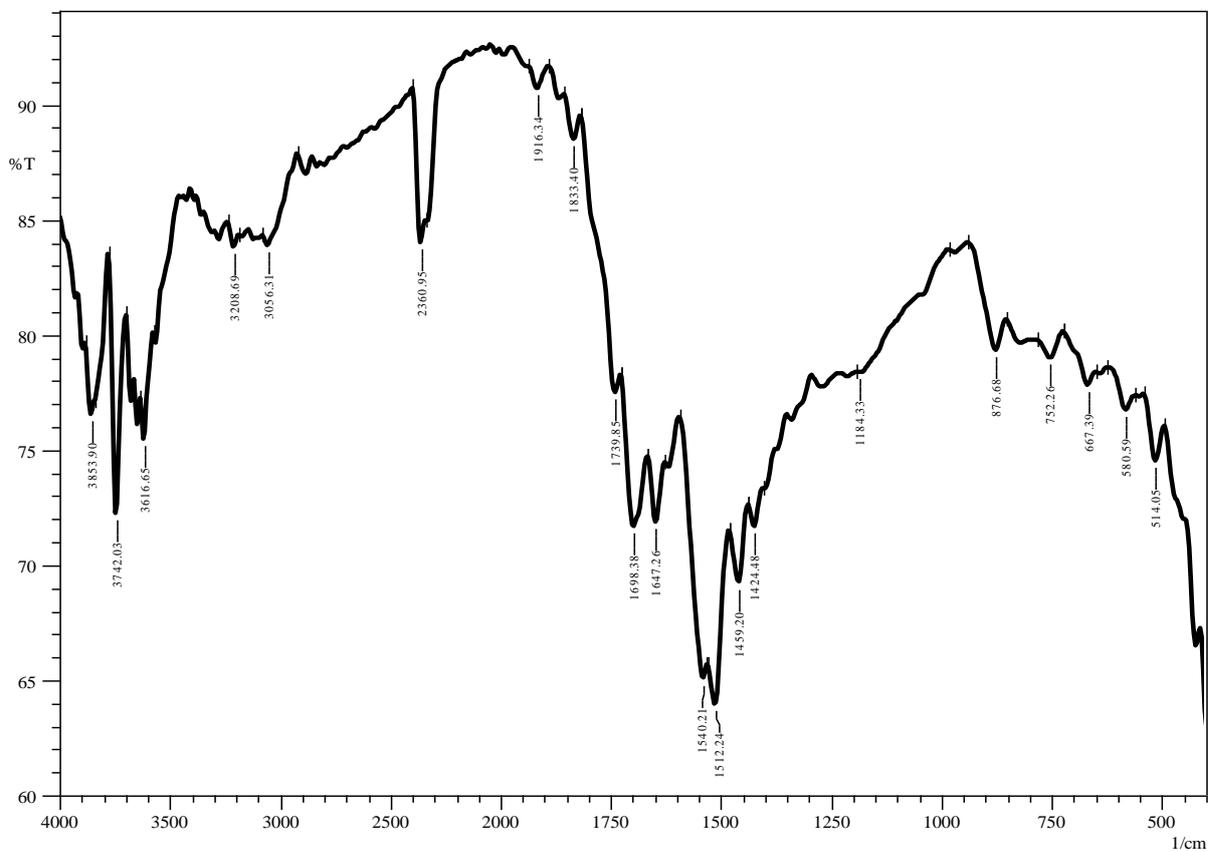


Figure 3: FTRI of Ad₁ after adsorption

Table 7: Comparison of Functional Group of Ad₁ Before and After Cu Adsorption

Sr.No	Functional Group	Ad ₁		Sr. No	Functional Group	Ad ₁	
		BA	AA			BA	AA
01)	Alkanes	1460	1459	04)	Amines	1540	1540
				05)	Carboxylic Acid/ Derivative (Amide)	1511 1648 1834	1512 1647 1833
02)	Alkenes	814	-----	06)	Phosphine	1188	1184
		877	876			2310	-----
		1914	1916			-----	2360
		3050	3056			2379	-----
03)	Alcohol & Phenol	-----	667	07)	Aldehydes	-----	1739
		755	752			08)	Aryl ketone
		1424	1424				
		-----	3208				
		3615	3616				
		3742	3742	9)	Organic Halogen	576	580
3851	3853	-----	514				

(BA: Before adsorption, AA: After adsorption)

The basic equilibrium study data for the removal of Cu ion by Ad₁ is represented in Table 8 and is showing final concentration of Cu ion (C_t) and adsorption capacity (q_t) after various contact time t (0-300 minutes) for different initial concentration of Cu solution (10-50 ppm). The said data was utilized for the determination of equilibrium concentration (C_e) and equilibrium adsorption capacity (q_e) for each initial concentration of Cu solution used in the study. The obtained values of C_e and q_e was further exploited for the computation of log(q_e- q_t), t/q_t, C_e/q_e, log C_e, log q_e at various contact time for each initial concentration of Cu solution required in the kinetics and isotherm study

Table 8: Equilibrium Study Data for Removal of Cu Ion at Different Initial Concentration

Time (t) (Minutes)	Initial Cu Solution Concentration (C _i) in ppm									
	10 ppm		20 ppm		30 ppm		40 ppm		50 ppm	
	Final Cu Solution Concentration (C _t) in ppm and adsorption capacity q _t (mg/g) at time t									
	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t	C _t	q _t
0	9.92	-	19.68	-	29.64	-	39.36	-	49.3	-
10	3.14	1.36	10.8	1.78	18.6	2.21	27.12	2.45	36.7	2.52
20	2.64	1.46	10.16	1.90	17.52	2.42	26.56	2.56	35.8	2.70
40	2.24	1.54	9.28	2.08	16.44	2.64	25.76	2.72	35.1	2.84
60	1.96	1.59	8.64	2.21	15.9	2.75	24.8	2.91	34.3	3.00
90	1.62	1.66	8.36	2.26	15.48	2.83	24.16	3.04	33.1	3.24
120	1.5	1.68	8.16	2.30	15.12	2.90	23.36	3.20	32	3.46
150	1.5	1.68	8.2	2.30	15.18	2.89	23.36	3.20	32	3.46
180	1.54	1.68	8.16	2.30	15.12	2.90	23.52	3.17	32.1	3.44
210	1.5	1.67	8.16	2.30	15.12	2.90	23.52	3.17	32.2	3.42
240	1.56	1.67	8.24	2.29	15.18	2.89	23.68	3.14	32.1	3.44
270	1.6	1.66	8.16	2.30	15.24	2.88	23.6	3.15	32	3.46
300	1.6	1.66	8.24	2.29	15.3	2.87	23.6	3.15	32.1	3.44

The obtained data was also employed to study the effect of initial concentration of Cu solution and contact time on % removal of Cu by Ad₁ and is given in Fig. 4. It can be observed that the removal of copper (II) ions was initially fast for all the initial concentration (10-50 ppm) and later on gradually slow down as approaching towards equilibrium. The reason for the same was a large number of vacant surface sites were available on Ad₁ for complex formation with Cu ion during the early stage, and as the time lapsed the left over vacant surface sites were unable to take up the Cu ion due to repulsive forces between Cu ion on the Ad₁ and bulk phases (Ibrahim et al., 2010). Also the % removal of Cu ion was high (85 %) for low initial concentration (10 ppm) and less (35 %) for high initial concentration (50 ppm). A similar trend was observed by Hameed et al., 2009. At initial low concentrations of Cu ions there was an interaction of maximum Cu ions with Ad₁ as the proportion of surface active sites of adsorbent to the total metal ions in the solution was high. Therefore the high % of removal of Cu ion was achieved at initial low concentration of Cu solution. When the initial concentrations of Cu ions solution was high the ratio of surface active sites of adsorbent to the total metal ions in the solution was low and hence the low % of removal of Cu ion was observed [87]. The equilibrium was attended in 120 minutes for nearly all the studied initial concentrations.

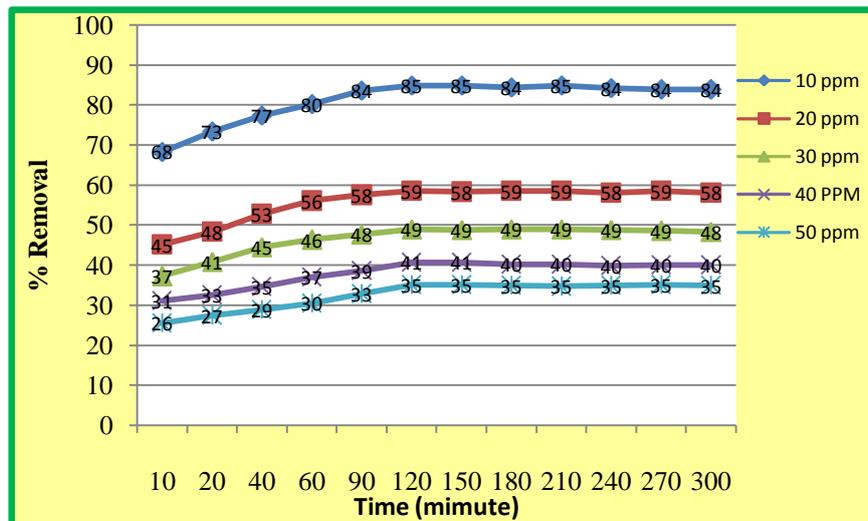


Figure 4: Effect of initial concentration of Cu solution and contact time on % removal of Cu by Ad₁

Fig. 5 and 6 is showing the Pseudo-first order kinetics plot and Pseudo-second order kinetics plot respectively for removal of Cu by Ad₁. Table 9 is showing values of various kinetics parameters for pseudo first order and pseudo second order models, comparison of experimental and calculated q_e , correlation coefficients for different initial concentration of Cu. The value of q_e was low at low initial concentration and high at high initial concentration whereas value of rate constant (k_1 or k_2) was high at low initial concentration and low at high initial concentration for both pseudo first order and pseudo second order models. Similar change in rate constant with changing initial concentration of adsorbate was observed by Hameed, B., 2009.

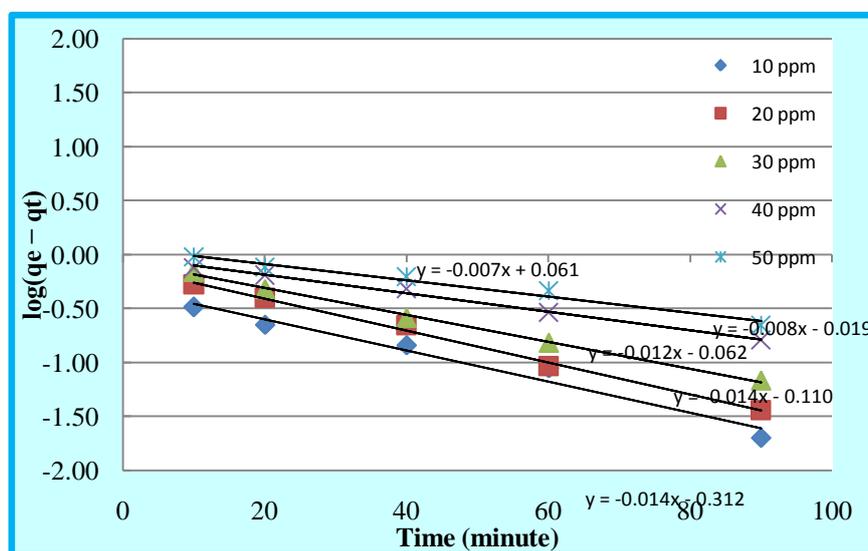


Figure 5: Pseudo-first order kinetics plot for removal of Cu by Ad₁

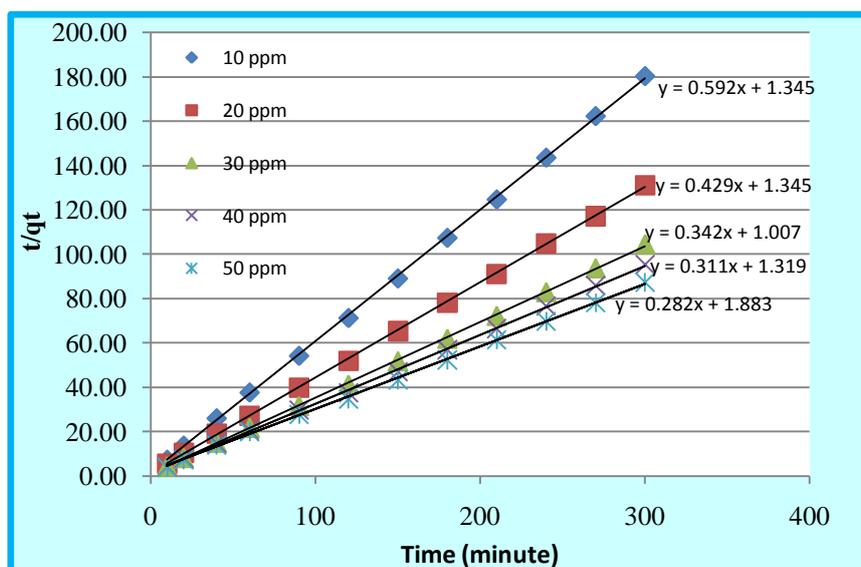


Figure 6: Pseudo-second order kinetics plot for removal of Cu by Ad₁

It can be observed that the correlation coefficient R^2 of the first order equation was considerably high (0.967-0.997) but the calculated q_e values from first order kinetic plot were deviating ($\% \Delta q_e$) much as compared to the experimental q_e values and does not shows good agreement between calculated and experimental q_e values. This shows that the removal of Cu(II) ions by adsorption on Ad₁ was not a first order reaction. However the values of correlation coefficient R^2 of the second order equation were very high (0.999) for all the initial concentration of Cu ion and also the theoretical determined q_e values were closer to the experimental q_e values for all the initial concentrations. This confirms that the removal of Cu(II) ions by adsorption on Ad₁ at different initial concentrations (10-50 ppm) follows the pseudo-second-order kinetic model [88]. The result is in accordance with findings of Anandkumar and Mandal, 2009 while removing during Cr(VI) from aqueous solution using Bael fruit (*Aegle marmelos correa*) shell as an adsorbent. This suggests that the rate-limiting step in the removal of Cu ion by biosorption with Ad₁ may be chemisorptions involving sharing or exchange of electrons between Ad₁ and Cu ion.

Table 9: Values of kinetics parameters for pseudo first order & pseudo second order models, comparison of experimental and calculated q_e , correlation coefficient for different initial concentration of Cu ion

Initial Cu ion Conc. (mg/l)	Exp. q_e (mg/g)	First Order Kinetics Parameter				Second Order Kinetics Parameter			
		q_e (mg/g) Cal.	$\% \Delta q_e$	k_1 (min^{-1})	R^2	q_e (mg/g) Cal.	$\% \Delta q_e$	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
10	1.68	0.487	70.8	0.032	0.967	1.69	0.6	0.260	0.999
20	2.30	0.776	66.1	0.032	0.995	2.33	1.3	0.137	0.999
30	2.90	0.867	70.0	0.0276	0.997	2.92	0.7	0.116	0.999
40	3.20	0.957	70.0	0.018	0.992	3.21	0.3	0.073	0.999
50	3.46	0.869	74.9	0.016	0.972	3.54	2.3	0.042	0.999

Fig. 7 is showing Langmuir adsorption isotherm plot for removal of Cu ion by Ad₁ and Table 10 is giving values of Langmuir separation factor calculated for various initial concentration of Cu ion solution. The adsorption equilibrium data correlate well with Langmuir model as coefficient of correlation was high ($R^2 = 0.987$) and showing a good linearity. The fit of the adsorption data into the Langmuir isotherm confirmed monolayer adsorption and the monolayer adsorption capacity was found to be 3.74 mg/g. The values of R_L for the studied system at different initial concentration were found to be between 0 and 1 for all the studied initial

concentration indicating the adsorption behaviour of Ad₁ was favourable for Cu ion under experimental conditions used in the study [89].

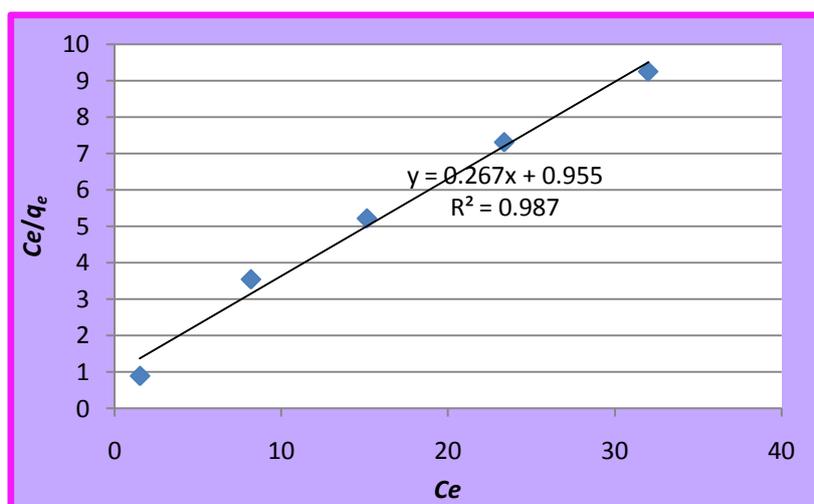


Figure 7: Langmuir adsorption isotherm plot for removal of Cu ion by Ad₁

Table 10: Langmuir Separation Factor

Initial Concentration	R _L
10	0.265
20	0.154
30	0.108
40	0.083
50	0.068

Fig. 8 is representing Freundlich isotherm plot for the said adsorption. The Freundlich isotherm model was also found suitable for the experimental data as showing good linearity with high coefficient of correlation ($R^2 = 0.982$). The fit of the adsorption data into the Freundlich isotherm verified multilayer adsorption. The value of $1/n$ was between 0 and 1 proving that the adsorption of Cu ions by Ad₁ was favorable under the stated investigational conditions.

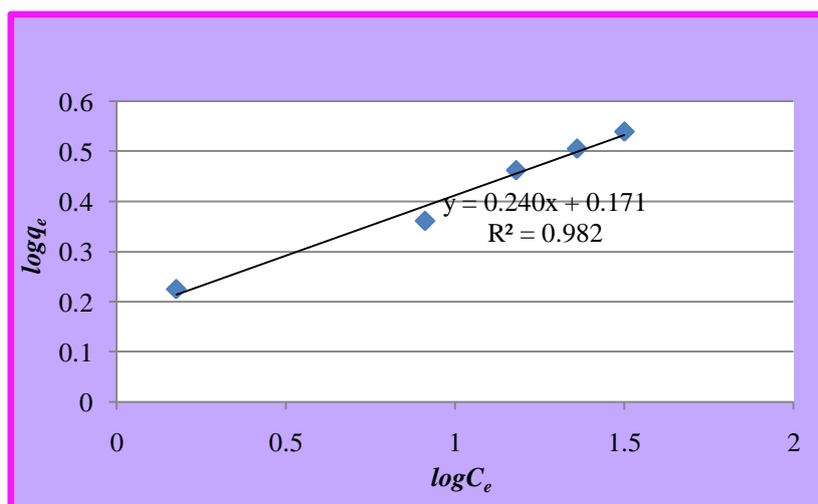


Figure 8: Freundlich adsorption isotherm plot for removal of Cu ion by Ad₁

Fig. 9 is demonstrating the equilibrium data tested for fitting in Temkin isotherm model. Temkin isotherm model is also showing considerable linearity with experimental data however the coefficient of correlation ($R^2 = 0.955$) was less as compared to Langmuir and Freundlich isotherm model.

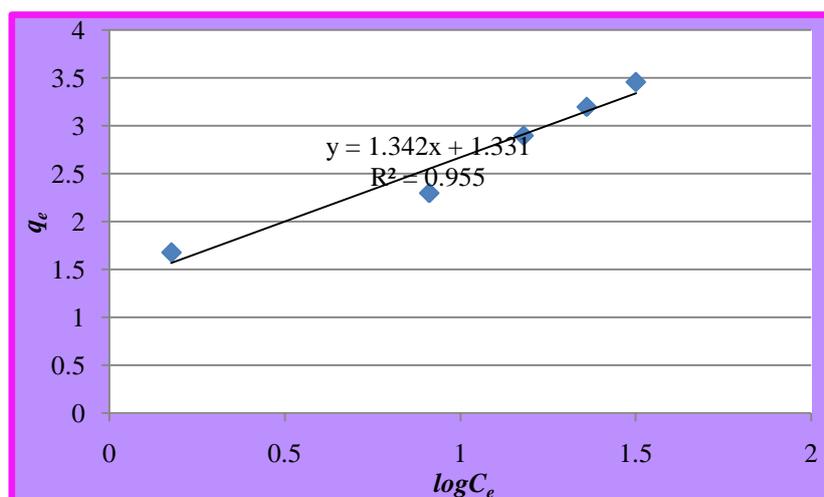


Figure 9: Temkin adsorption isotherm plot for removal of Cu ion by Ad₁

Table 11 is showing the values of various constants for Langmuir, Freundlich and Temkin Isotherm model applied to study equilibrium data. The Langmuir isotherm model is showing maximum adsorption capacity of 3.74 mg/g at studied conditions (constant temperature 60 °C).

Table 11: Values of Langmuir, Freundlich and Temkin Isotherm Constants

Langmuir Isotherm		Freundlich		Temkin		
$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0}$		$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$		$q_e = B \log kt + B \log C_e$ B = RT/b		
Q ⁰ (mg/g)	b (L/mg)	K _F (mg/g (L/mg) ^{1/n})	1/n	B	Kt (L/mg)	b (J/mol)
3.74	0.28	1.48	0.240	1.342	9.81	2063.01

The adsorption equilibrium studies revealed that the experimental data of Cu ions adsorption on Ad₁ fitted well not only to the Langmuir isotherm model but also to the Freundlich isotherm model and reasonably to the Temkin isotherm model. The order of fitness of data to isotherm models were: Langmuir > Freundlich > Temkin. In terms of R² as Langmuir equation provided better fitting as compared to Freundlich and Temkin hence considered desirable model for the said metal removal system. Wang et al.(2010) also found the well fitness of equilibrium data to Langmuir, Temkin and Freundlich isotherms model with better fitting with Langmuir isotherm while removing cadmium (II) ions from aqueous solution by a new low-cost adsorbent bamboo charcoal.

IV. Conclusions

- 1) The adsorbent (Ad₁) obtained by the heating Tur dal husk in air tight container had considerable carbon content, porosity, specific surface area and functional groups to remove metal ions from its aqueous solution.
- 2) The equilibrium study data for removal of Cu(II) ions from its solution of various initial concentration (10-50 ppm) by developed adsorbent revealed the % removal of Cu ion was high with low initial concentration and low for high initial concentration.
- 3) The kinetic modeling of studied adsorption system (removal of Cu(II) ions by Ad₁) confirmed that the experimental data were following the pseudo-second-order model suggesting a chemisorptions process.
- 4) The fitting of equilibrium data was found to be satisfied by Langmuir, Freundlich and Temkin isotherm in order Langmuir > Freundlich > Temkin therefore the most suitable isotherm model to fit the equilibrium data well for the studied adsorption system was Langmuir.
- 5) The work concluded that the studied adsorbate (Cu(II) ions)/adsorbent (Ad₁) system was a favorable adsorption.

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