Study of Metal Adsorbent Prepared from Tur Dal (*Cajanus cajan*) Husk: A Value Addition to Agro-waste

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Abstract: *The aim of the present investigation was to develop metal adsorbent from agro-waste (husk) of tur dal (Cajanus cajan) for their value addition and to improve the effectiveness of developed adsorbent by optimizing the conditions of adsorption for complete removal of Cu ions from its 50 ml, 50 ppm solution. The washed and dried tur dal husk was carbonized in air tight container at 500 ^{0}C for 1 hr. to get its carbon form possessing adsorption property. The physicochemical characterization of prepared adsorbent was done for yield, bulk density, conductivity, particle size, moisture, ash, water soluble content, pH, calorific value, trace elements, crystal nature and structural morphology. The optimum parameters for adsorption was studied by varying pH (2-10), agitation speed (50-250 rpm), temperature (10-60 ^{0}C), adsorbent dose (0.25- 2.75 g) and contact time (0.5-4 hr.). The study concludes tur dal husk can be exploited for the preparation of metal adsorbent. The prepared adsorbent was found to be most effective in an adsorption condition of 6 pH, 150 rpm agitation speed, 60 ^{0}C temperature, 2.75g adsorbent dose and 3 hr. contact time. The thermodynamic study revealed adsorption by the developed adsorbent was endothermic (positive ΔH^0), non spontaneous (positive ΔG^0) and increasing randomness at the adsorption sites (positive ΔS^0).*

Keywords: *Adsorption, copper, optimization, thermodynamic, tur dal husk*

I. Introduction

Toxic heavy metal ions are being added to the aquatic streams by means of various industrial activities at much higher concentration than the prescribed limits, possessing a serious threat to aquatic life and leading to the environmental degradation [1]. The conventional methods (ultra filtration , reverse osmosis, chemical precipitation, ion exchangers etc.) to remove metal ions from aqueous solutions however are not much preferable many times due to their own limitations such as production of sludge, less efficiency, high cost [2]. Adsorption process is considered better as compared to various available water pollution control technologies, because of convenience, ease of operation and simplicity of design. Adsorption is nothing but the accumulation of a substance at the interface solid and liquid or solid and gas. Adsorbate is the substance that accumulates at the interface ,and the solid on which adsorption occurs is known as adsorbent. The adsorption mainly occurs due to the unbalanced forces (van der Waals, electrostatic) at the surface of the solids [3].

Efficient and environment friendly adsorbents are still in high demand which reduces heavy metal content in waste water to acceptable level at affordable costs. The researchers are always in search for low-cost adsorbents, to be prepared from a wide variety of raw materials which can be easily activated, cheap, abundant, having low inorganic content and high organic (carbon) content. Living microorganisms or dead biomass of microorganisms and agricultural waste can be used as biosorbents. The use of living microorganism as biosorbent however has practical limitations as their growth is inhibited when the significant amount of metal ions are absorbed by microorganisms or when the concentrations of metal ions are high. Plant wastes are inexpensive as they have no or very low economic value. Abundant waste materials or products from industrial and agricultural activities can be potential alternatives for heavy metal removal [4,5].The use of agricultural residues as biosorbent is therefore receiving considerable attention as large quantities are readily and cheaply available as a byproduct of various industries, economic and eco-friendly due to their unique chemical composition, renewable and more efficient [6,7].Agro-waste basically composed of cellulose and lignin along with other components like water, starches, hemicelluloses, simple sugars, proteins, some lipids, extractives (low molecular organic substances soluble in neutral solvent), resin of terpenes, fat, waxes, fatty acids, alcohols, tannins, flavonoides, colour pigments, low molecular weight hydrocarbons, ash and many other compounds which carries a variety of functional groups having capability of complexing heavy metal ions which facilitate their removal by adsorption. The functional group present in the agro-biomass are acetamido, alcoholic, carbonyl, hydroxyl, carboxyl, phenolic, ether, amido, amino, sulphydryl, phosphoryl, esters, lactones, structural polysaccharides and many [8-10]. Cassava waste [11], tamarind wood [12], waste tea leaves [13], banana and

orange peels [14], olive stone waste [15], walnut shell [16],soybean hulls [17] and various other ago-waste in their raw form have been studied extensively and found suitable for metal removal.

The application of raw agricultural waste or untreated plant wastes as adsorbents however reported to have low adsorption capacity due to low surface area and porosity [18, 19]. The plant wastes need to be modified or treated to boost its performance before being applied for the decontamination of heavy metals [20]. The processing of agro-waste for their modification into carbon form is needed as in this form the agro-waste possesses high porosity and large surface area making it more effective for metal adsorption process [21].

Tur dal (*Cajanus cajan)* husk which is about 8 percent of the pulse grain and is the low cost byproduct or waste of pulse processing industry. The husk of tur dal is reported to contain about 5.6 percent crude protein, 0.3 percent fat, 31.9 percent crude fiber, 3.5 percent ash and 58.7 percent carbohydrates and posses potential to be used as metal adsorbent [22]. Merely throwing Tur dal husk for cattle feed is the wasteful way of utilizing this material. As tur dal husk have no or little value and available in large quantity, it is better to do some effort for their value addition. It would be an act of value addition if tur dal husk are converted into their carbon form and utilize as adsorbent for heavy metals removal. The conversion of tur dal husk into adsorbent carbon also help in reducing the cost of waste disposal o this material and provide a potentially inexpensive alternative to the existing commercial activated carbon [23, 24]. Very few researchers have studied the metal adsorption ability of dal husk (Black gram, Bengal gram, *Lathyrus sativus*) [25, 26]. N. Ahalya, et al., investigated raw husk of tur dal (*Cajanus Cajan*) as a new biosorbent for the removal of Ferric (III) and Chromium (VI) ions from aqueous solutions. However the carbon form of tur dal husk is still not prepared and investigated for metal adsorption purpose.

The aim of present work was to optimize the condition of copper ion adsorption from its solution by adsorbent carbon prepared from tur dal husk for value addition to ago-waste.

II. Materials And Methods

The tur dal husk waste was obtained from local pulse processing industry Niki Agro Products Pvt. Ltd, M.I.D.C, Jalgaon, Maharashtra state, India. A copper (II) ion stock solution was prepared by dissolving appropriate amount of copper sulfate in double distilled water. The analytical grade chemicals of standard brand were procured from local chemicals supplier and used for analysis purpose.

2.1 Preparation of Metal Adsorbent from Tur Dal Husk

The metal adsorbent from the Tur dal husk was prepared by slight modification in method described by E.-S.Z. El-Ashtoukhya et al., 2008 [27].The obtained husk waste was first washed with tap water repeatedly to remove dirt and other particulate matter and then with double distilled water. The washed husk was subjected for drying in hot air oven at 105 degree centigrade for six hours. The dried material was then cooled and gently ground in a grinder ground husks were then subjected to carbonization in an air tight stainless steel container by heating in muffle furnace at 500 degree centigrade for one hour. The produced carbonized material was cooled and washed with 0.1 molar hydrochloric acid to remove ash. The acid washed material was then drained with double distilled water until the pH of the filtrate reached above 5.0 and again dried at 105 degree centigrade for 6 hours in hot air oven. The material ultimately was gently crushed and sieved to particle size ranging 0.25–0.15 millimeter and stored in air tight container. The prepared adsorbent was referred as Ad_1 for further study for the adsorption of copper ion. The yield of Ad_1 was calculated as follows given in equation 1:

$$\text{Yield} = \frac{Wc}{Wo} \times 100$$

(1)

Where, W_o= Mass of the original material before carbonization, and W_c = Mass of the material remaining after carbonization.

2.2 Characterization of Adsorbent

The Ad_1 was analysed for various physicochemical parameters such as bulk density and ash as per CEFIC (European Chemical Industry Council) methods [28]. Bulk Density apparatus (DBK 5028-7) was used in the analysis of density. The particle size, moisture, water soluble content and pH was analysed based on Bureau of Indian Standards method IS 877: 1989 [29].Electrical conductivity was determined by IS 14767: 2000 method [30] using Conductivity Meter of Systronic (Model 304). Calorific value of adsorbent sample was estimated using Digital Bomb Calorimeter (Rajdhani Scientific, Model: RSB 6). The traces of elements in adsorbent were determined using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), Model: VARIAN 720-ES. The presence of carbon in the prepared adsorbent and nature and shape of its crystals was confirmed by X-Ray Diffraction (XRD), performed in a XRD of BRUKER (Germany), Model: D8 ADVANCE with scintillation detector. The morphological study of raw husk and $Ad_1$was carried out by

Scanning Electron Microscope (SEM) of HITACHI (Model: S-4800,TypeII)coupled with Energy Dispersive X-ray Spectroscopy (EDS) of BRUKER.

2.3 Preliminary Adsorption Study

Initially the rough trial was taken to check whether prepared adsorbent (Ad_1) remove Cu ion from its solution or not. The batch adsorption was carried out under the conditions given in Table 1. The appropriate amount of Cu solution and adsorbent was taken in 100 ml capped conical flasks and agitated in Orbital Shaking Incubator (REMI) for 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5 and 8 hr. providing sufficient time to establish equilibrium. After each contact period the suspension was filtered through Whatman No.42 filter paper to separate the suspension of Ad_1 and the Cu solution. The filtrate was then diluted to appropriate dilution with double distilled water for the analysis of residual Cu concentration using Atomic Absorption Spectrophotometer (SL 176, ELICO Ltd., Hyderabad, India). The % Removal or Adsorption of Cu was calculated as follows shown in equation 2:

$$\%.\text{Removal} = \left\{ \frac{C_i - C_e}{C_i} \right\} \times 100 \qquad (2)$$

Where, C_i is initial concentration of heavy metals ions and C_e is final or equilibrium concentration of heavy metal ion in milligram per liter [31].

Table 1: Initial Adsorption Trial

Batch Parameter	First Trial	Second Trial	Third Trial
Concentration of Cu ion solution	100 ppm	50 ppm	50 ppm
Volume of Cu ion solution	50 ml	50 ml	50 ml
pH of Cu ion solution	5.63 (Natural)	5.78 (Natural)	5.78 (Natural)
Adsorbent dose	0.1 g	0.1 g	0.25 g and 0.5 g
Particle size of Adsorbent	0.25-0.15 mm	0.25-0.15 mm	0.25-0.15 mm
Agitation speed	150 rpm	150 rpm	150 rpm
Temperature	30 ^{0}C	30 ^{0}C	30 ^{0}C
Contact Time	0.5 – 8 hr. (with time interval 0. 5 hr.)	0.5 – 8 hr. (with time interval 0. 5 hr.)	0.5 – 8 hr. (with time interval 0. 5 hr.)

2.4 Optimization of Adsorption Condition

Based on the result of initial trial the batch adsorption study was planned for the optimization of pH, agitation speed, temperature and adsorbent dose, keeping the other parameter of adsorption such as initial concentration of Cu solution (50 ppm), volume of solution (50 ml), particle size (0.25-0.15 mm) and contact time (4 hr.) constant. The pH optimization study was carried out by varying pH by 1 from 2 to 10 pH, keeping agitation speed 150 rpm, temperature 30 ^{0}C and adsorbent dose 0.5 gram. The pH of solutions was maintained using 0.1-0.5 M solution of HCl or NaOH. After agitation of mixture the suspension was filtered and filtrate analysed for residual Cu ion concentration. In the optimization of agitation speed the agitation speed varied from 50- 250 rpm keeping pH at optimized level, temperature at 30 ^{0}C and adsorbent dose 0.5 gram. The optimized condition of temperature was obtained by changing temperature from 10 ^{0}C to 60 ^{0}C while keeping pH and agitation speed at optimized level and adsorbent dose 0.5 gram. The valuable information on the mechanism of adsorption is provided by thermodynamic analysis. Thermodynamic studies were therefore carried out to evaluate the feasibility of the adsorption process by estimating the standard Gibb's free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0).

The ΔG^0 in J/mol was computed using thermodynamic equilibrium constant (K_C) by equation 3:

$$\Delta G^0 = -RT \ln K_C \qquad (3)$$

Where, R is ideal gas constant (8.314 J/mol K), T is temperature in K

The K_C is related to C_∂ and C_e by the equation 4:

$$K_{C=} C_\partial / C_e \qquad (4)$$

Where, C_∂ is milligram of Adsorbate adsorbed per liter(mg/L)and C_e is the equilibrium concentration of solution in milligram per liter(mg/L).

C_∂ was calculated on the basis of following relation given in equation 5:

$$C_\partial = C_i - C_e \qquad\qquad \textbf{(5)}$$

Where, C_i is the initial concentration of solution in milligram per liter(mg/L) and C_e is is the equilibrium concentration of solution in milligram per liter(mg/L).

According to Van't Hoff equation ΔG^0 is related to ΔH^0 and ΔS^0 by the relation presented in equation 6:

$$\ln K_C = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad\qquad \textbf{(6)}$$

The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot of $\ln K_C$ versus 1/T [32, 33].

The adsorbent dose optimization study was carried out by altering dose from 0.25 to 2.75 gram keeping pH, agitation speed and temperature all at optimum condition. The adsorption capacity (q_e milligram per gram) was determined by the equation 7:

$$q_e = V\frac{(C_i - C_e)}{W} \qquad\qquad \textbf{(7)}$$

Where, C_i is initial concentration of heavy metals ions and Ce is final or equilibrium concentration of heavy metal ion in milligram per liter, V is the volume of the solution in liter and W is the mass of the Adsorbate in gram [34, 35].

Eventually at the end of study the contact time was optimized, carrying out the adsorption at achieved optimum conditions.

III.   Results And Discussions

3.1 Adsorbent Characterization

The result of physical analysis of prepared adsorbent is shown in Table 2. The yield of adsorbent on dry raw husk mass basis was 31.73 %. The bulk density of adsorbent was found to be 0.6085 gram per cubic centimeter (g/cm^3) and electrical conductivity (specific conductance) 276.75 milli Siemens per meter (mS/m). The particle size data shows that Ad_1 had majority of particles between 210 to 250 micron.

Table 2: Physical Characteristics of Adsorbent (Ad$_1$)

Parameter	Result
Yield (%)	31.73 ± 0.32
Bulk density in g/cm^3	0.6085 ± 0.0
Conductivity (mS/m)	276.75
Particle size	
210-250 micron	51.84 %
180-210 micron	9.82 %
150-180 micron	38.34 %

Values are Mean (± SEM) of 3 determinations

Table 3 is representing the chemical characteristics of adsorbent Ad_1. The adsorbent had 4.54 % moisture, 5.16 % ash. The water soluble content with adsorbent was found to 0.52 %. The calorific value of adsorbent was 7047.94 Calories per gram (Cal/g). The pH of adsorbent solution as measured with Deluxe (EI) pH meter was observed to be 7.71.

Table 3: Chemical Characteristics of Adsorbent Ad$_1$

Parameter	Result
Moisture (%)	4.54 ± 0.04
Ash (%)	5.16 ± 0.10
Water soluble content (%)	0.52 ± 0.02
Calorific value (Cal/g)	7047.94 ± 2.92
pH	7.71 ± 0.01

Values are Mean (± SEM) of 3 determinations

The traces of some elements found with Ad_1 are given in Table 4. The result predicted minerals responsible for ash in adsorbent to be of Magnesium (Mg), Calcium (Ca), Sodium (Na), Ferrous (Fe), Manganese (Mn), Zinc (Zn), Copper (Cu) and Lead (Pb).

Table 4: Trace Element Analysis of Adsorbent Ad_1

Element	Mg	Ca	Na	Fe	Zn	Cu	Mn	Pb
Result (ppm)	3503.04	1423.61	1169.62	70.41	57.17	19.66	14.75	6.23

The XRD pattern of adsorbent is represented in Fig. 1. The peak obtained for adsorbent was compare with the standard peak for carbon and found matching. The result thus confirms that after carbonization adsorbent raw tur dal husk was transformed to adsorbent carbon. The XRD result also showed the nature of crystals in adsorbent as hexagonal and a mixture of 29.6 % crystalline and 70.4 % amorphous crystals.

Fig. 2 and 3 is showing the scanning electron microscope pictures of raw tur dal husk and adsorbent Ad_1. It is clear from the SEM images that raw husk had very less pores of small sizes whereas carbonized form of husk (Ad_1) had many pores of bigger sizes. The porous structure of Ad_1 explains why it was more suitable for adsorption of metals ion as compare to raw husk.
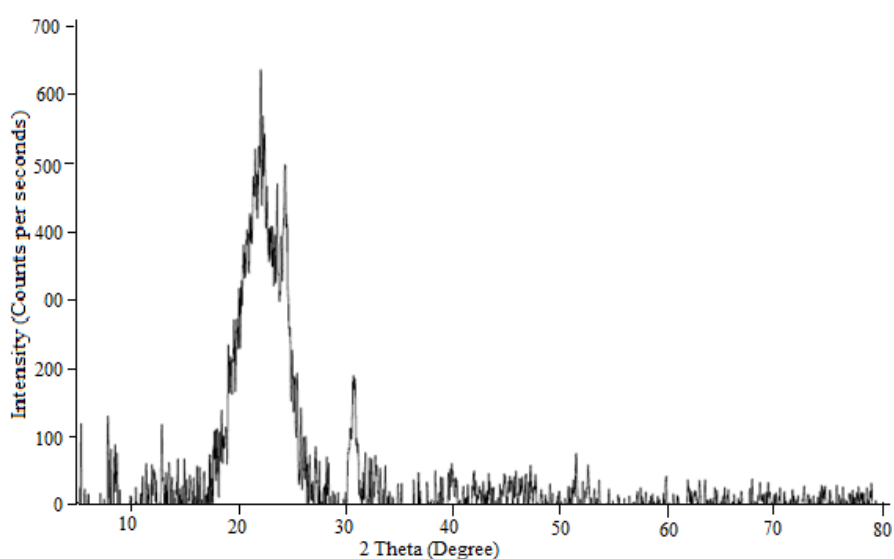

Figure 1: XRD pattern of Ad_1

S-4800 5.0kV 8.2mm x1.80k SE(M)   30.0um

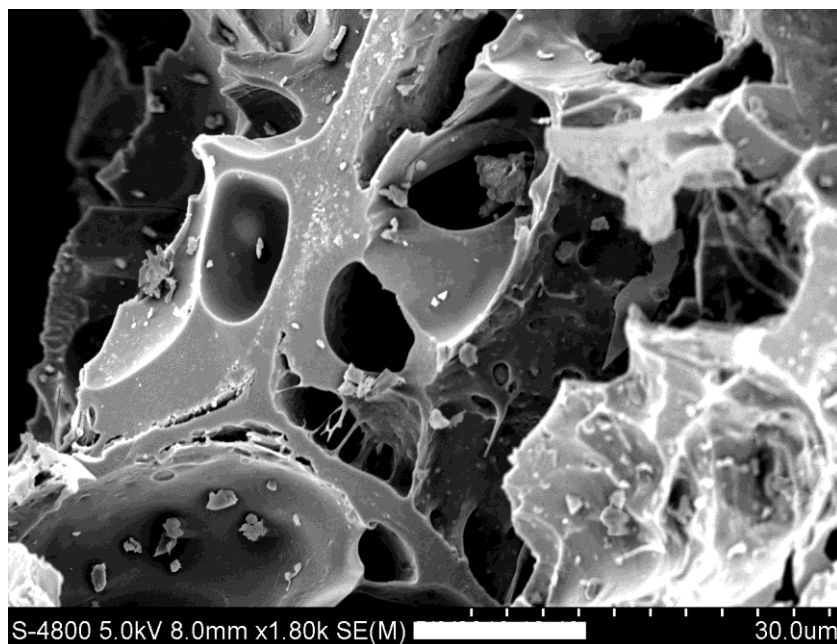**Figure 2: Scanning electron microscope image of raw tur dal husk**

Figure 3: Scanning electron microscope image of Ad$_1$

3.2 Initial Adsorption Trial

   The findings of adsorption study of Cu ion by developed adsorbent from tur dal husk in without optimization of adsorption condition is shown in Table 5. The result of first trial revel removal of Cu ion from it's solution of 100 ppm with 0.1 g adsorbent was low (8.3 %). The second trial was therefore planned with 0.1 g adsorbent but reducing the initial concentration of Cu solution to 50 ppm. The result of second trial in term of % removal was also not satisfactory as only 16.4 % removal of Cu ion was observed. The third trail was carried out keeping initial concentration of Cu ion solution same (50 ppm) and increasing the adsorbent dose (0.25 & 0.5 gm). The % removal was 28.1 % and 36.8% with adsorbent dose 0.25 and 0.5 g respectively.According to Indian Environment (Protection) Rule the permissible maximum limits of copper in industrial effluent for discharge in inland surface water, public sewers and in marine costal area is maximum 3.0 ppm [36]. In order to utilize the developed adsorbent for the industrial effluent treatment, there was need to achieve more than94 % removal in the said planned experiments. Many researchers already have attempted to enhance the adsorption performance of metal adsorbent by optimization of adsorption condition and achieved drastic improvement in adsorption [37]. The optimization of adsorption conditions was therefore felt essential for improving the performance of adsorbent.

Table 5: Result of Initial Adsorption Trials

Parameter	First Trial	Second Trial	Third Trial	
			0.25 g	0.5 g
Equilibrium Time	2.0 hr.	1.5 hr.	2.5 hr.	3.5 hr.
Residual Cu ion concentration at equilibrium	90.6 ppm	41.5 ppm	35.5 ppm	31.2 ppm
% Removal of Cu ion	8.3 %	16.4 %	28.1 %	36.8%

3.3 Optimization of Adsorption Condition
3.3.1 Effect of pH on Adsorption

   Fig.4 represents the effect of pH on Adsorption. The adsorption takes place by various mechanisms, and one of the import mechanisms is electrostatic force of attraction between metal ion (possessing positive charge) and adsorbent surface (carrying negative charge). The pH of the aqueous solution is considered to be most important parameter affecting adsorption of metal ion at the solid-liquid interfaces as changing the charges on the adsorbent surface. It was observed as the pH increased the % removal of Cu also increased linearly. The adsorption was very low at pH 2 & 3 (2.6 and 4.5 % removal respectively) and then increased rapidly up to pH 6 (24.7 % at 4, 35.6 % at 5 & 41.7 % at 6 pH). The concentration of H^+ in the solution and the surface charge of the adsorbent was the cause for the found effect. At acidic pH, excess H^+ ions in the solution compete with the metal ion present in the solution for the adsorption sites of the adsorbent and prevent the metal ion from reaching the adsorption site. Thus at low pH adsorbent surface was more protonated and posses positive charge as the surface of adsorbent was completely covered with H^+ ions. The said condition was therefore not allowing

adsorption of positively charged species in solution by adsorbent because of their repulsion by adsorbent surface. Retardation in diffusion of Cu species due to such repulsion was also the cause for the lower adsorption at lower pH. As the pH of the system increased, the number of positively charged sites decreased and the number of negatively charged sites increased on the surface of adsorbents [38]. Due to said change in the surface charge of the adsorbent, as the pH increased beyond 3 the competition from the hydrogen ions decreased and the positively charged ions present in the solution (Cu^{2+}) now adsorbed at the negatively charged sites of the adsorbent. At pH 7 and above the precipitation of Cu ion was observed due to formation of metal complex as hydroxide. The % removal at pH 7 and above was high (94.5 % at 7, 97.0 at 8, 98.2% at 9 and 99.2 at 10) because of both the combine effect of precipitation as well as of adsorption mechanism. B.M.W.P.K Amarasinghe and R.A. Williams (2007) obtained the same type of result while adsorbing Cu ion with tea waste as low cost adsorbent. H. Ye et al., 2012 also found the effect of pH in similar trend for removing Cu(II) from aqueous solution using modified rice husk [39]. Other researchers also received the same kind of result with adsorbent material coca shells, orange waste [40, 41]. Even at 6.5 pH very slight precipitation was observed. Therefore to support the removal of Cu ion only by adsorption and not by precipitation, the optimum pH for the adsorption was fixed at 6.0.
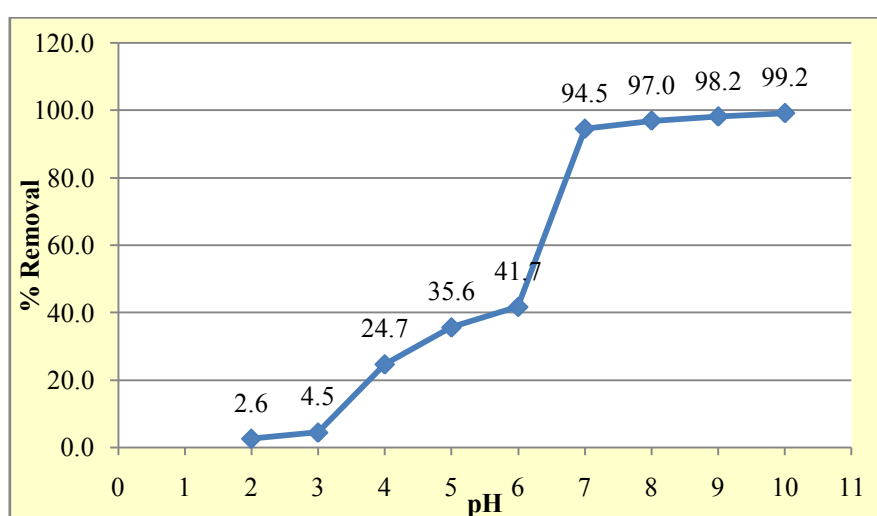

Figure 4: Effect of pH on Cu adsorption by Ad_1

3.3.2 Effect of Agitation on Adsorption

The effect of agitation on Cu uptake is shown in Fig. 5. The data revel as the agitation speed increased the adsorption efficiency also increased until it reached peak value (41.1 % removal) and then further increase in agitation had no benefit on adsorption. It was observed, % removal of Cu increased progressively as the agitation speed increased from 50 to 150 rpm (36 %, 39.5 % & 41.1 % removal at 50, 100 & 150 rpm respectively). The reason behind the same is mass transfer phenomenon which is generally observed during adsorption. The adsorbate molecules first migrate from the bulk of the solution towards the adsorbent surface, the diffusion of adsorbate then takes place through the boundary layer to the adsorbent surface. After this only the actual adsorption of adsorbate occur on adsorption site of adsorbent. The adsorption takes place not only on the surface of adsorbent, the adsorbate molecules further diffuse in the bulk of adsorbent and there also again the adsorption occur [42]. At lower agitation speeds, the fluid film around the adsorbate particle was thicker due to which the difficulty in crossing the boundary layer was faced by adsorbent particle, resulting low adsorption [43]. The justification of increase in adsorption due to increase in the agitation speed lies in the fact as the agitation speed increased the turbulence also increased and it overcame the boundary layer resistance and facilitate the migration of Adsorbate molecules from the bulk solution to the surface of adsorbent. Also as the rate of transfer of Adsorbate molecules toward the adsorption surface increased, in turn it forced the diffusion of adsorbate inside adsorbent mass. It is concluded as the agitation speed increase the adsorption also increase due to improvement in migration rate of adsorbate towards the adsorbent and the forcing of diffusion of adsorbate inside the adsorbent bulk. The findings of Y.C. Sharma et al. (1991) also agreed with result while using tamarind seed for adsorbing cadmium [44].However the adsorption was found to be low at 200 rpm (40.7 % removal)and 250rpm (40.3 % removal) as compare to 150 rpm (41.1 % removal). The reason for the same may be the improper contact between Cu^{2+} ion and the binding site of Ad_1. A.V. AjayKumar et al., 2009 had also received similar type of result when tried to remove various heavy metals (Cd^{2+}, Cu^{2+}, $N^{2+}i$, Zn^{2+}) using activated sludge [45]. As the shaking speed 150 rpm was sufficient to ensure the availability of all the binding

sites of the adsorbent for uptake of maximum Cu^{2+} ion present in solution, the optimized agitation speed was therefore selected as 150 rpm.
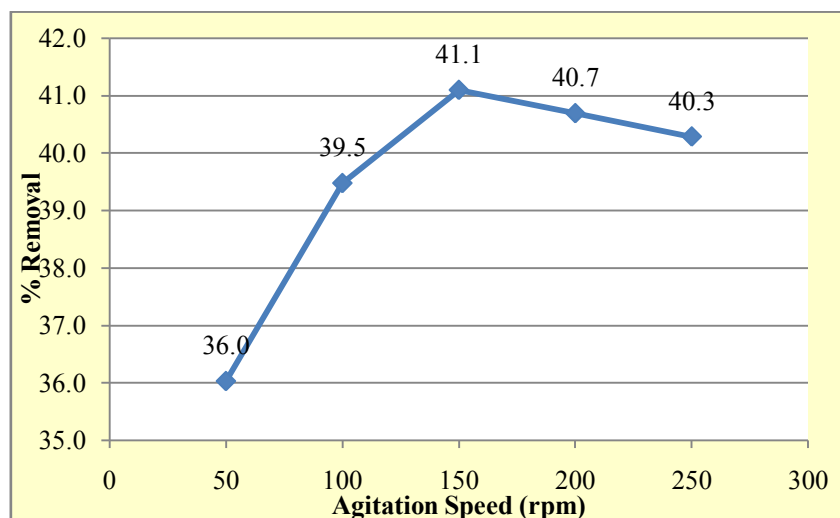

Figure 5: Effect of agitation speed on Cu adsorption by Ad$_1$

3.3.3 Effect of Temperature on Adsorption
The effect of temperature on Cu removal is given in Fig. 6. The % removal of Cu was 35.8%, 38.3%, 41.3%, 42.7 %, 44.9 %, 45.5 % at 10, 20, 30, 40, 50 and 60 ^{0}C respectively. The adsorption of Cu was observed to be facilitated by increase in temperature. It means the adsorption reaction was absorbing heat to occur. The adsorption of Cu by the adsorbent was considered endothermic in nature. The predicted cause for improvement in % removal with increase in temperature may be due to the formation of new binding sites on and near the surface of Ad$_1$ as a result of breaking of some internal bonds. Increase in the kinetic energy of adsorbate was also thought as the another possible reason for the increase in adsorption that facilitated diffusion of Adsorbate within pores of adsorbent [46]. Diffusion also increased due to decrease in viscosity of solution as a consequence of increasing temperature and enlargement of pore size. The similar result was obtained by S.H. Hasan et al., 2008 in an attempt to adsorb Cr(VI) by agricultural waste (maize bran) [47]. The increase in adsorption efficiency with increase in temperature was observed by X.S. Wang et al. (2010), while removing metal ion (chromium) with adsorbent carbon derived from wheat-residue [48].

S. Sun, and A. Wang (2006) had also received the same result of increase in adsorption with increase in temperature while removing Cu(II) ions using N, O-carboxymethyl chitosan [49].The 60 ^{0}C temperature was thus optimized for the said adsorption.
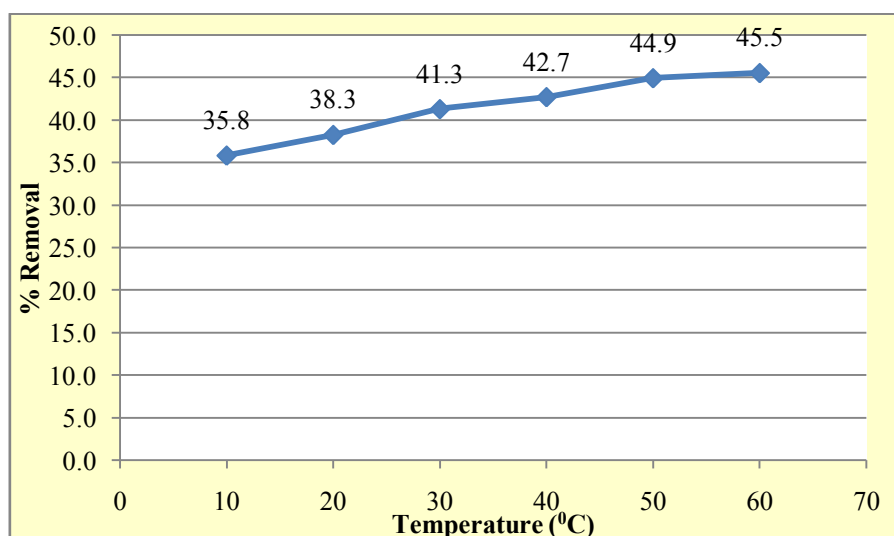

Figure 6: Effect of temperature on Cu adsorption by Ad$_1$

The estimation of standard Gibb's free energy of adsorption at different temperature is shown in Table 6. The ΔG^0 was found to be 1371.14, 1165.78, 886.14, 764.00, 545.48 and 426.78 J/mol for the temperature 10, 20, 30, 40, 50 and 60 ^{0}C respectively. The ΔG^0 was observed to be decreasing with increase in temperature but remain positive for all the temperature. The obtained positive values of ΔG^0 at all studied temperatures conclude that adsorption process was endergonic (non-spontaneous) [50]. The result is in accordance with the study done by G. Moussavi, and B. Barikbin (2010) where ΔG^0 obtained was positive during adsorption of Cr(VI) by pistachio hull powder.

Table 6: Standard Gibb's Free Energy of Adsorption at Different Temperature

Temperature (^{0}C)	Temperature T (K)	1/T	Initial Concentration of Cu solution (C_i) (mg/L)	Equilibrium Concentration of Cu solution (C_e) (mg/L)	$C_\partial = C_i - C_e$ (mg/L)	$K_C = C_\partial / C_e$	$\ln K_C$	$\Delta G^0 = -RT \ln K_C$ (J/mol)
10	283	0.0035	49.40	31.7	17.7	0.5584	-0.58	1371.14
20	293	0.0034	49.40	30.5	18.9	0.6197	-0.48	1165.78
30	303	0.0033	49.40	29	20.4	0.7034	-0.35	886.14
40	313	0.0032	49.40	28.3	21.1	0.7456	-0.29	764.00
50	323	0.0031	49.40	27.2	22.2	0.8162	-0.20	545.48
60	333	0.0030	49.40	26.6	22.8	0.8571	-0.15	426.78

Fig.7 is the plot of $\ln K_C$ versus 1/T for determining the values of ΔH^0 and ΔS^0. The value of $\ln K_C$ was found to decrease linearly with increase in value of 1/T. The line had equation y = -819.2x + 2.324 with slope -819.2 and y-intercept 2.324. The data of line was found to fit satisfactory as coefficient of determination (R^2) was closer to unity (0.989). The slope of line and y-intercept was used in Van't Hoff equation to calculate ΔH^0 and ΔS^0 and is given in Table 7. The value of ΔH^0 and ΔS^0 was found to be 6810.82 J/mol and 19.32 J/mol K respectively. Both ΔH^0 and ΔS^0 were found to be positive for the said adsorption. The positive value of ΔH^0 again confirms that the adsorption was endothermic. The positive value of ΔH^0 and ΔS^0 tells the adsorption reaction was unfavorable for enthalpy but favorable for entropy. The positive value of ΔS^0 revel increased randomness at the solid/solution interface during adsorption and the system became more disordered through adsorption process. The similar finding(positive ΔH^0 and positive ΔS^0) was reported in a study of the adsorption of nitrate from aqueous solutions by activated carbons prepared from sugar beet bagasse activated chemically with ZnCl$_2$ [51].When adsorbing copper from aqueous solutions using watermelon shell, positive ΔH^0 and positive ΔS^0 was also observed by K. Banerjee et al., 2012 [52].
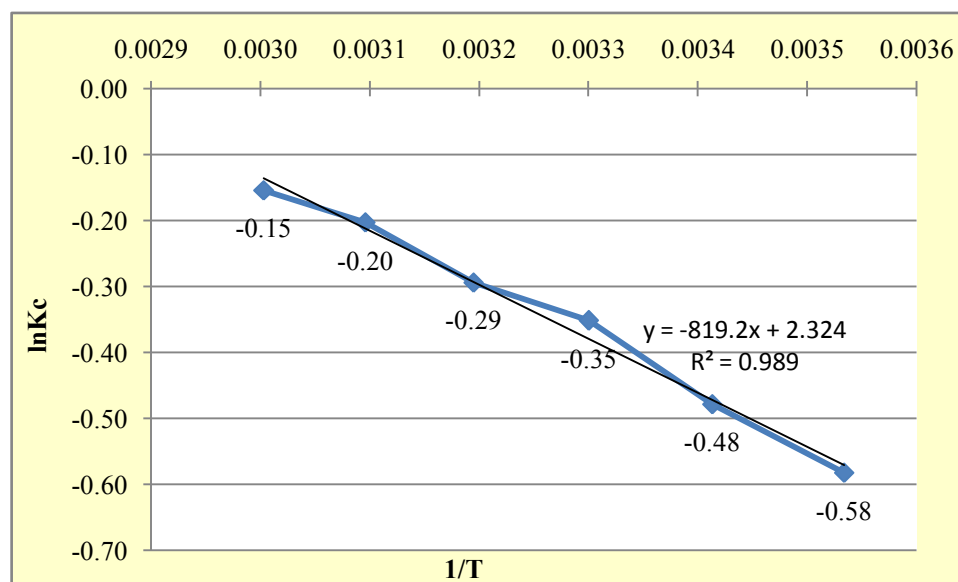

Figure 7: Plot of $\ln K_C$ versus 1/T

Table 7: Standard Enthalpy Change (ΔH^0) and Entropy Change (ΔS^0) of Adsorption

Van't Hoff Equation		Equation of line with Corelation coefficient	Slope	Y Intercept	ΔH^0 (J/mol)	ΔS^0 (J/mol K)
$\ln K_C = -\dfrac{\Delta G^0}{RT} = -\dfrac{\Delta H^0}{RT} + \dfrac{\Delta S^0}{R}$		y = -819.2x + 2.324 R² = 0.989	-819.2	2.324	6810.82	19.32

3.3.4 Effect of Adsorbent Dose on Adsorption

The effect of adsorbent dose on Cu adsorption is depicted in Fig.8. The % removal was found to be 34.8, 45.1, 53.4, 61.1, 75.3, 85.0, 94.9 and 100 % for adsorbent dose 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5 and 2.75 g respectively. The adsorbent capacity of 3.4, 2.2, 1.8, 1.5 1.2, 1.1, 0.9, 0.9 mg of Cu per g of adsorbent was observed for adsorbent dose 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5 and 2.75 g respectively. The % removal of Cu was found to be increasing with increase dose of Ad_1 whereas the adsorption capacity q_e found to be decreasing with increasing dose of adsorbent. Earlier study by other researchers also confirms the same trend in % removal and adsorption capacity as consequence of increase amount of adsorbent dose for the removal of adsorbate [53, 54].The % removal increased with increasing level of adsorbent due to the availability of large surface area which increased more numbers of adsorption sites. It was observed that with 0.25 g the % removal was 34.8 % but when the adsorbent dose was doubled (0.5 g) the % removal obtained was not double, instead it was less (45.1%). This less prominent adsorption which was also the cause for decrease in q_e with increase in the adsorbent dose may be related with the fact as the blocking of some of the adsorption sites, non availability of adsorbent surface due to their masking with formed adsorbent agglomerates (M.N. Ibrahim Mohammed et al., 2010) and lengthening of diffusion path. The saturation of adsorption sites as adsorption proceeds with increasing dose of adsorbent was also the reason for the decrease in adsorption capacity. As minimum 2.75 g dose required for compete removal of Cu species from 50 ml (50 ppm) Cu solution, it was considered optimum for said adsorption.
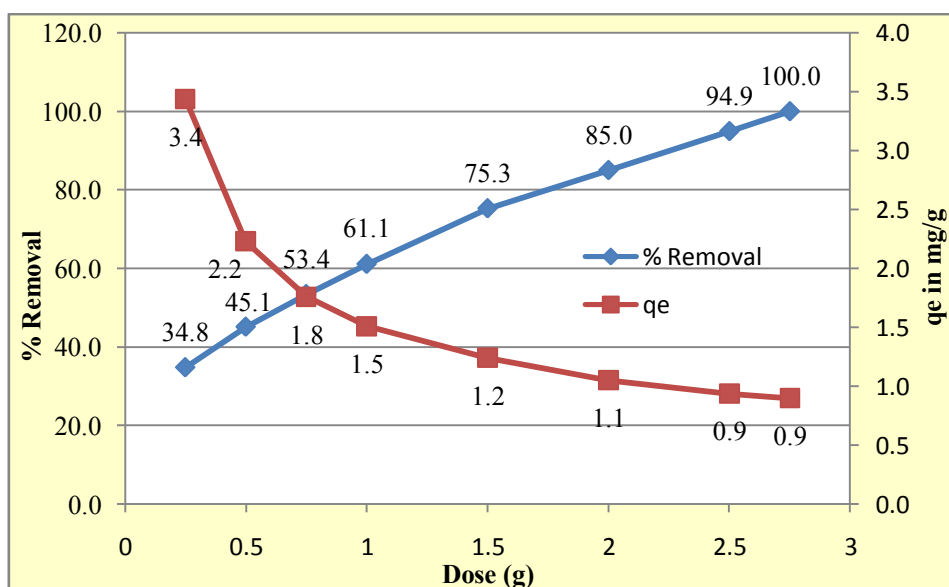

Figure 8: Effect of dose of Ad_1 on Cu adsorption

3.3.5 Contact Time Optimization

The optimization of contact time was done at all the achieved optimized parameter for adsorption (pH 6, agitation speed 150 rpm, temperature 60 ^{0}C and adsorbent dose 2.75 g) and in shown in Fig.9. The % removal was found to be 85.4, 90.3, 93.9, 96.4, 98.8, 100, 100 and 100% for contact time 0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 4 hr. respectively. The adsorption observed to be increasing with increasing contact time. Initially the removal of Cu was high due to the availability of large surface area. As the adsorption commenced with time there was exhaustion of adsorption sites with adsorbent. At his stage the phenomenon of migration of Adsorbate from the exterior to the interior sites of the adsorbent particles took the control of adsorption and the adsorption observed was less effective [55, 56]. The result agrees with the findings of A.V. AjayKumar et al., 2009 while removing heavy metals on activated sludge. The other researchers also found the increase in adsorption with increasing contact time till the equilibrium time is attend [57]. The complete adsorption was achieved in 3 hr., which was a minimum time for 100% removal of Cu. The contact time of 3 hr. was finalized as the optimum time for the considered adsorption.
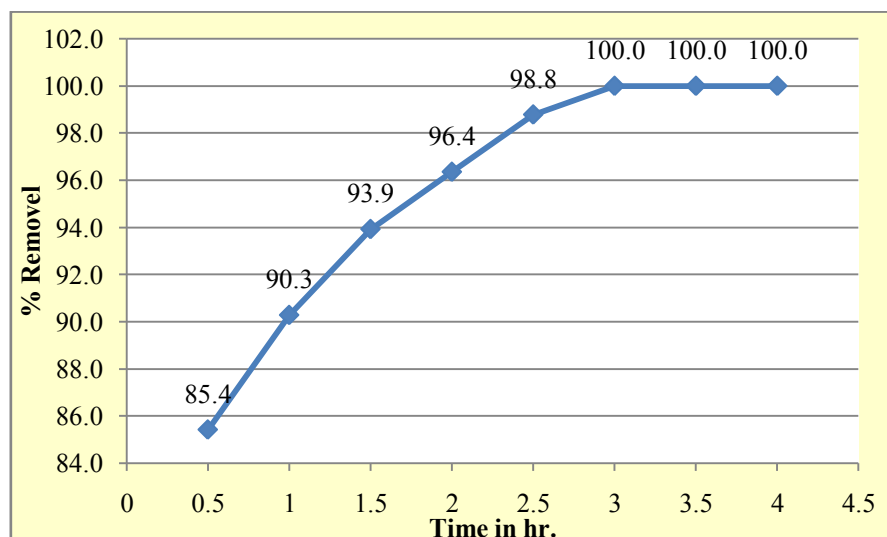
Figure 9: Effect of contact time on adsorption of Cu by Ad$_1$

IV.   Conclusion

The effective metal adsorbent can be prepared from tur dal (*Cajuns Cajon)* husks simply by their carbonization. The optimum condition required to remove complete Cu ions from 50 ml, 50 ppm Cu solution using developed adsorption is pH 6, agitation speed 150 rpm, temperature 60 ^{0}C, adsorbent dose 2.75 g and contact time 3 hr. However the metal adsorption by the prepared adsorbent is endothermic in nature, non-spontaneous and increases randomness at the adsorption site. The findings of present the work may be useful in designing the process of waste water treatment for removing heavy metals particularly copper by adsorption.

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