Utilization of Pulse Processing Waste (*Cajanus cajan* Husk) for Developing Metal Adsorbent: A Value-added Exploitation of Food Industry Waste

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Abstract India is the largest producer of pulses (edible legume) in the world. Pigeon pea or Tur (*Cajanus cajan*) is the second most major pulse produced in India and is mainly processed to convert into product known as "Tur dal". The manufacturing industries of Tur dal generate considerable amount of byproduct/waste in the form of husk. The present investigation explores the possibility of exploiting activated carbon prepared from the Tur dal husk for removing heavy metal. The objective of the work was to enhance the performance of prepared activated carbon by carrying out batch experiments study to optimize the condition of adsorption for complete removal of Cu ions from its 50 ml, 50 ppm solution. The char was produced by carbonizing the washed and dried Tur dal husk in air tight container at 500°C for 1 hr. The obtained char was then activated by soaking in concentrated sulfuric acid (1:1 ratio) for 24 hr. at room temperature to get activated carbon. The physicochemical characterization of achieved activated carbon was done for various parameters along with analysis of trace elements (ICP), crystal nature (XRD) and structural morphology (SEM). The optimum condition for adsorption was studied by altering pH (2-10), agitation speed (50-250 rpm), temperature (10-60°C), adsorbent dose (0.1- 2.25 g) and contact time (0.5-4 hr.). The work concludes activated carbon prepared from Tur dal husk possess considerable metal adsorption property and showing maximum activity in an optimum condition of 6 pH, 200 rpm agitation speed, 10°C temperature, 2.25 g adsorbent dose and 3 hr. contact time. The examination of thermodynamic data confirmed the adsorption by the developed activated carbon was exothermic (positive ΔH^0), changing from spontaneous to non-spontaneous with increase temperature (both negative and positive ΔG^0), making system ordered and feasible (positive ΔS^0) through adsorption. The work suggests way of giving value addition to pulse processing industry waste for their better utilization in eco-friendly and economical way.

***Keywords:** adsorption, copper, food waste, activated carbon, tur dal husk*

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1. Introduction

Food derived from plant source contain inedible portion in the form of stone, peels, seed coat and husk. One of the purposes of the processing of raw agricultural commodity is to make them consumable by remove this uneatable portion. The separated scraps are sometimes subject to cattle feed as by product of the industry and mostly thrown as waste. The agro food industry creates huge amount waste and is matter of concern due their potential of creating environmental pollution. Under the provision of various environmental acts the food processing industrial waste needs to be disposed safely and require significant investment on such waste disposal. The cost on such treatments and disposal however can be reduced if the produced leftover is utilized for some useful purpose instead of throwing [1].

The agro food industry has the tremendous potential to remove heavy metals from effluent by adsorption. The heavy metal adsorption properties of agro waste is natural and is due to the presence of various functional groups carried by cellulose, hemicelluloses, lignin, starches, sugar, protein, lipid present in agro based garbage. These functional groups have the capability of complexing heavy metals [2] and remove them by process of adsorption. The metal adsorption capacity of agro waste can be improved by their heating in controlled condition to produce its carbon (extremely porous). The adsorption performance of this agro based carbon can be further enhanced by their activation (alteration in surface functional groups and their charges) with various agents such as oxidizing agent (hydrogen peroxide), organic compounds (ethylenediamine, formaldehyde), organic acid (tartaric acid, citric acid, sulfuric acid, hydrochloric acid, nitric acid), base solutions (calcium or sodium hydroxide, sodium carbonate) [3].

The natural aquatic systems is getting polluted due to the introduction various toxic heavy metal ions such as Hg, As, Pb, Cr, Fe, Se, Co, Ni, Cd, Zn, Cu at a much higher concentration than the prescribed limits, coming from the waste water of mining, refining ores, fertilizer tanneries, batteries industries [4,5]. According to Indian Environment (Protection) Rule, 1986 [6], 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. The available techniques to remove heavy metals like precipitation, ion exchange, reverse osmosis and electrolytic methods have limitations (high cost, production of sludge in huge quantity) and not much popular [7]. The removal of heavy metals by adsorption using activated carbon on the other handis more reliable method. The large surface area, chemical nature, micro-porous structure makes activated carbon ideal for the said purpose [8]. The activated carbon are always in high demand but prove expensive some times, if prepared from costly raw materials. The cost of activated carbon produced from agro food industrial waste is less as large quantities are readily and cheaply available [9]. The various agro based materials investigated for their metal adsorption property and reported to be successful. Husk or bran of rice, wheat flour, maize, corn, black gram husk, pearl millet, Shells and/or stones of coconut, almonds, apricots, peanuts, olive wastes, cherries, bael fruit, Brazil nut, hazelnut, wood apple, chestnut, Peels of different fruits such as, orange, banana, watermelon, garlic, cassava, mango, jack fruit, Wastes resulting from the production and processing of tea, coffee, as well as sugar cane bagasse, coir pith, grape bagasse, Agro waste from papaya seeds, sunflower, palm seed coat, pineapple stem, maize cob, pine bark, tamarind seed, barley straw already have been proved effective for metal adsorption purpose [10].

India is the largest consumer and producer of pulses (edible legume) in the world, which is around 15% of the total grain in country. Dal is a major form in which pulses are consumed in India. Dal is also popular in other Asian countries like Nepal, Pakistan, Sri Lanka and Bangladesh. Dal is a prepared by separating pulse (dried seeds) from their outer hulls and split. There are large number of dal mills scattered in the India which process more than 75% of the pulses produced. Chickpea (*Cicer arietinum*) also known as Bengal gram (chana) is the major pulse produced in India followed by Pigeon pea (*Cajanus cajan*) also known as Tur (arhar) or tropical green pea or yellow Pigeon pea or Red gram. Pigeon pea is mainly consumed in the form of split pulse as "Tur dal" in India. The processing of Pigeon pea to produce Tur dal involve two steps 1) Loosening of husk or seed coat and 2) Dehusking and splitting into cotyledon. The loosening of husk is facilitated by prolong sun drying as it is effective and economical. The loose husk then separated from the grain by imparting friction with grooved rollers in machine. Tur dal industry generate considerable amount of husks which is around 8% of this pulse [11]. Tur dal husk which is the low cost by product of this industry is generally considered for cattle feed only. During processing many times due to use of lime water, alkali and other chemicals the husk become unfit even for cattle feed. The Tur dal husk which is basically cellulosic material can be very well exploited for the preparation of activated carbon in economical way. Earlier investigators mainly studied *Cicerarientinum* husk for metal adsorption but in their raw form [12-17]. Their study confirms husk of *Cicerarientinum* to be an excellent material for biosorption of metals if present in low concentration in water. Husk of pulse *Lathyrussativus* (Indian pea) was studied by Panda, et al., 2006 [18]. Mungbean (*Phaseolus aureus/ Vignaradiata*) husk an agro waste material was evaluated by Saeed, A., et al., 2009 [19] as a new sorbent for the removal of cadmium (II) from aqueous solution. The hulls of *Vignaradiata* and *Cicer arietinum* have been exploited for the preparation activated carbon [20,21]. The referred literature review reveled that only Ahalya et al., (2007) carried out work on the raw husk of Tur dal as a new biosorbent for the removal of Ferric (III) and Chromium (VI) ions from aqueous solutions. Their study concludes Turdal husks in their raw form has potential to treat wastewaters containing low concentration of metal ions. The preparation of activated carbon from Tur dal husk is still not attempted.

The present investigation was carried out with the aim to prepare activated carbon from pulse processing industrial waste (Tur dal husk) and to study its adsorption potential for the effective removal of metal (Cu ion) from its aqueous solution.

2. Materials and Methods

Stock solution of copper (II) ion (1000 ppm) was made by dissolving 3.9295 g of copper sulfate ($CuSO_4.5H_2O$) in one liter of double distilled water. This prepared stock solution was used to prepare desired concentration of fresh Cu solution by appropriate dilution. The chemicals required for analysis were procured from Jinendra Scientific, Jalgaon (Maharashtra state, India) and of analytical grade from standard brands (MERCK, SDFCL). Niki Agro Products Pvt. Ltd., a local pulse processing industry located at M.I.D.C, Jalgaon, was contacted to obtain Tur dal husk.

2.1. Preparation of Activated Carbon

The activated carbon from Tur dal husk was prepared by slight modification and combining the methods described by El-Ashtoukhya et al., 2008 [22], Sivaraj et al., 2010 [23] and EI-Sayed et al., 2011 [24]. The husk was first carbonized and the resulting char was then activated by treating with sulfuric acid as given in Figure 1.

2.2. Characterization of Activated Carbon

The prepared activated carbon was analysed for various physicochemical parameters, crystallography and morphological structure by standard methods using sophisticated instruments given in Table 1.

2.3. Initial Adsorption Study

Initially the batch adsorption experiments were carried out to find out roughly the adsorption potential of prepared activated carbon Ad$_3$ in adsorbing Cu ion from its solution. The whole sets of experiments were carried out changing Cu solution concentration and adsorbent carbon dose at natural pH. The other parameters for

adsorption like volume of Cu ion solution (50 ml), particle size of adsorbent (0.15-0.25 mm), agitation speed (150 rpm) and temperature (30°C) were kept constant during preliminary study. First experiment carried out using Cu solution of 100 ppm (natural pH 5.63) and 0.1 g of adsorbent dose. Second experiment was performed keeping adsorbent dose same (0.1 g) but lowering the concentration of Cu solution to 50 ppm (natural pH 5.78). In third experiment concentration of Cu solution was kept same i.e 50 ppm but adsorbent dose increased to 0.25 g. Forth experiment was conducted in the same manner as third only changing adsorbent dose to 0.5 g.
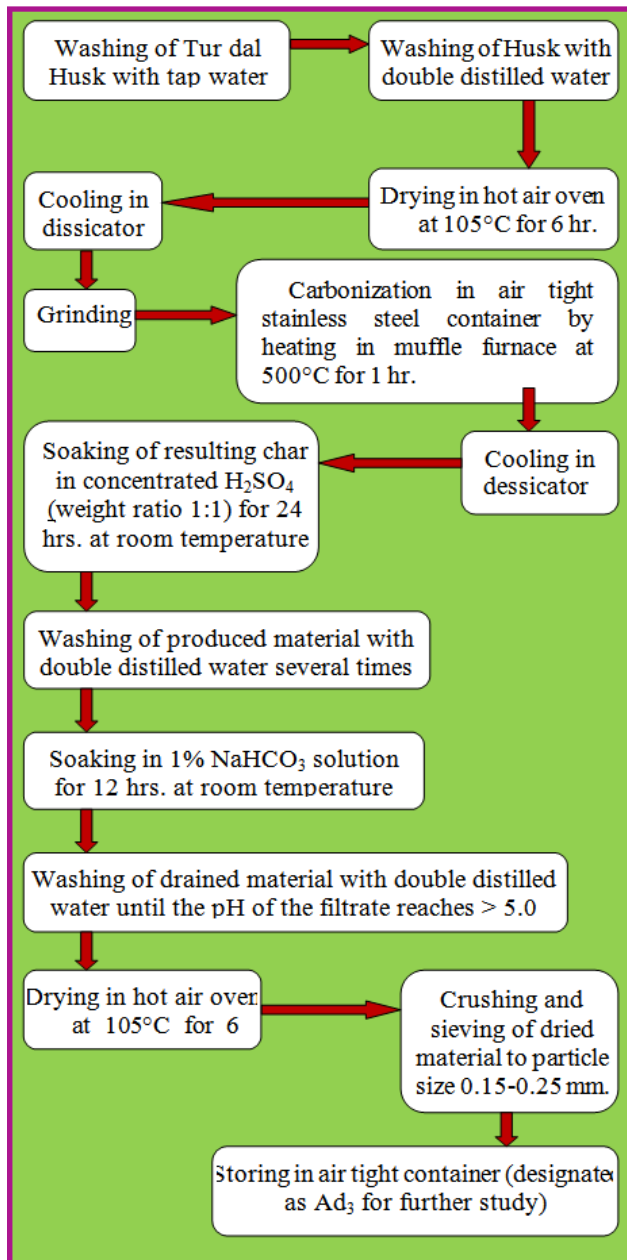

Figure 1. Method of preparation of adsorbent ad₃ from Tur dal husk

All the experiments were carried out in 100 ml capped conical flasks adding required amount of Cu solution and adsorbent dose. The flasks were 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. The flasks were 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. After every treatment period 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) [28]. The% Adsorption/ Removal of Cu was calculated as per equation 1:

$$\%.\,Adsorption = \left\{ \frac{C_i - C_e}{C_i} \right\} x\ 100 \qquad (1)$$

Table 1. Analysis Methods and Instruments for Physicochemical Characterization of Ad₃

Parameter	Equipment/ instrument	Analysis Method
Moisture	Hot air oven	Bureau of Indian Standards method (IS 877: 1989) [25]
Water soluble content	Weighing balance (AND, Model HR-200)	
pH	pH Meter (Deluxe 101 (EI))	
Particle Size	IS Sieve & Sieve Shaker	
Conductivity	Conductivity Meter (Systronic, Model 304)	Bureau of Indian Standards method (IS 14767: 2000) [26]
Ash	Muffle furnace (Tempo Instruments and Equipment Pvt. Ltd.)	European Chemical Industry Council (CEFIC) methods, 1986 [27]
Bulk density	Bulk Density apparatus (DBK 5028-7)	
Yield	Weighing balance (AND, Model HR-200)	El-Ashtoukhya et al., 2008
Calorific value	Digital Bomb Calorimeter (Rajdhani Scientific, Model: RSB 6)	
Traces of elements	Coupled PlasmaOptical Emission Spectrometer (ICP-OES) (Model: VARIAN 720-ES)	
Adsorbent nature and shape of crystals	X-Ray Diffraction (XRD) (BRUKER, Germany, Model: D8 ADVANCE)	
Adsorbent morphology	Scanning Electron Microscope (SEM) (HITACHI, Model: S- 4800TypeII), Coupled with Energy Dispersive X-ray Spectroscopy (EDS) of BRUKER	

Where, C_i and C_e is initial and equilibrium concentration of Cu ions solution respectively in mg/L [29,30].

2.4. Study of Effect of Adsorption Conditions

The optimization study of adsorption parameters was planned on the basis of findings of preliminary batch adsorption trial. The effect of pH, agitation speed, temperature and adsorbent dose on adsorption capacity of Ad₃ was observed by keeping the other parameters of adsorption such as initial concentration of Cu solution (50 ppm), volume of Cu solution (50 ml), particle size of adsorbent (0.15-0.25 mm) and contact time (4 hr.) constant. The effect of pH was studied by adjusting the pH of solutions at 2, 3, 4, 5, 6, 7, 8, 9, 10 using 0.1-0.5 M solution of NaOH or HCl. The pH adjusted solutions were stirred at 150 rpm at 30°C with 0.5 g Ad₃ dose. The obtained optimum pH was then maintained in all the further study of adsorption. The effect of agitation on adsorption was examined by shaking the suspension of copper solution containing 0.5 g Ad₃ dose at various speed (50, 100, 150, 200 and 250 rpm) in an incubation temperature of 30°C. The temperature effect on Cu removal was observed by maintaining temperature at 10, 20, 30, 40, 50 and 60°C keeping pH and agitation speed at optimized level and Ad₃ dose 0.5 g. The effect of adsorbent dose was studied by shaking Cu solution with various dose of Ad₃ (0.1, 0.25, 0.5, 0.75, 1, 1.5, 2.0 and

2.25 g) keeping pH, agitation speed and temperature at optimum condition. The adsorption capacity q_e (mg/g) was determined by the equation 2:

$$q_e = V \frac{(C_i - C_e)}{W} \quad (2)$$

Where, C_i and Ce is initial and equilibrium concentration of Cu ions solution respectively in mg/L, V is the volume of the Cu solution in liter and W is the mass of the Ad$_3$ in g [31].

The study ended with the optimization of contact time, carrying out the adsorption at achieved optimum conditions.

2.5. Thermodynamic Study

The feasibility of the adsorption process was predicted by estimating thermodynamic parameters such as standard Gibb's free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) from the adsorption data obtained during temperature optimization.

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

$$\Delta G^0 = -RT \ lnK_C \quad (3)$$

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

Equation 4 is showing how the K_C is related to C_∂ and C_e

$$K_C = C_\partial / C_e \quad (4)$$

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

C_∂ was computed using equation 5:

$$C_\partial = C_i - C_e \quad (5)$$

Where, C_i is the initial concentration of Cu solution and C_e is is the equilibrium concentration of Cu solution both in mg/L.

Equation 6 represents Van't Hoff equation giving relation between ΔG^0 and ΔH^0 and ΔS^0.

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

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

3. Results and Discussions

3.1. Characterization of Ad$_3$

The physicochemical characterization of developed adsorbent Ad$_3$ is given in Table 2. The moisture in Ad$_3$ was found to be 6.17%, ash 6.95% and water soluble content 0.91%. The calorific value of prepared adsorbent carbon was 7172.67 Cal/g. The observed pH of Ad$_3$ solution was 5.44 and may be due to treatment of prepared carbon with H_2SO_4. The recovery of Ad$_3$ from dried husk

(yield) was 31.31%. The bulk density of Ad$_3$ was 0.5479% whereas conductivity 297.25 mS/m. The particles found in Ad$_3$ mixture was of size 210-250 µm (60.66%), 180-210 µm (9.12%) and 150-180 µm (30.22%).

Table 2. Physicochemical Characteristics of Adsorbent Ad$_3$

Parameter	Result
Moisture (%)	6.17 $\pm$ 0.06
Ash (%)	6.95$\pm$0.08
Water soluble content (%)	0.91 $\pm$0.02
Calorific value (Cal/g)	7172.67 $\pm$1.20
pH	5.44 $\pm$ 0.01
Yield (%)	31.31 $\pm$ 0.31
Bulk density (g/cm^3)	0.5479 $\pm$3.32
Conductivity (mS/m)	297.25
Particle size	
210-250 µm	60.66%
180-210 µm	9.12%
150-180 µm	30.22%

Values are Mean ($\pm$ SEM) of 3 determinations

Table 3 is showing the trace amounts of various elements present in Ad$_3$. The elemental analysis confirms the presence of Mg, Na, Ca, Fe, Zn, Cu, Mn and Pb in prepared activated carbon responsible for ash.

Table 3. Trace Element Analysis of Adsorbent Ad$_3$

Element	Result (ppm)	Element	Result (ppm)
Mg	3092.66	Na	3040.84
Ca	1441.89	Fe	145.70
Zn	46.11	Cu	18.26
Mn	13.17	Pb	5.16

Figure 2 is showing the standard XRD pattern of carbon whereas XRD of Ad$_3$ is given in Figure 3.
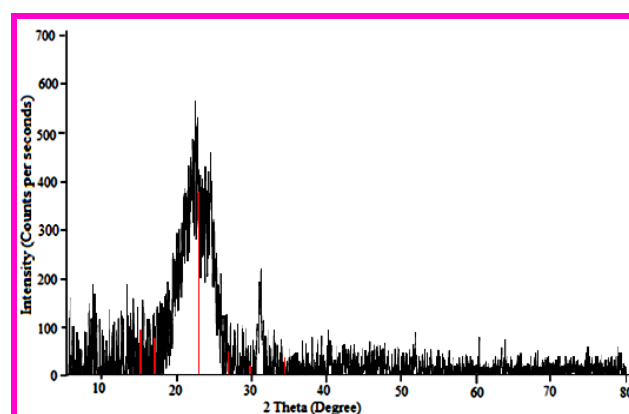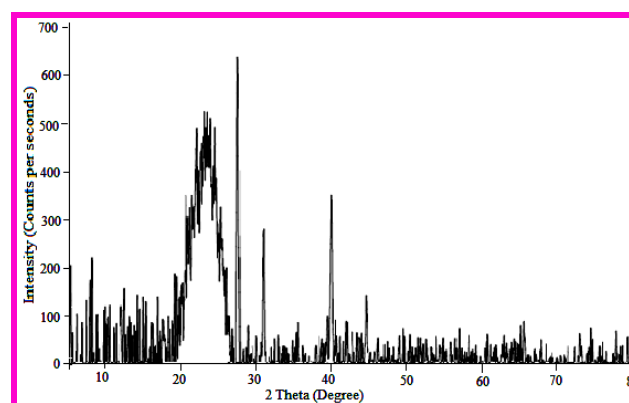

Figure 2. Standard X-ray diffraction of carbon

Figure 3. X-ray diffraction of Ad$_3$

The standard XRD peak for carbon was found to matching with XRD peak obtained for Ad$_3$ and verifies the produced material was carbon. The XRD result also

confirmed the obtained activated carbon was a mixture of 60.6% amorphous and 39.4% hexagonal shaped crystalline crystals.

Figure 4 and Figure 5 is representing the porous structure in raw Tur dal husk and Ad₃ respectively when observed through SEM. It can be seen that raw husk surface had no or very few pores and thus acquiring less surface area whereas surface of Ad₃ was characterized by many pores and exhibiting large surface area.
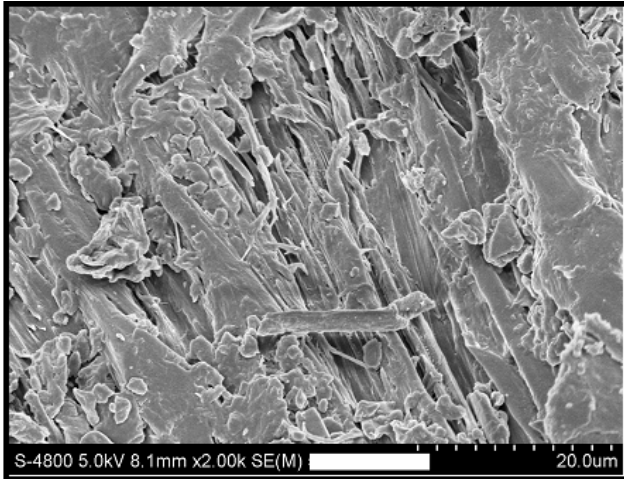

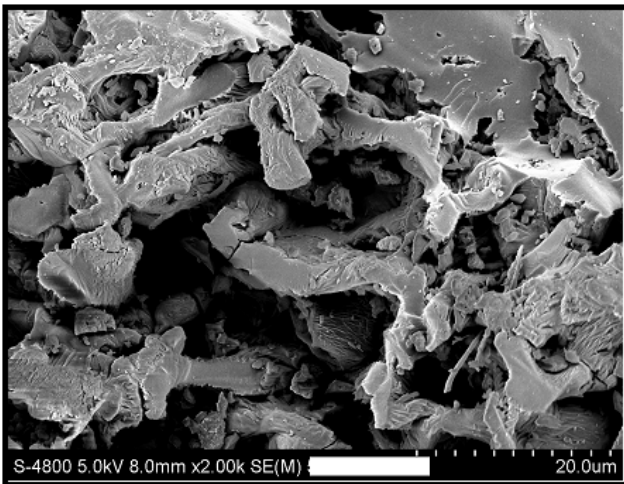
Figure 4. SEM image of raw tur dal husk

Figure 5. SEM image of Ad₃

Further treatment of this porous char with H_2SO_4 developed high porosity [33]. The developed activated carbon Ad₃ with its porous structure and large surface area was predicted to be effective metal adsorbent.

3.2. Initial Adsorption Trial

Table 4 illustrates the outcome of initial adsorption trial performed by varying the initial concentration of Cu solution and the dose of Ad₃. The adsorption of Cu ion from its 100 ppm solution by 0.1 g Ad₃ dose was low (10.5%) in first adsorption experiment. The second experiment conducted with same dose (0.1 g) but lowering initial Cu solution concentration to 50 ppm, shown improvement in Cu adsorption (18.8%). The third experiment carried out with 0.25 g dose and 50 ppm initial Cu solution concentration was also found to increase the adsorption performance (32.2%). Further to increase the adsorption, the fourth experiment carried out with 0.5 g

dose and 50 ppm initial Cu solution concentration however shown no extreme progress in adsorption (39.1%). Based on the findings of preliminary adsorption study the optimization of adsorption condition was planned as investigation carried out by the previous researchers reported drastic change in the performance of adsorbent by the optimization of adsorption condition [34,35,36].

Table 4. Preliminary Adsorption Trials

Parameter	First Trial	Second Trial	Third Trial	Fourth Trial
Residual Cu ion concentration at equilibrium	88.4	40.1	33.5	30.1
% Adsorption of Cu ion	10.5	18.8	32.2	39.1
Equilibrium Time	3.0 hr	2.5 hr	3	3.5

3.3. Study of Effect of Adsorption Condition

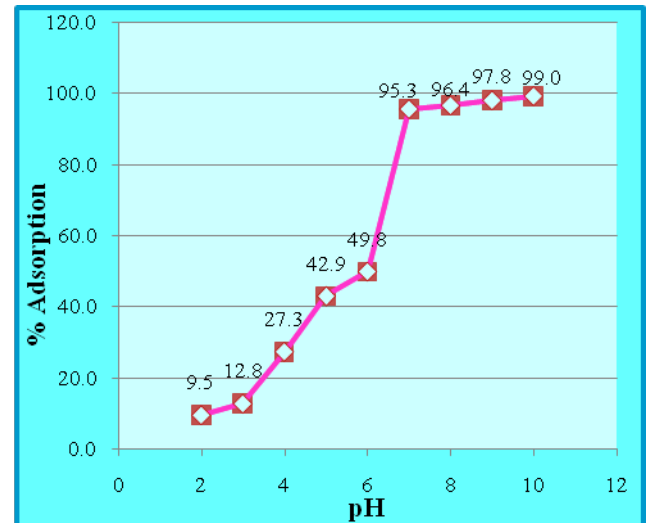### 3.3.1. Effect of pH on Adsorption

Figure 6. Effect of pH on Cu adsorption by Ad₃

The initial pH of metal solution is considered most important as it alter the charges on the adsorbent surface and affect adsorption. The effect of pH on adsorption is shown in Figure 6. The adsorption of Cu ion was found to increase linearly with increase in pH. The adsorption was observed to be low at pH 2 (9.5%) and 3 (12.8%). The moderate adsorption was found at pH 4, 5 and 6 (27.3%, 42.9% & 49.8% respectively). Very high adsorption was achieved at pH 7, 8, 9 and 10. The adsorption of metal ions by activated carbon is mainly due to electrostatic attraction between positively charged metal ions and negative charges on the surface of activated carbon. At low pH (2 & 3) the metal ion solution carried H^+ ions in high amount. As the Ad₃ added in the Cu solution the surface of Ad₃ completely got covered with H^+ ions. The shield of H^+ ions on the surface of Ad₃ was preventing the Cu ion (positively charged) from reaching to the adsorption sites of Ad₃ by repulsion, resulting less adsorption [37]. However the number of H^+ ions decreased as the pH increased (4, 5 & 6), due to which Cu ion became more accessible to negative charged sites on the Ad₃ and significant adsorption occurred. The obtained result was in accordance with the data found by Boonamnuayvitaya et al., 2004 [38] while removing

heavy metals (Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+} and Ni^{2+}) by coffee residues. The very high removal of Cu at pH 7 and above was not due to adsorption only but because of precipitation of Cu ion as copper hydroxide [39,40]. Practical point of view for the application of adsorption, 6 pH was selected as optimum without precipitation of Cu.

3.3.2. Effect of Agitation on Adsorption

Figure 7 is viewing the effect of agitation speed on Cu adsorption by Ad_3.
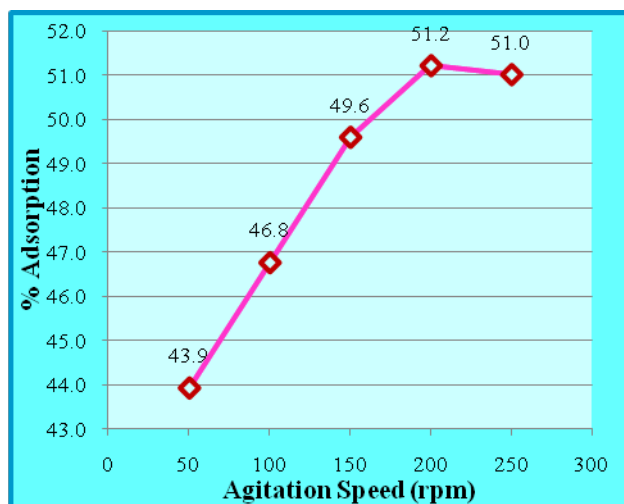

Figure 7. Effect of agitation speed on Cu adsorption by Ad_3

The adsorption found to increase with increase in agitation speed and after attending optimum speed start declining. The adsorption was 43.9%, 46.8%, 49.6%, 51.2% and 51.0% for agitation speed 50, 100, 150, 200 and 250 rpm respectively. The maximum adsorption was obtained at 200 rpm agitation speed and optimized for further study. The adsorption occur when adsorbate particle reach on the surface of adsorbent by crossing resistance offered by bulk of solution and boundary layer surrounding adsorbent surface. The adsorption further continues as Adsorbate molecules diffuse in the bulk of adsorbent [41]. The thickness of fluid film surrounding Ad_3 particle was greater when the agitation set to low rpm. The Cu ions were unable to cross this thick layer easily and diffusion of Cu ions within Ad_3 pores were also less, due to which low adsorption occurred [42]. As the agitation speed increased the thickness of fluid film surrounding Ad_3 reduced due to increase in turbulence and adsorbate particles (Cu ions) reaching easily to the Ad_3 surface as experiencing less resistance crossing the boundary layer. Also the diffusion of Cu ions wasat its extreme causing high adsorption [43]. The result agree with the data obtained by Zouboulis et al., 2007 [44] while removing toxic metals from an aqueous mixture containing zinc, copper and nickel exploiting microbes as biosorbent. The adsorption found to be almost same at 250 rpm as obtained at 200 rpm. This shows 200 rpm agitation speed was sufficient to make available all the binding sites of the Ad_3 for adsorbing Cu^{2+} ion in solution. Increasing agitation beyond 200 rpm was unable to establish the proper contact between Ad_3 and Cu^{2+} ion, also desorption at some sites occurred due to possible break-up of the Cu ions and Ad_3 bonding, resulting no further improvement in adsorption. The similar result i.e. increase in adsorption with increase in shaking speed up to certain rpm and then

decreasing beyond optimum rpm, was also reported by other researchers [45,46].

3.3.3. Effect of Temperature on Adsorption

Figure 8 is showing the effect of temperature on adsorption of Cu by Ad_3. The adsorption was 54.9%, 53.2%, 51.0%, 49.6%, 46.6% and 44.7% at 10, 20, 30, 40, 50 and 60°C respectively. The Cu adsorption was fund to be decreasing with increasing temperature. This shows the process of adsorption of copper by Ad_3 was exothermic in nature. The possible cause for the observed effect may be due to the breaking of some internal bonds with increasing temperature, resulting lessening of few adsorption sites on Ad_3 surface and within pores [47]. Similar phenomenon was observed by other investigators while carrying out adsorption of metals or dyes by various biosorbents [48], [49]. Among all the studied temperature, low temperature (10°C) was optimized as most suitable temperature for the said adsorption.
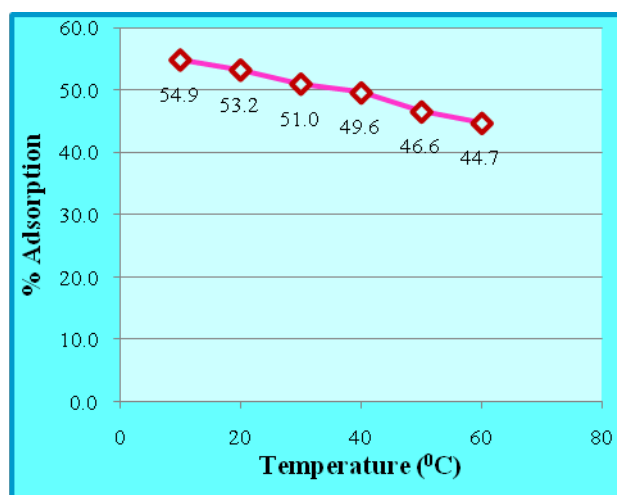

Figure 8. Effect of temperature on Cu adsorption by Ad_3

3.3.4. Effect of Adsorbent Dose on Adsorption
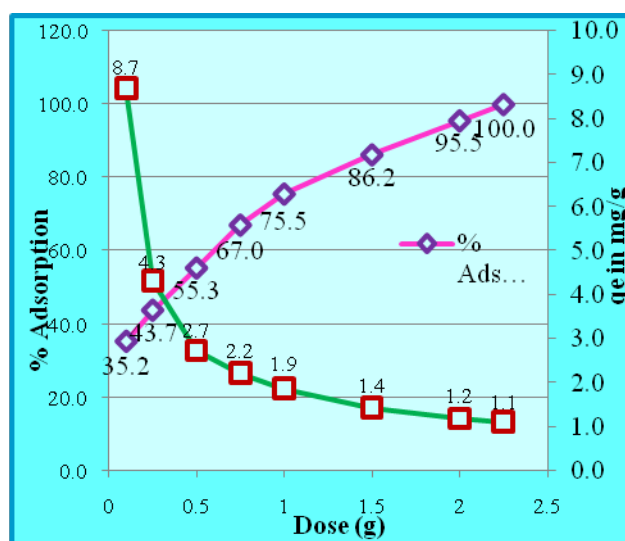

Figure 9. Effect of dose of Ad_3 on Cu adsorption

The effect of amount of Ad_3 for adsorbing Cu is depicted in Figure 9. The adsorption of Cu for Ad_3 quantity 0.1, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0 and 2.25 g was 35.2, 43.7, 55.3, 67.0, 75.5, 86.2, 95.5 and 100%

respectively and adsorption capacity 8.7, 4.3, 2.7, 2.2, 1.9, 1.4, 1.2 and 1.1 mg/g respectively. The adsorption capacity q_e found to be decreasing and% adsorption increasing with increasing application of Ad_3 amount [50]. The corresponding increase in number of adsorption sites with the elevated doses of Ad_3 was the cause for improved adsorption. However as the amount of Ad_3 increased the formation of agglomerates due to interaction of various Ad_3 particles occurred. The formed agglomerates was overlapping Ad_3 surface, making it unavailable for adsorption. Some adsorption sites also got obstructed with this over-crowding of Ad_3 particles resulting low adsorption capacity with increasing dose of Ad_3 [51,52], Similar result was also reported by Bansala, et al., 2009 [53] in an attempt to exploit pretreated rice husk for adsorbing Cr (VI) from its aqueous solutions.

3.3.5. Contact Time Optimization

Finally the contact time optimization was done by conducting adsorption experiment at all achieved optimized condition i.e. 2.25 g adsorbent dose, 10°C temperature, 200 rpm agitation speed and 6 pH. The effect of contact time under said optimized conditions is given in Figure 10. The adsorption was 86.0, 92.3, 95.7, 97.8, 99.2 for contact time 0.5, 1.0, 1.5, 2.0 and 2.5 hr. respectively. The adsorption found to be increasing with increasing contact time and complete adsorption (100%) was achieved for contact time 3.0 hr. and above. During initial period of adsorption the effective adsorption was observed as large surface area of Ad_3 with all vacant adsorption sites was available for adsorption. The less prominent adsorption was observed as the contact time increased. The reason behind the same was as the time lapse the available adsorption sites on the surface of Ad_3 got saturated due to bonding with Cu ion. At this stage the adsorption became independent of adsorption sites on surface and dependent on the migration of Cu ions for further adsorption on adsorption sites within pores of Ad_3 [54,55,56]. Research conducted by previous workers Arivoli, et al., 2009 [57], Dorriset al., 2000 [58] also confirms the same trend in adsorption with respect to contact time. The minimum time observed to achieve complete adsorption was 3 hr. and hence optimized as the optimum time for the considered adsorption.
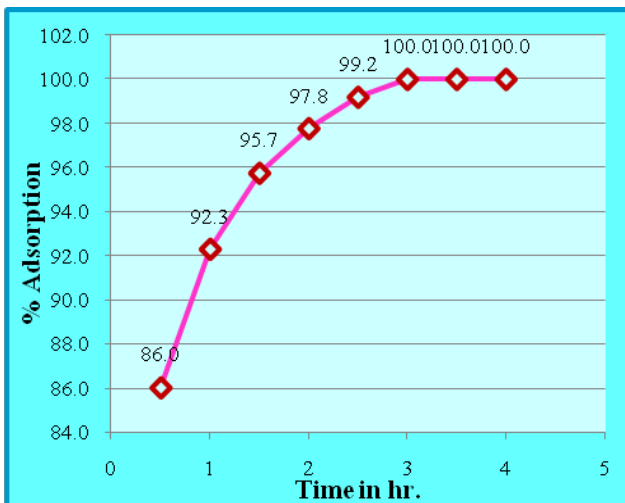
3.3.6. Thermodynamic Study

Table 5 is showing the estimated values of standard Gibb's free energy at various temperature. The ΔG^0 at temperature 10, 20, 30, 40, 50 and 60°C was calculated to be -458.68, -316.04, -102.00, 42.14, 370.24 and 585.02 J/mol respectively. The ΔG^0 was found to be increasing with increasing temperature but remained negative upto 30°C and thereafter positive. The adsorption process found to be feasible and spontaneous (exergonic) [59] up to 30°C as ΔG^0 was negative and then became non-spontaneous (endergonic) as ΔG^0 was positive [60,61] for all the temperature above 30°C. Meena et al., 2005 [62] also found the negative and positive value of ΔG^0 while removing various heavy metals (Cd, Cu, Ni & Zn) using carbon aerogel as an adsorbent. ΔG^0 was found to increase gradually with increasing temperature, indicating spontaneity decreases with the rise in temperature.

Table 5. Standard Gibb's Free Energy of Adsorption at Different Temperature

Temperature(°C)	C_e(mg/L)	K_C	lnK_C	ΔG^0 =$-RT lnK_C$ (J/mol)
10	27.1	1.2152	0.19	-458.68
20	26.3	1.1385	0.13	-316.04
30	25.2	1.0413	0.04	-102.00
40	24.5	0.9839	-0.02	42.14
50	23	0.8712	-0.14	370.24
60	22.1	0.8095	-0.21	585.02

The slope and Y-intercept of line obtained by ploting of lnK_C versus 1/T is presented in Figure 11. With increasing 1/T, lnK_C also found to increase linearly. The slope and Y-intercept of the obtained line was used in Van't Hoff equation to calculate the values of ΔH^0 and ΔS^0 Figure and is given in Table 6.

Table 6. Standard Enthalpy Change (ΔH^0) and Entropy Change (ΔS^0) of Adsorption

Equation of line with Corelation coefficient	ΔH^0 (J/mol)	ΔS^0 (J/mol K)
y = 775.5x - 2.525 R² = 0.984	-6.4475x10³	-20.99

Figure 10. Effect of contact time on adsorption of Cu by Ad_3
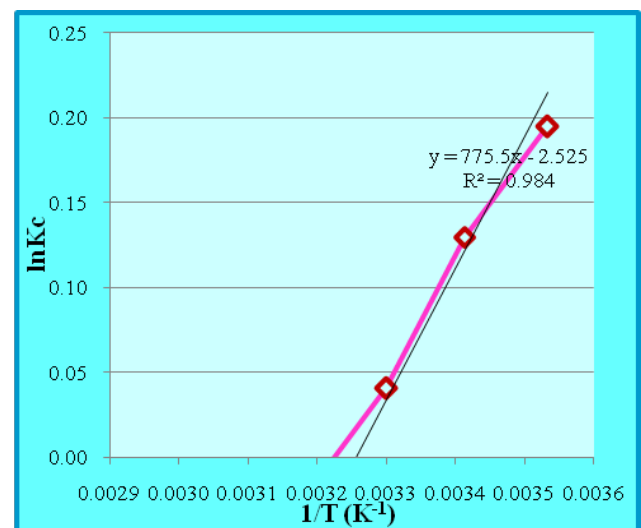
Figure 11. Plot of lnK_C versus 1/T

The value of ΔH^0 and ΔS^0 was found to be -6.4475×10^3 J/mol and -20.99 J/mol K respectively. Both ΔH^0 and ΔS^0 were negative in the given adsorption. The exothermic nature of the said adsorption can be again authenticated by negative value of [63]. The negative value of ΔH^0 and ΔS^0 reveals the adsorption reaction was favorable for enthalpy but unfavorable for entropy. The favoring of adsorption for enthalpy and not for entropy also confirms the reaction became less spontaneous as temperature increased. The negative value of ΔS^0 imply less randomness at the solid/solution interface during adsorption and the system became more ordered through adsorption process i.e. probability of favorable adsorption [64]. The result (both negative ΔH^0 and ΔS^0) agree with the findings of Liang et al., 2010 [65] while removing Cu ions using orange peels as adsorbents.

4. Conclusion

The activated carbon prepared from the waste of pulse processing industry (*Cajanus cajan* Husk) by the process of carbonization and activation with sulfuric acid had the potential to adsorb metal. The optimization of adsorption condition further enhanced efficiency of the prepared activated carbon. In an experimental batch adsorption the optimum condition found to remove complete Cu ions from its 50 ml, 50 ppm solution applying 2.25 g of developed activated carbon was 10°C temperature, 200 rpm agitation speed, 6 pH and 3 hr. contact time. The thermodynamic study of the said adsorption reveled the adsorption was exothermic, feasible and favorable, spontaneous at low temperature (10-30°C) and non-spontaneous at high temperature (40-60°C). The outcome of work may be utilized for designing adsorption process to control water pollution due to heavy metals particularly copper, as one of the possible value addition to Tur dal processing waste.

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