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ADSORPTION OF COPPER FROM AQUEOUS SOLUTION USING LOW-COST ADSORBENT

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ABSTRACT

In this study activated carbon prepared from *Adathoda vasica* stem was used as adsorbent to remove Cu^{2+} from an industrial waste water. For this purpose, high grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used as heavy metal sample. Laboratory experimental investigation was carried out to identify the effect of pH (1.50 – 5.5), agitation time (30-240 min) varying temperature (30-50°C) and varying biomass quantities (2,4,6,8,10 g/L) and other co-existing ions were also examined. The kinetics of interactions were tested with pseudo first order –Lagergren equation and first order reversible –Bhattacharya Venkobachar equation. The Langmuir & Freundlich adsorption isotherm models fitted the experimental data best with regression coefficient $r^2 > 0.95$ for the Cu(II) ions. The adsorption was endothermic and the computation of the parameters ΔG° , ΔH° & ΔS° indicated that the interactions were thermodynamically favorable. The results showed that *Adathoda vasica* stem carbon (AVSC) was an effective & economical biosorbent material for the removal and recovery of heavy metal ions from waste water.

(Keywords: *Adathoda vasica*, Activated carbon, Heavy metals, Langmuir, Freundlich, Wastewater)

INTRODUCTION

Heavy metal pollution in wastewater has always been a serious environmental problem, because heavy metals are not biodegradable and can be accumulated in living tissues [1]. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams. Elevated environmental levels of Cu(II) comes from variety of sources. Mining, metal cleaning, plating baths, pulp, paper and paper board mills, refineries, fertilizer industries etc., are the potential sources of Cu(II) in industrial effluents [2]. Copper, a widely used metal in industry, is an essential trace element for human health and play an important role in carbohydrate and lipid metabolism & in the maintenance of heart and blood vessel activity. According WHO, the maximum acceptable concentration of Cu(II) in drinking water is 1.5 mg/L. The adult human body contains 100-150 mg of Cu(II), but excess amounts in the body can be toxic [3]. In aqueous environments, the speciation of the metal is dependent both on ligand concentration & pH. If the excessive amount of Cu(II) is allowed to enter into the environment, can cause serious health issues such as nausea, headache, dizziness, respiratory difficulty, hemolytic anemia, massive gastrointestinal bleeding, liver & kidney failure & even death[4-7]. Removal of metal ions from wastewater in an effective manner has become an important issue. Efficient methods for the removal of metals have resulted in the development of new separation techniques. Precipitation, ion-exchange, flocculation, adsorption, electro-chemical processes, electro-

dialysis, nano-filtration and reverse osmosis are commonly applied for the treatment of wastewater [8]. However, these methods are either inefficient or expensive when heavy metals exist in low concentrations [9]. Additionally, these methods may also affect the generation of secondary wastes, which are difficult to treat. Adsorption is an alternative technology in which increased amount of study has been focused because of cost effectiveness, local availability & technical feasibility for the removal of heavy metal ions from the wastewater [10]. Different factors affecting the adsorption as the contact time, adsorbent dose, pH and temperature were examined to optimize the adsorption equilibrium and the kinetic data are fitted using different models and parameters.

MATERIALS AND METHODS

Experimental

Adsorbent

Adathoda Vasica Activated Carbon (AVAC) was prepared by treating air-dried *Adathoda vasica* stem with concentrated sulphuric acid in a weight ratio of 1:1. The resulting black product was kept in a furnace maintained at 500 °C for 12 h followed by washing with water until free from excess acid and dried at 150 ± 5 °C. The Carbon product thus obtained was ground and it was sieved to select particles of size 0.75 μm for use.

Preparation of copper solution

The solution of Cu(II) was prepared by diluting a 100 ppm stock metal ion solution obtained by dissolving 0.393 g of hydrated copper sulphate ($\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$) in 1L distilled water. The range of concentration of prepared Cu(II) solution was 1–100 mg/L. The range of pH selected was 1.5–5.5. The pH of each solution was adjusted to the required value with 1M HCl & 1M NaOH before mixing the adsorbent with the solution.

Adsorption studies

A known quantity of adsorbent powder was contacted with a known concentration of metal bearing solution (2 g adsorbent in 100 ml metal ion solution in an Erlenmeyer flask). Samples were taken out at specific duration of time and centrifuged to 5000 rpm for 10 min. The supernatant liquid was separated and analyzed for Cu(II) ions.

Analysis of Cu(II) ions

Perking Elmer 2380 atomic absorption spectrophotometer was used to determine the concentration of Cu(II) in the solution.

RESULT AND DISCUSSION

Characterization of the Adsorbent

Activated carbon is widely used as an adsorbent due to its high surface area, high adsorption capacity, micro porous structure and high degree of surface respectively.

The physico- chemical properties of the chosen adsorbent are listed in following table 1.

TABLE-1

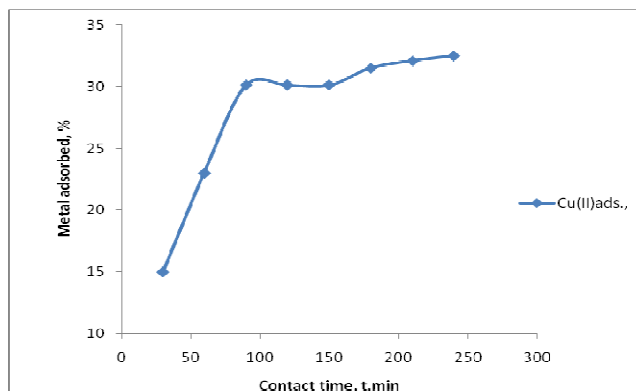
PROPERTIES	AVAC
Particle size (μm)	0.75
Bulk density (g/cc)	0.79
Moisture content (%)	0.601
Ash content (%)	11.42
Fixed Carbon content (%)	73.41
Matter soluble in water (%)	2.14
Matter soluble in acid (%)	2.8
pH	6.19
Surface area, (m^2/g)	120.6
Iron content (%)	0.4

Effect of agitation time on adsorption

The agitation time was evaluated as one of the most important factors affecting the adsorption efficiency. The relationship of percentage metals removal by adsorbent with contact time was plotted and presented in figure-1. The

amount of the adsorbed metal ion increased as the time increases, and after 240 min adsorption becomes constant and attains equilibrium. There is no change in adsorption on further increase in contact time.

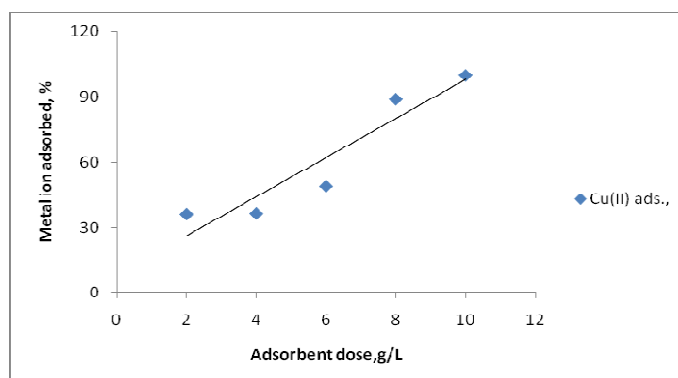
Fig. 1. Effect of contact time on percent Cu(II) removal



Effect of Adsorbent dose

Adsorption experiments were also performed at different adsorbent dosages namely (2.0, 4.0, 6.0, 8.0 & 10.0 g/L) of AVAC. The adsorption efficiency increased with an increasing adsorbent dosage and presented figure-2. This is due to an increase in the surface area of the adsorbent which in turn increases the number of binding sites.

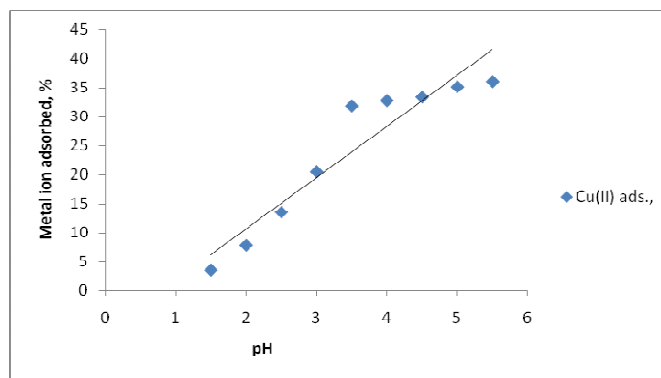
Fig-2 Effect of adsorbent dose on percent Cu(II) removal



Effect of pH

The pH of the metal solution played an important role in the adsorption of Cu(II). With an increase in pH from 1.5 to 5.5, percentage sorption and uptake also increased. At lower pH values, the surface charge on the adsorbent is positive and adsorption was not favorable and also the H^+ ions compete strongly with metal ions for active sites in adsorbent [11]. Increase in pH result in the electro static repulsion between the cations and surface sites, there by the competing effect of the H^+ ions decreases and the positively charged Cu(II) ions get adsorbed on the free binding sites, resulting an increase in the total metal uptake, as shown in figure-3.

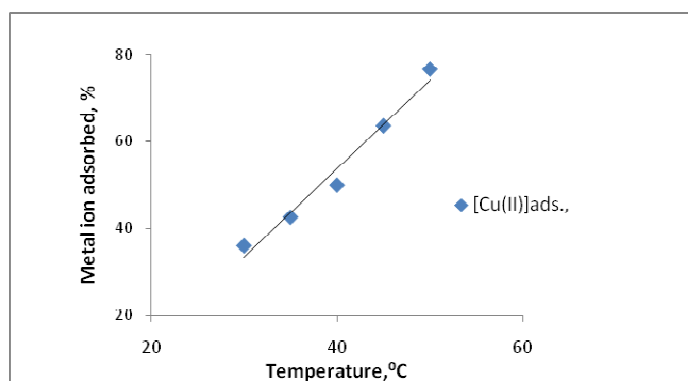
Fig-3 Effect of pH on percent Cu(II) removal



Effect of temperature

The adsorption of Cu(II) at different temperatures namely 30, 35, 40, 45 and 50°C were studied. The adsorption was found to increase with increase in temperature as shown in figure-4. It reveals that the adsorbate-adsorbent system is endothermic in nature for which the evaluation of thermodynamic parameters was carried out.

Fig-4 Effect of temperature on percent Cu(II) removal



Evaluation of thermodynamic parameters

Thermodynamic parameters namely ΔG° , ΔH° & ΔS° were calculated at different temperatures using the following relations.

$$\Delta G^\circ = -RT \log K_o ; \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Where $K_o = C_{\text{solid}} / C_{\text{liquid}}$; C_{solid} = Solid phase concentration at equilibrium (mg/L); C_{liquid} = liquid phase concentration at equilibrium (mg/L); T = Temperature; R = gas constant

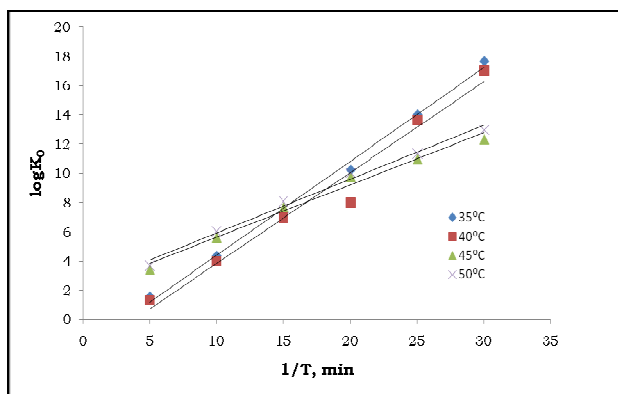
Fig.5 shows the plot of $\log k_o$ versus $1/T$ at different initial Cu(II) concentrations and the values of estimated thermodynamic parameters are given in Table-2. The negative values of ΔG° confirm the feasibility of the reaction and the spontaneous nature of the sorption and the positive values of ΔH° indicate the sorption reaction to be in agreement with the endothermic nature of interaction and governs the possibility of physical adsorption [12,13]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of adsorption increases which rules out the possibility of chemisorption [13]. The enhancement of adsorption capacity of the activated carbon at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface [14,15].

Table-2 Thermodynamic properties for the adsorption of Cu(II) at different concentration

[Cu(II)] _{ini} , mg/L	K _o				ΔG°				ΔH°	ΔS°
	35°	40°	45°	50°	35°	40°	45°	50°		
5	2.16	2.38	2.77	2.99	-1.97	-2.25	-2.70	-2.94	20.93	74.23
10	1.28	1.39	1.51	1.61	-0.64	-0.86	-1.09	-1.28	12.57	42.78
15	1.05	1.11	1.16	1.21	-0.13	-0.27	-0.40	-0.51	7.64	25.24
20	0.95	0.99	1.01	1.06	+0.12	+0.01	-0.06	-0.17	5.72	18.13
25	0.78	0.80	0.83	0.86	+0.62	+0.57	+0.49	+0.37	4.91	13.85
30	0.69	0.73	0.76	0.77	+0.92	+0.81	+0.71	+0.69	4.53	11.88

ΔH° (kJ/mol), ΔS° (J/K/mol), ΔG° (kJ/mol)

Fig-5 Equilibrium constants and thermodynamic parameters



KINETICS OF ADSORPTION

The first order kinetic equation like Lagergren (Lagergren, 1898) and Bhattacharya-Venkobachar (Bhattacharya-Venkobachar, 1984) equations were applied to the adsorption data are shown in table-3.

Lagergren equation : $\log (q_e - q) = -(k_{Lager}/2.303) \times t + \log q_e$
 Bhattacharya-Venkobachar equation : $\log (1 - U_t) = -(k_{Bhat}/2.303) \times t$

Where q_e & q = amount of Cu(II) ions adsorbed at equilibrium time & time t , respectively (mg/g); $U_t = [(C_i - C_t)] / C_i - C_e$; C_i, C_t & C_e = Concentration of Cu(II) ions at time zero, equilibrium ions concentration (mgL^{-1}); k_{Lager} & k_{Bhat} = first order adsorption rate constant (min^{-1})

The r-values indicate the applicability of these kinetic equations and the first order kinetic nature of adsorption of Cu(II) ions on AVAC as given in table-3.

Table-3 Kinetic of adsorption for removal of Cu²⁺ onto AVAC at 30 ± 1°C

Model Parameter	Cu ²⁺ ions
Lagergren Rate Constant, 10 ⁴ x k (s ⁻¹)	4.222
r-value	0.982
Bhattacharya- Venkobachar Rate Constant, 10 ⁴ x k (s ⁻¹)	3.838
r-value	1.000

Fig-6 Lagergren plot for the adsorption of Cu(II) by AVAC

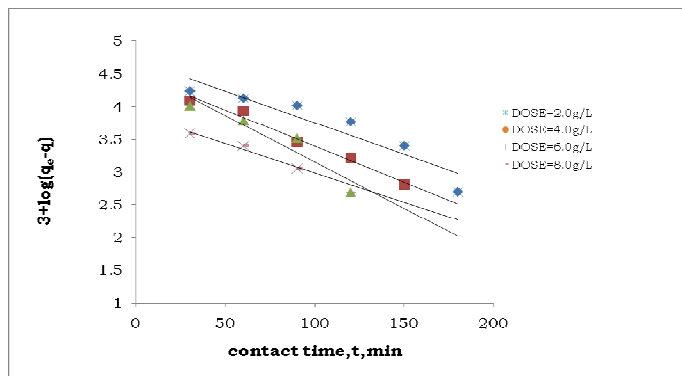
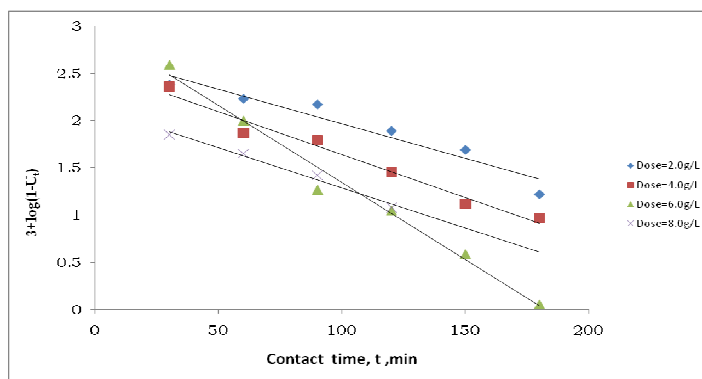


Fig-7 Bhattacharya-Venkobachar plot for the adsorption of Cu(II) by AVAC



ADSORPTION ISOTHERMS

Two types of adsorption isotherm models namely Langmuir isotherm & Freundlich isotherm were tested. The Langmuir isotherm model is given as follows:

$$C_e/Q_e = 1/Q_m b + C_e/Q_m$$

Where, C_e = Concentration of copper(II) at equilibrium (g/l); Q_e = amount of copper(II) adsorbed at equilibrium($mg\ g^{-1}$); Q_m & b = Langmuir constants- Adsorption capacity and Adsorption energy respectively.

The linear plots of C_e/Q_e versus C_e suggest the applicability of Langmuir isotherms shown in Fig.8. The values of Q_m & b were determined from the slopes and intercepts of the plots and are presented in Table- 4.

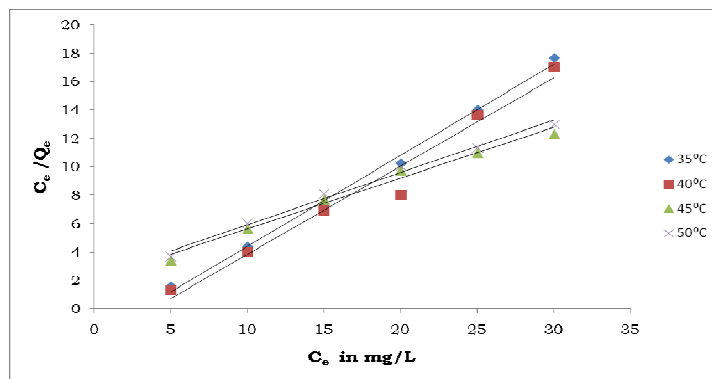
Table-4 Langmuir Isotherm Results

Temp., °C	Statistical Parameters /Constants		
	r^2	Q_m	b
35	0.9846	17.53	0.1089
40	0.9843	17.36	0.1190
45	0.9813	17.12	0.1319
50	0.9898	17.09	0.1416

It was observed in table-4 that, the Langmuir maximum adsorption capacity Q_m is 17.09 and the equilibrium constant b is 0.1416. The essential features of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor (R_L). The value of R_L indicates the shape of the isotherms to either unfavorable ($R_L > 1$), linear ($R_L < 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

In the present study, the computed values of R_L are found to be fraction in the range of 0-1 (for Cu^{2+} is 0.079), indicating that the adsorption process is favorable for this adsorbent (AVAC) for the removal of toxic metal ions.

Fig-8 Langmiur isotherm for the adsorption of Cu(II) ion by AVAC



Freundlich isotherm model

The logarithmic form of Freundlich isotherm model is given as follows,

$$\log Q_e = \log k_F + 1/n \log C_e$$

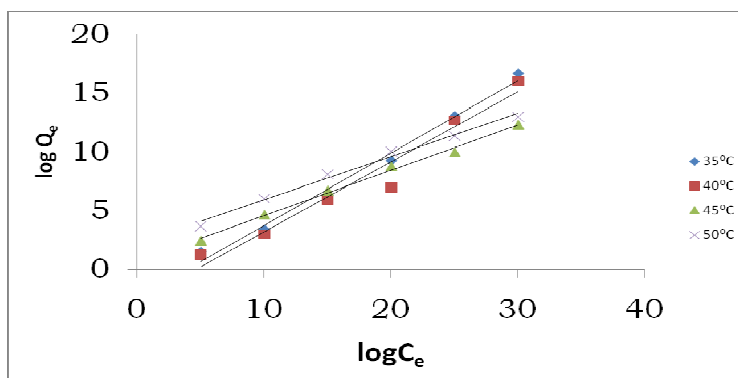
Where, Q_e = amount of Cu(II) sorbed at equilibrium (mg/g) ; C_e = concentration of the Cu(II) at equilibrium (g/L) ; k_F = adsorption capacity (L/g) ; n = intensity of adsorption.

Linear plots of $\log Q_e$ versus $\log C_e$ shows that the adsorption of metal ions obeys the Freundlich adsorption isotherm (Fig-9). The values of k_F & n given in table-5 shows that the increase in negative charges on the adsorbent surface that makes electrostatic force like van der Waal’s between the carbon surface and metal ion. The values clearly show the dominance of adsorption capacity [16]. The intensity of adsorption is an indication for the bond energies between metal and adsorbent. However, the value of n is greater than one indicating that the adsorption is much more favorable.

Table-5 Freundlich constants and statistical parameter

S.No.	Temp., °C	k_F	1/n	R^2
1	35	3.8786	0.4984	0.9720
2	40	4.2682	0.4885	0.9687
3	45	4.7251	0.4814	0.9725
4	50	4.9669	0.4911	0.9742

Fig-9 Freundlich isotherm for the adsorption of Cu(II) ion by AVAC



CONCLUSION

Adsorption is a potentially attractive technique for the treatment of heavy metals such as Cu(II) from wastewater. The present work was carried out using *Adathoda vasica* stem activated carbon as adsorbent. The adsorption capacity strongly depend on the contact time, adsorbent dosage, pH and temperature. The kinetics of adsorption of Cu(II) were tested with pseudo-first order Lagergren and Bhattacharya–Venkobachar models. The experimental data well fitted to the Langmuir and Freundlich equations, with good correlation coefficients. The study of the thermodynamic parameters indicated that the adsorption process was thermodynamically spontaneous under natural conditions and the adsorption is endothermic in nature.

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