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Review Article

LOW COST ADSORBENT AS ACTIVATED CARBON FOR REMEDIATION OF CU(II) IONS FROM WATER

A. Shajudha Begum

PG and Research Department of Chemistry,
Periyar E.V.R College (Autonomous) Tiruchirapalli, Tamil Nadu, India.

ABSTRACT

In this study activated Carbon produced from Betelnut was used as adsorbent to remove Copper from a waste water. For Laboratory experimental investigation was carried out to identify the effect of pH (1.5 – 5.5), agitation time (30-240min), varying temperature (35-55˚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 –Lagergran equation and first order reversible –Bhattacharya Venkobachar equation. The Langmiur & Freundlich adsorption isotherms models fitted the experimental data best with regression coefficient $r^2 > 0.9$ 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 betel nut was an effective & economical biosorbent material for the removal and recovery of heavy metal ions from waste water. Conclusions have been drawn from the literature reviewed and suggestions for future research are proposed.

Keywords: Activated carbon, Heavy metals, Kinetic study and wastewater.

INTRODUCTION

Saving water to save the planet and to make the future of mankind safe is what we need now. 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 effulence[2]. Copper, a widely used metal in industry, is a 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 1.5mg/L. The adult human body contains 100-150mgs 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 potential health issues such as nausea, headache, dizziness, respiratory difficulty, hemolytic anemia , massive gastrointestinal bleeding, liver & kidney failure & even death[4,5,6,7]. Removal of metal ions from waste water is an effective manner has become an important issue. Efficient methods for the removal of metals have resulted in the development of new separation technologies. Precipitation, ion-exchange, flocculation, adsorption, electro-chemical processes, electro dialysis, nano-filtration & 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 form the wastewater[10]. Different factor affecting the adsorption as the contact time, adsorbent dose, pH and temperature were examined to optimize the adsorption equilibrium and kinetic data are fitted using different models & process parameters.

Experimental section

Adsorbents

Carbon was prepared by treating air – dried *Betel nut* 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 hours 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 to select particles 0.75 mµ in size for use.

Preparation of Copper solution

The solution of Copper(II) were prepared by diluting a 100ppm stock metal ion solution obtained by dissolving 0.393 g of hydrated Copper sulphate ($CuSO_4.7H_2O$) in 1L distilled water. The range of concentration of prepared Cu(II) solution was 1 – 100 ppm. The range of pH selected was 1.5 – 6.0. The pH of each solution was adjusted to the required value with 1M HCl & 1M NaOH before mixing the adsorbent with the solution.

Analysis of Copper(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.

PROPERTIES	BNAC
Particle size(µm)	0.72
Bulk density(glcc)	0.71
Moisture content(%)	0.509
Ash content(%)	10.42
Fixed Carbon content(%)	63.41
Matter soluble in water(%)	1.14
Matter soluble in acid(%)	3.8
pH	6.0
Surface area,m^2/g	315.4
Iron content(%)	0.3

1. 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 become constant and attains equilibrium. Further increase in contact time, there is no change in adsorption.

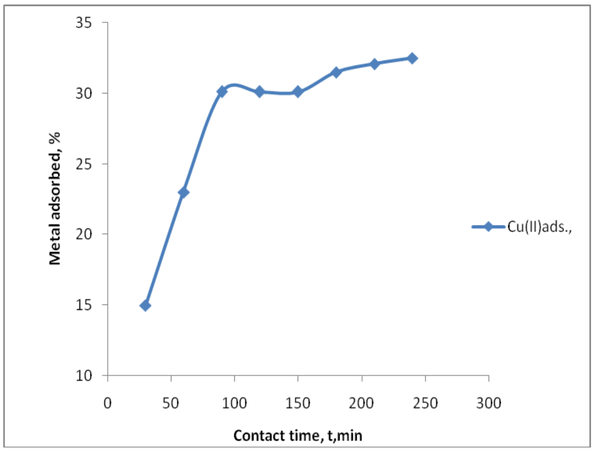

Fig. 1: Effect of contact time on percent Cu(II) removal

2. 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) *BNAC* powder , 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 inturn increases the number of binding site.

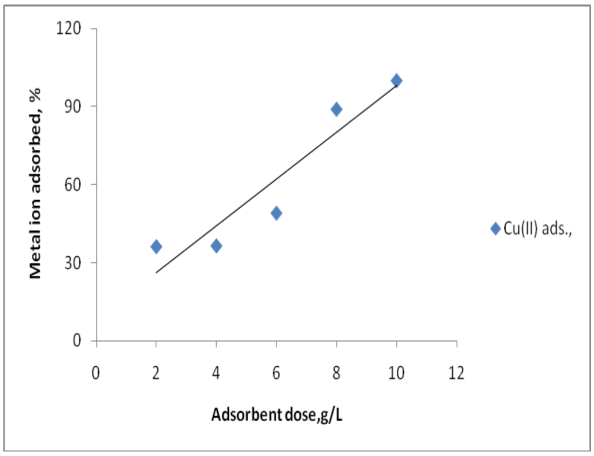

Fig. 2: Effect of adsorbent dose on percent Cu(II) removal

3. Effect of pH

The pH of the metal solution played on important role in the adsorption of Cu(II), with an increase in pH (1.5-5.5), 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 completes strongly with metal ions for active sites in adsorbent [11]. Increase in pH result in the electro static repulsion between the cat ions 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.**

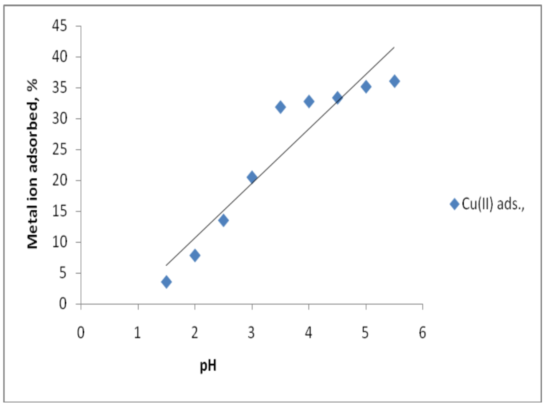

Fig. 3: Effect of pH on percent Cu(II) removal

4. Effect of temperature

The adsorption of Cu(II) at different temperatures namely 35˚C, 40˚C, 45˚C , 50˚C & 55, ˚C, were studied. The adsorption was found to increase with increase in temperature shown in figure-4. It reveals that the adsorbate – adsorbent system is an endothermic in nature for which the evaluation of thermodynamic parameters was carried out.

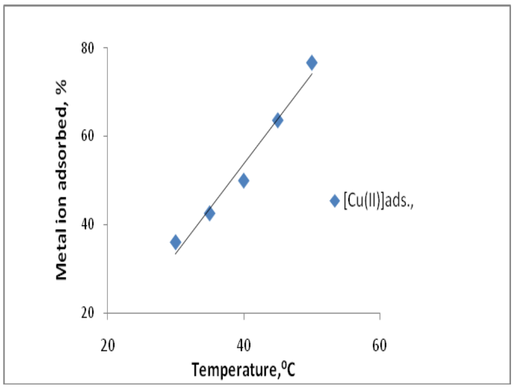

Fig. 4: Effect of temperature on percent Cu(II) removal

5. Evaluation of thermodynamic parameters

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

$\Delta G^\circ = - RT\log k_o$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Where $k_o = C_{solid} / C_{liquid}$

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 & the values of estimated thermodynamic parameters are given in Table-2. The negative value of ΔG° confirms the feasibility of the reaction and the spontaneous nature of the sorption & the positive value of ΔH° indicates the sorption reaction to be agreement with the endothermic nature of interaction & 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, this rules out the possibility of chemiosorption[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]

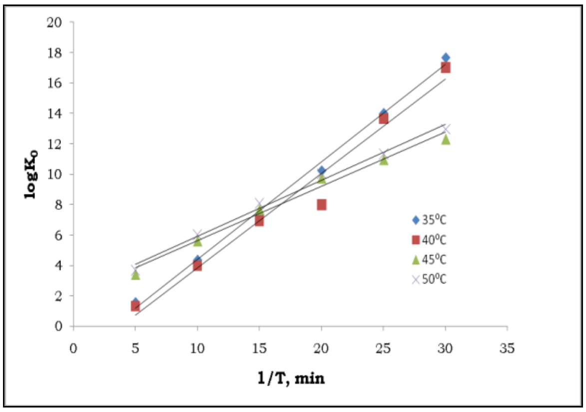

Fig. 5: Equilibrium constants & Thermodyanamic parameters

KINETICS OF ADSORPTION

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

Lagergren equation:

$$\log (q_e - q) = -(k_{lager}/2.303) * t + \log q_e$$

Bhattacharya-Venkobachar equation : log $(1-U_t) = -(k_{Bhatt}/ 2.303)*t$.

q_e & q = amount of Cu(II) ions adsorbed at equilibirium time & time t, respectively(in mg/g).

$$U_t = [(C_i\text{-}C_t)]/ C_i\text{-}C_e)]$$

C_i,C_t &C = Concentration of Cu(II) ions at time zero, equilibriumions concentration(in mgL^{-1}).

kl_{ager} & k_{Bhat}= first order adsorption rate constant

The r-values (correlation coefficient close to unity) indicate the applicability of these kinetic equations and the first order kinetic nature of adsorption of Cu(II) ions on BNAC shown in table-3.

Table 3: Kinetic of adsorption for removal of Cu^{2+} onto BNAC

Model Parameter	Cu^{2+} ions
Lagergen equation 10^4 k (s^{-1}) r-value	 3.222 0.882
Bhattacharya-venkobachar equation 10^4 k (s^{-1}) r-value	3.938 1.000

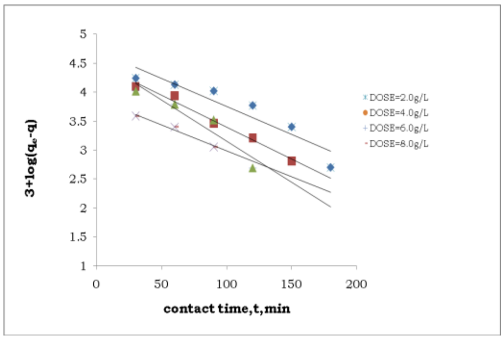

Fig. 6: Lagregren equation for the adsorption of Cu(II) by BNAC

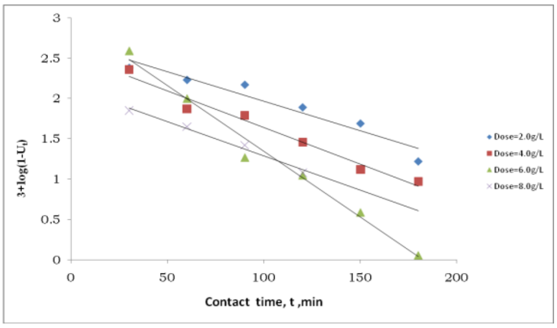

Fig. 7: Bhattacharya-Venkobachar equation for the adsorption of Cu(II) by BNAC

ADSORPTION ISOTHERMS

Two types of adsorption isotherm models namely Langmuir isotherm & Freundlich isotherm were tested. The Langmiur 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 = Langmiur constants- Adsorption capacity and Adsorption energy respectively.

The linear plots of C_e /Q_e versus C_e suggest the applicability of Langmiur 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: Langmiur Isotherm Results

	Temperature	Statistical Parameters / Constants		
	^{0}C	r^2	Q_m	B
copper ion adsorption	35	0.9946	16.53	0.1090
	40	0.9743	16.36	0.1189
	45	0.9913	15.12	0.1233
	50	0.9898	17.10	0.1324

It was observed in table-4 that, the Langmiur maximum adsorption capacity Q_m is 17.10 and the equilibrium constant b is 0.1324. The essential features of Langmiur 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, indicating that the adsorption process is favorable for this adsorbent (BNAC) for the removal of toxic metal ions.

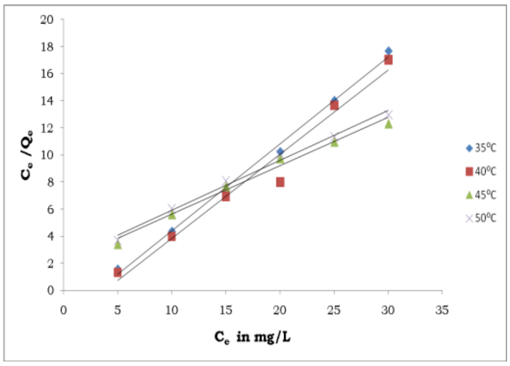

Fig. 8: Langmiur isotherm for the adsorption of Cu(II) ion by BNAC

Freundlich isotherm model

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

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

Q_e = amount of Cu(II) sorbed at equilibrium (mg g^{-1})
C_e = concentration of the Cu(II) at equilibrium (g.l^{-1})
k_F = adsorption capacity (l.g^{-1})
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-6 shows that the increase in negative charges on the adsorbent surface that makes electrostatic force like Vanderwaal's between the carbon surface and metal ion. The values clearly show the dominance of adsorption capacity. 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.

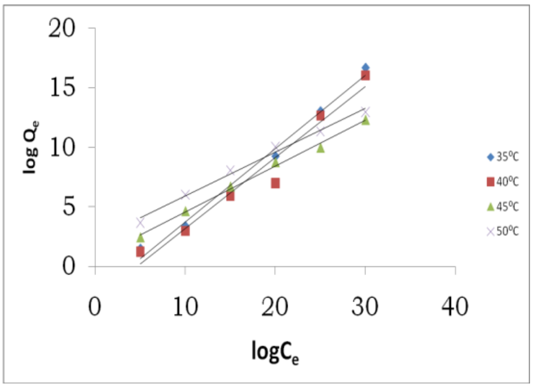

Fig. 9: Freundlich isotherm for the adsorption of Cu(II) ion by BNAC

CONCLUSION

Adsorption is a potentially attractive technology for the treatment of heavy metals such as copper(II) from wastewater. The present work was carried out using BETEL NUT powder as adsorbent. The adsorption capacity strongly dependent on the contact time, adsorbent dosage, pH & temperature. The kinetics of adsorption of copper(II) were tested with pseudo-first order Lagregren and Bhattacharya –Venkobachar model. The experimental data well fitted to the Langmiur & 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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