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Removal of Copper (II) by Adsorption on Biomass Carbon Derived from Pongamia (*Pongamia pinnata*) Leaf

A.Anitha[1]*, K.Kohilavani[2], R.Murugalakshmi[3]

[1,2,3]Department of Chemistry, V.V.Vanniaperumal College for Women, Virudhunagar-626 001, Tamil Nadu, India.

**Corresponding Author*

Abstract

The present study was conducted in order to investigate the feasibility and reliability of chemically activated *Pongamia pinnata* leaf carbon for the removal of copper (II) ions in the aqueous solution. Effect of parameter like pH, adsorbent dose, contact time, temperature and initial metal ion concentration were also determined. The optimum conditions obtained were 30 min contact time, 1.0g adsorbent dose, 40 ^{0}C, 0.1M Cu and pH 6 for copper removal. The maximum Cu adsorption capacity was found to be 84.9% on using activated pongamia leaf derived carbon. The adsorption process of copper (II) is tested with Langmuir and Freundlich adsorption isotherm models. The results revealed that copper is considerably adsorbed on pongamia leaf derived carbon and it could be economic method for the removal of copper from aqueous solutions. Moreover this study gives a value added utilization of biomass to remove Cu from waste water.

Keywords: adsorbent adsorption; biomass carbon; copper(II); pongamia leaf;

INTRODUCTION

Chemical substances such as heavy metals, organic and synthetic compounds generated from industrial activities have resulted in deterioration of the ecosystem due to improper discharge. Unlike other pollutants, heavy metal contamination has gained relatively more significance in view of their persistence, bio-magnification and toxicity. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, radiator manufacturing, smelting, alloy industries and storage batteries manufacture [1]. Among different toxic metals copper is of particular concern in wastewater treatment.

Copper as an essential element plays an important role in all living organisms. It is widely used in industries due to its high electrical and thermal conductivity, good corrosion resistance, ready availability, high recyclability and attractive appearance [2]. Copper (II) is one of the heavy metals most toxic to the living organisms and it is one of the widespread heavy metal contaminants of the environment. Intake of Cu contaminated water can causes hemolysis, hepatotoxic and nephrotoxic affects vomiting, cramps, convulsions, or even death [3].

Treatment processes for metal removal from wastewaters include precipitation, membrane filtration, ion exchange, adsorption and co-precipitation/adsorption. Cost-effective alternative technologies or adsorbents for the treatment of metal-containing wastewaters are needed. Natural materials that are available in large quantities, or certain waste plant products, may have potential as inexpensive adsorbents. Due to their low cost, after these materials have been expended, they can be disposed of without regeneration. Generally, adsorbents can be assumed as low cost if they require little processing, are abundant in nature, or are a by-product or waste material from another industry [4]. Reports have appeared on the preparation of activated carbons derived from rice husk [5], rice hull [6], palm kernel shell [7], saffron leaves [8], sorgum vulcaris dust [9], coir pith[10], couroupita guianensis [11], pongamia pinnata leaf [12] and sunflower stem [13] have been used to remove metal ions from water solution.

Pongamia leaf is a low cost adsorbent which is biodegradable and agro-waste which may act as a significant material for copper adsorption. Pongamia leaf waste is discarded all over the world as useless material. It is causing waste management problems though it has some compost, medicinal and adsorbent potentiality. It is an abundant, readily available, low cost and cheap, environment friendly bio-material. Considering the above criteria, pongamia leaf was selected to prepare the biomass carbon.

Thus the purpose of this work was to investigate the adsorption capacity of activated carbon from pongamia leaves to remove copper ions from the aqueous solution. The experiments were done to evaluate the effectiveness of adsorbent dosage, pH, contact time, initial metal ion concentration and temperature for the maximum removal of copper from aqueous solutions and the results were presented in a simplified and systematic way. The Langmuir and Freundlich adsorption isotherms were used to verify the adsorption.

EXPERIMENTAL

PREPARATION OF PONGAMIA LEAF ACTIVATED CARBON (PLAC)

Pongamia leaf used as raw material in this work was procured from a local garden. The midrib, which divides the blade into two lamina halves is removed with little hand pressure. The precursor was washed exhaustively with distilled water to remove adhering impurities from the surface, air-dried, cut to 1-2 cm size. Pretreated biomass was soaked in a concentrated solution of

ZnCl2 in the weight ratio of 1:1 biomass: $ZnCl_2$. The contents are stirred well in a magnetic stirrer at 60 ^{0}C for two days and dried in an air oven. The dried mass was finally heat treated in a furnace at 350 ^{0}C for 2 hours. The heat treated sample was washed several times with dilute HCl followed by de-ionized water until the washings are neutral to pH and its conductivity is minimal. On adding few drops of dilute NaOH solution and AgNO3 solution separately into the washings, no formation of white precipitate ensures the absence of Zn^{2+} and Cl^- ions. Absence of Zn^{2+}, Cl^-, neutrality in pH and low conductivity of the washings ensures thorough washing of the sample. The final mass of carbon lump was dried, ground and sieved to 250 mesh size. The powder prepared in this way is called Pongamia Leaf Activated Carbon (PLAC).

PREPARATION OF ADSORBATE SOLUTION

The copper stock solution (0.5M) was prepared using analytical grades of $CuSO_4{\cdot}5H_2O$. The test solutions were prepared by dilution to the desired concentrations of copper solution. The pH of the solution was adjusted using 0.1M HCl and NaOH solutions. All biosorption experiments in this study were carried out in 250 ml Erlenmeyer flasks with a working volume of 100 ml Cu(II)solution. The flasks were agitated on a rotary shaker set at 120 rpm speed and at 35oC temperature. The biomass free supernatant obtained was analyzed for residual Cu(II) concentration was found out volumetrically using EDTA as titrant and muroxide indicator. The amount of metal ion adsorbed per gram of the biomass and was calculated using the equation below:

$$qe = (Ci - Ce)V/M$$

where qe is the amount of metal ion biosorbed per gram of the biomass in mg/g, Ci is the initial concentration of the metal ion in mg/L, Ce is the equilibrium concentration of the metal ion in mg/L, M is the mass of the biomass in grams and V is the volume of the metal ion in litres. The experiment was performed in triplicate and the mean value taken for each parameter.

RESULTS AND DISCUSSION

EFFECT OF CONTACT TIME ON Cu (II) ADSORPTION

The effect of contact time on the adsorption of Cu ions using PLAC was studied and the results are shown in fig.1. All parameters such as dose of adsorbent, temperature, initial metal ion concentration and pH of solution were kept constant.

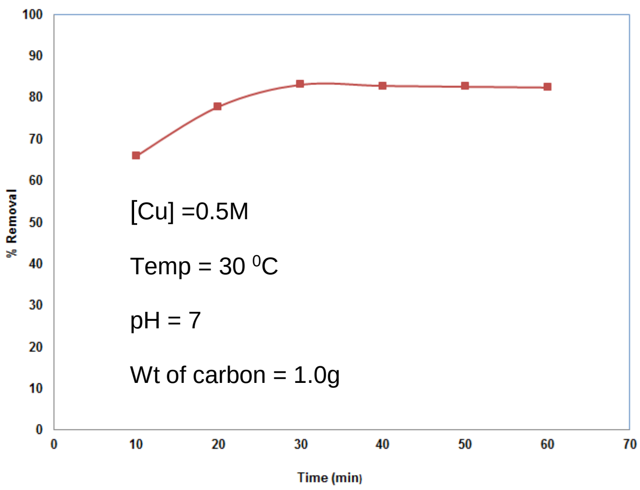

Figure 1. Effect of contact time on adsorption of Cu

Activated carbon sample must reach adsorption equilibrium to measure its total adsorptive capacity. In adsorption system, the contact time plays an important role among many experimental parameters, and influences the adsorption kinetics. Fig.1 depicts that there was an appreciable increase in percentage removal of Cu (II) up to 30 minutes, due to the availability of large number of sites for the adsorption of copper ions to occur, thereafter further increase in contact time does not increase the removal of copper due to the saturation of sites. Thus the effective contact time (equilibrium time) taken as 30 minutes. This result is important because equilibrium time is one of the important parameters for an economical wastewater treatment. The amount of heavy metal ion increases as time increases upto certain extend and thereafter remains constant. Similar results are recorded by other researchers [14, 15].

EFFECT OF ADSORBENT DOSE ON Cu (II) ADSORPTION

The adsorption of copper by PLAC at different dosages 0.8 to 1.3g for the copper removal was investigated.

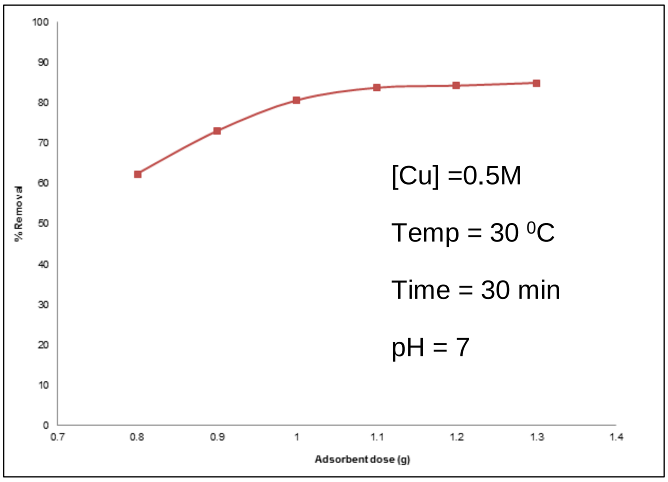

Figure 2. Effect of adsorbent dose on adsorption of Cu

Fig.2 showed that the copper removal increases with the increase in adsorbent dosage, this is mainly due to the greater availability of adsorbent. Percentage of Cu(II) removal from 62 to 85% acquired by the increase of adsorbent dosage. The adsorption capacity increases with the increase of adsorbent dosage because of the increase in surface area. This result also suggests that after a certain dose of adsorbent, the equilibrium conditions reached and hence the amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent. Our report was same as others [15, 16].

EFFECT OF INITIAL METAL ION CONCENTRATION ON Cu (II) ADSORPTION

The initial concentration of copper provides the important forces to overcome all mass transfer resistance of metal ions between the aqueous and solid phases. The effect of initial copper concentration on the copper adsorption rate was studied in the range of 0.06-0.16M (variation of 0.02M) at pH 7, temperature 30°C, 1.0g of adsorbent dose and 30 min contact time. The results obtained are represented in fig. 3.

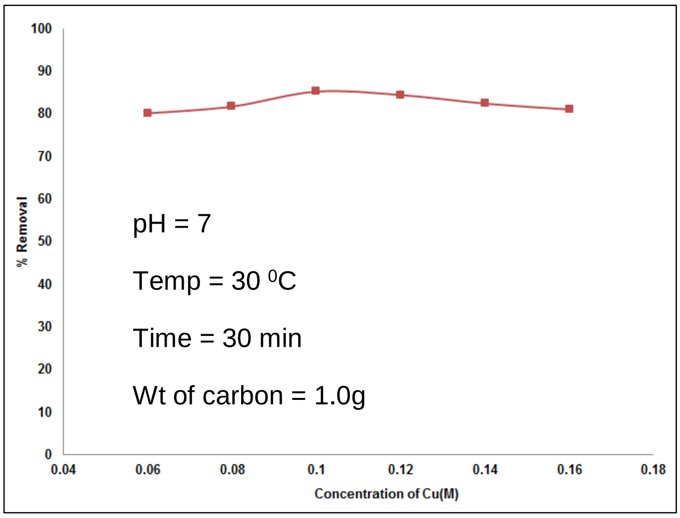

Figure 3. Effect of initial metal ion concentration on adsorption of Cu

From the fig. 3, it was observed that the percentage removal decreased with increase in initial copper concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of copper to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial copper concentration. Therefore it was evident from the results that copper adsorption was dependent on the initial metal concentration. Earlier studies [17, 18] showed the similar results.

EFFECT OF pH ON Cu (II) ADSORPTION

The effect of pH on the adsorption of Cu ions using PLAC was studied and the results are represented in fig. 4.

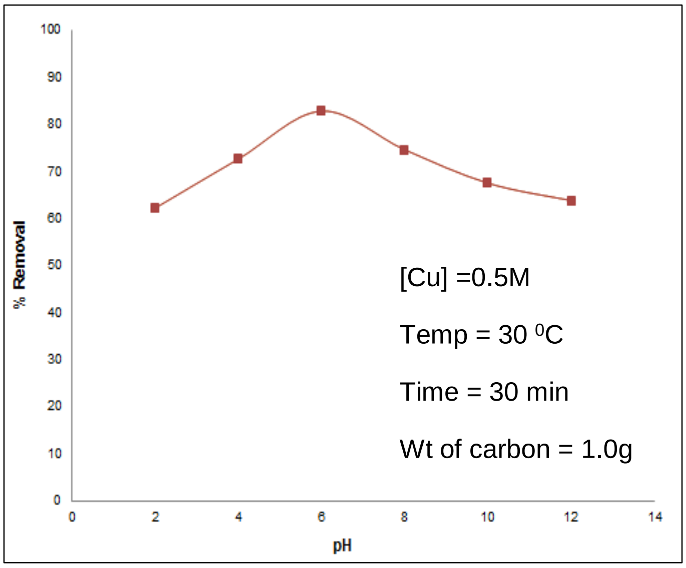

Figure 4. Effect of pH on adsorption of Cu

The pH of the solution is the important controlling factor for the adsorption of copper from the aqueous solution. The removal of Cu (II) increases from 62% at pH 2 to 82% at pH6. After that the adsorption capacity decreases from pH 6 to 14. The adsorption at pH 2 observed to be low due to the higher concentration of fast moving H^+ ions [19]. Increase in metal removal with increase in pH can be explained on the basis of the decrease in competition between proton and metal cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. After pH 6 there is a decrease in the adsorption capacity due to the precipitation of copper. After pH 6 there are three species present, Cu^{2+} in very small quantities, $Cu(OH)^+$, $Cu(OH)_2$ in large quantities. It has significant effect on adsorption of metal [20]. Maximum copper removal at pH 6 using pongamia leaf was supported by the other investigation [21].

EFFECT OF TEMPERATURE ON CU (II) ADSORPTION

The effect of temperature on removal of copper ion using PLAC was studied within the range of 35 to 60 ^{0}C and the results are represented in fig. 5. Other parameters such as dose of adsorbent, pH, metal ion concentration, contact time and pH of solution were kept constant. The temperature dependence of the adsorption process is related with several thermodynamic parameters.

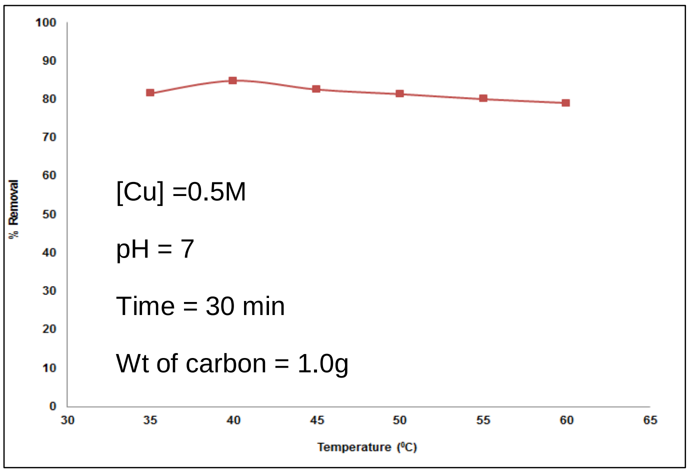

Figure 5. Effect of temperature on adsorption of Cu

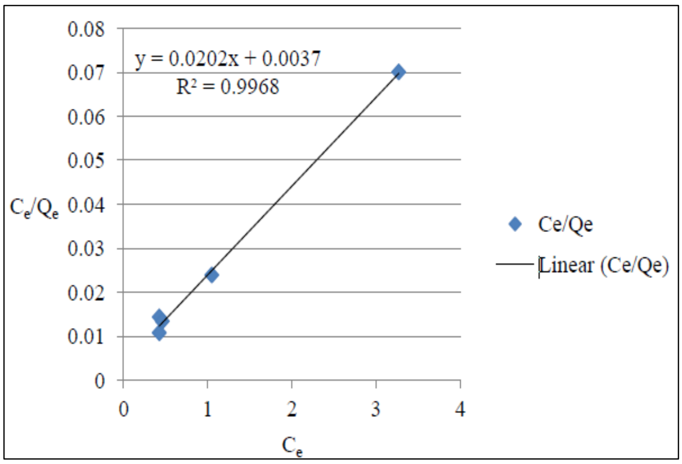

Figure 6. Langmuir adsorption isotherm for Cu adsorption

The temperature showed the negative effect on adsorption of copper using PLAC. With increase in temperature from 40 to 60 ^{0}C the removal of copper ions was decreased from 85 to 79% for PLAC. From the figure 4 it is clear that the low temperatures are in favour of copper ion removal. This may be due to a tendency for the copper ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The result shows that adsorption mechanism related with removal of copper is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in general related with low adsorption heat. This implies that the adsorption process was exothermic in nature. Similar findings are also reported by other researchers [22, 23].

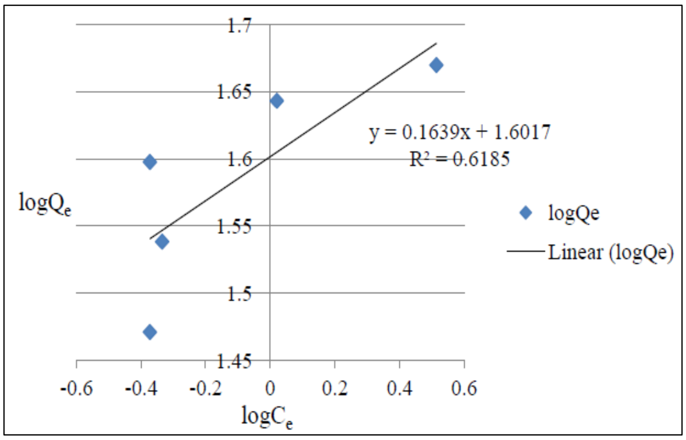

Figure 7. Freundlich adsorption isotherm for Cu adsorption

Adsorption isotherm Models

Isotherms models give the mathematical relationship used to describe the adsorption behaviors and adsorption capacity [24]. The relationship between the amount of Cu (II) ion and its equilibrium concentrations are described using the Freundlich and Langmuir models and the plots are represented in fig. 6 and 7. Langmuir adsorption isotherm is drawn by plotting the values C_e/Q_e Vs C_e gave a straight line and the linearity is due to the formation of monolayer of Cu (II) on the surface of the pongamia leaf carbon. It can be seen from the graph, copper adsorption is best represented by Langmuir isotherm (highest R^2 value) The Freundlich isotherm is empirical and heterogeneous layer is formed by plotting the values, graph log Q_e Vs log C_e gives slope and intercept. Langmuir isotherm constants and Freundlich isotherm constants were determined and are given in Table 1.

Table 1: Langmuir and Freundlich parameters for Cu (II) ion removal at 298 K

Adsorption Models	K_L	K_F	q_m(mg/g)	R^2	n
Langmuir	5.459		0.495	0.998	
Freundlich		39.967		0.6185	6.1013

Langmuir and Freundlich isotherms models are best fitted with an equilibrium data. Langmuir model in terms of R^2 value gives 0.9968 this indicates the monolayer of copper on the surface of adsorbent. A value of slope indicates normal Langmuir adsorption. The values of Freundlich exponent n,value is greater than unity showed the favourability of adsorption by Pongamia leaf carbon while 1/n is below 1 is indicative of normal Freundlich isotherm [25].

A partial list of biomass carbon utilized for adsorptive removal of metals is given in table 2 and the Cu removal efficiency of PLAC is comparable with the other biomass carbon.

Table 2: Efficiency of biomass carbon on metal adsorption

Biomass	**Metal ion**	**% removal**
Rice husk [5]	Cr(VI)	88
Rice hull [6]	Cu(II)	98
Rice hull [7]	Cd(II)	97
Palm kernel shell [7]	Cu(II)	86
Saffron leaf [8]	Cu(II)	76
Saffron leaf [8]	Cd(II)	91

Biomass	Metal ion	% removal
Saffron leaf [8]	Ni(II)	97
Sorgum Vulcaris dust [9]	Cu(II)	95
Coir pith [10]	Hg(II)	100
Coir pith [10]	Pb(II)	100
Coir pith [10]	Cd(II)	100
Coir pith [10]	Ni(II)	92
Coir pith [10]	Cu(II)	73
Couroupita guianensis [11]	Cu(II)	98
Pongamia pinnata leaf [12]	Cr(VI)	82
Sunflower stem [13]	Cr(VI)	82
Pongamia pinnata leaf (present work)	Cu(II)	85

To summarize, we have described how biomass carbon powder from GREEN biomass waste namely PONGAMIA LEAF can be produced and attempted to evaluate its potential as an adsorbent for removal of copper from waste water. The work also stresses Green Environment from Waste concept, which is the want of the hour.

CONCLUSION

The present investigation is carried out to study the suitability of a novel indigenous adsorbent, pongamia leaf derived activated carbon (PLAC) for the removal of heavy metal such as copper fromthe wastewater.

1. Influence of process parameters such as pH, adsorbent dosage, temperature, contact time, initial metal ion concentration were at moderate levels such that they can affect the removal efficiencies of the Cu were concerned.
2. The optimum pH of solution for Cu removal was found to be 6.
3. Within the scope of the experimental investigation the optimum temperature was found to be 40 ^{0}C.
4. The optimum time for adsorption of copper was found to be 30 minutes.
5. Initial metal ion concentration showed the negative effect on adsorption efficiency i.e. at lower levels the adsorption was higher.
6. Adsorbent dosage showed the positive effect on adsorption efficiency i.e. at higher adsorbent dose the adsorption was higher.
7. Our research work is designed in such a way of take waste, make products, and turns them to resources which is the reverse of the global scenario of take resources, make products, and turn them to waste.

The present research concludes that there is no need of complex activation procedure for the preparation of biomass carbon with superior adsorption behaviour. Thus the usage of biomass waste materials/residues as precursors of carbons as adsorbent offers significant potentials for reducing the cost and environmental damage resulting from uncontrolled disposal of these residues. This approach is thus interesting as it deals simultaneously with the water treatment and recycling of environmental waste. *Thus the study provides an effective way to value-added utilization of discarded biomass in the area of GREEN ENVIRONMENT.* However, further research should attempt to improve the adsorption capacity of adsorbents and apply this method to the removal of metals in large scale.

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