Activated Carbon from Morindacitrifolia Leaf as a Novel Adsorbent for Removal of Copper (II) Ions

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ABSTRACT

The current worldwide environmental problem is the contamination of water by toxic heavy metals. To remove the heavy metals from water sources, waste withered out leaves are used as affordable adsorbents. In this work, activated carbon was derived from the *Morindacitrifolia* leaf to remove the toxic Cu (II) ions from the contaminated water. Effect of adsorption parameters like contact time, pH, temperature, adsorbent dose and initial metal ion concentration were investigated.The optimum conditions were found to be 50 min contact time, pH 6, temperature 50 ^{0}C, 0.8g adsorbent dose and initial metal ion concentration of 0.14 M Cu. *Morindacitrifolia* Leaf derived Activated Carbon (MLAC) has the maximum Cu adsorption capacity of 94.6%. Equilibrium data were well represented by the Freundlich and Langmuir isotherm model for all tested adsorption systems. Due to zero cost and high efficiency *Morindacitrifolia* leaf activated carbon could be an easily available and renewable biological adsorbent for the removal of copper from waste water.

Keywords:Adsorption, Bioadsorbent, Biomass Carbon, Copper (II), MorindaCitrifolia Leaf

1. INTRODUCTION

The pollution of water resources by toxic heavy metals is one of the environmental issues worldwide. The group of elements with atomic density value greater than 6g/cm^3 [1] is termed as heavy metal. Heavy metals like nickel(Ni), arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), zinc (Zn), manganese (Mn) and mercury (Hg) mainly pollutes the fresh water reserves [2] because of their non-biodegradable, persistent and toxic nature. Most of the metals are teratogenic, carcinogenic and pose severe health problems like reduced growth and development, organ damage, oxidative stress and nervous system impairments [3]. Heavy metals are introduced into the environment including water, soil [4], air and biosphere due to rapid industrial growth. The main industrial sources are smelting, mining, surface finishing and electroplating industry [5]. Copper is required by humans in trace amounts for its role in enzyme synthesis, bones and tissues development [6]. Conversely, the divalent copper (Cu^{2+}) is carcinogenic and toxic on excess consumption. Excess intake of Cu^{2+} results in deposition over liver which in turn creates vomiting, headache, respiratory problems, abdominal pain, liver and kidney failure and finally gastrointestinal bleeding [6]. Moreover it produces detrimental deleterious effects to many plant species viz., Acacia holosericea and Eucalyptus crebra [7]. The presence of excess Cu^{2+} in water reserves affect the osmoregulatory mechanism of the aquatic animals [8] and leads to mutagenesis in humans [9]. Huge amounts of Cu^{2+} are let out to the environment as untreated waste from industries [7].

The permissible Cu^{2+} limit of industrial effluent is 1.3 mg/L as per United State Environmental Protection Agency [9] scale, whereas World Health Organization (WHO) sets the permissible Cu^{2+} limit as 1.5 mg/L for drinking water [10]. Copper (Cu^{2+}) contaminated wastewaters are released from various industries extensively to the water bodies, enters into food chains which in turn leads to serious health problems like carcinogenicity and mutagenesis in living systems. A wide range of technologies are currently in use to remove Cu^{2+} from wastewater.

Innumerable technologies are practiced and adapted to maintain the environmental safety by removing excess Cu^{2+} from the industrial effluents. Each technology has their own cons and pros; obviously adsorption is one of the promising methods to remove the heavy metals from wastewater. The advantages of adsorption process are flexibility in design, availability of sustainable, cost effective and eco-friendly adsorbents and removal of heavy metal from industrial effluent.

Moreover, as adsorption is a reversible phenomenon regeneration of adsorbents can be done by desorption process. As adsorbent can be regenerated, adsorption is the zero cost process. Recently adsorption using biomass derived adsorbents (biosorbents) has gained its importance due to the value added utilization of waste biomass to the most needed water purification process.

Many adsorbents are developed from cheap biomass and tested its utility for heavy metal ion removal. The efficiency of adsorption depends on the nature of the adsorbent used. Biomass derived adsorbents like Irish Peat moss [11], pine cone powder [12], kenaffiber [13], sugar beet pulp [14], tea [15] and many others have been used for heavy metal removal. But the efficiency of Activated Carbon (AC) derived from biomass is higher than the biosorbents for heavy metal removal. This is because of the salient features of the AC like high surface area enriched with micropores and mesopores. These features of AC claim the high removal efficiency of heavy metals from wastewater.

Thus the current research explores the possible application of AC derived from Morindacitifolia leaves for Cu^{2+} removal. Morindacitifolia leaves are available in bulk at free of cost along the road sides of Virudhunagar district. AC was prepared from Morindacitrifolia leaves by simple procedure without make use of high temperature and pressure conditions and expensive catalyst. The AC thus prepared in this manner was used for the adsorption of Cu^{2+} from waste water by varying pH, initial concentration of Cu ions, adsorbent dosage, temperature and contact time and the results are presented in systematic way.

2. EXPERIMENTAL

2.1 Preparation of Morindacitrifolia Leaf Activated Carbon (MLAC)

The raw material of this work was collected from the trees on the road side. The main vein of the leaf was removed with hand pressure. The precursor was washed using distilled water to remove the dust and sticky impurities on the surface. It was cut to 1-2 cm size and then shade dried for about a week and then oven dried at 100 ^{0}C for an hour. The dried mass was crushed and heated in a furnace at 350 ^{0}C for 2 hours. The heat treated sample was washed several times with de-ionized water, until the washings are free from coloured impurities. The final mass of carbon was dried, ground and sieved to 250 mesh size. Thus Morinda Leaf Activated Carbon (MLAC) was prepared.

2.2 Preparation of adsorbate solution

The wastewater was artificially prepared in lab. The stock solution (0.5M) of copper was prepared with analytical grades of $CuSO_4 \cdot 5H_2O$. The test solutions of copper were prepared to the desired

concentrations by dilution. The solution was adjusted to suitable pH using 0.1M HCl and NaOH solutions. All the adsorption experiments of this study were carried out in 250 ml Erlenmeyer flasks with 100 ml working volume of Cu (II) solution. The flasks were shaked on a rotary shaker set at 120 rpm speed and at 35 ^{o}Ctemperature. The biomass free supernatant liquid was analyzed for residual Cu(II) concentration by titration against EDTA as titrant and murexide as indicator. The amount of metal ion adsorbed per gram of the biomass was calculated using the equation:

$$q_e = (C_i - C_e)V/M$$

where q_e is the amount of metal ion biosorbed per gram of the biomass in mg/g, C_i is the initial concentration of the metal ion in mg/L, C_e 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 done in triplicate and the mean value was taken for each parameter.

3. RESULTS AND DISCUSSION

3.1Effect of Contact Time on Cu (II) Adsorption

The adsorption of Cu ions using MLAC was studied at various contact time. All other parameters like dose of adsorbent (0.5g), temperature (35 ^{o}C), initial metal ion concentration (0.1M) and pH (7) of solution were maintained constant during the study. The effect of contact time on adsorption was shown in Fig (1).
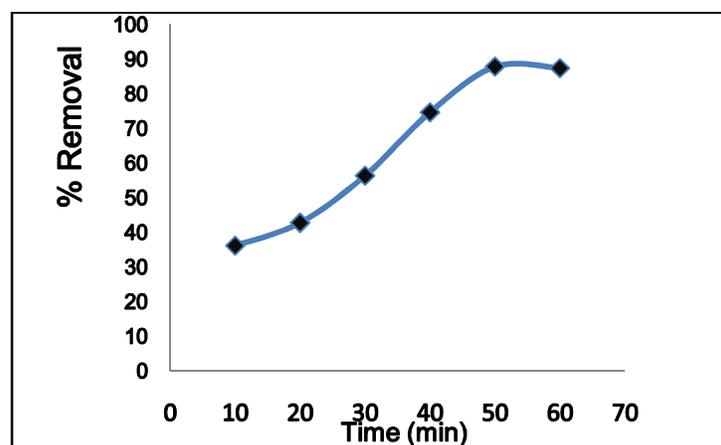

Figure 1. Effect of contact time on adsorption of Cu

On the observation of results, it was found that the adsorption increases rapidly till 50 minutes, after that there was no significant change in the adsorption. The initial rapid adsorption is due to the availability of plenty of vacant sites and after 50 minutes, equilibrium state was achieved. From fig (1), it is informed that the removal of metal ions removal increases with increasing contact time before the attainment of equilibrium. On increasing the contact time from 10 to 50 minutes, removal of Cu (II) ions increases from 36% to 87% on the usage of MLAC as adsorbent. After 50 minutes, desorption predominates, which infers that the optimum time for the maximum adsorption of Cu (II) ions was 50 minutes. From literature, it was known that the equilibrium time is one of the key parameter for waste water treatment and it varies with the nature of biomass used to prepare the activated carbon. Rengaraj et al [16] and Alinnor and Nwachukwu [17] analyzed the sorption of phenol onto palm seed coat activated carbon and nitrophenol onto fly ash with the equilibrium time of 2 hours.

3.2 Effect of pH on Cu (II) Adsorption

The effect of pH variation from 2 to12 on the adsorption of Cu ions using MLAC was studied by keeping all other parameters like contact time (50 min), temperature (35 ^{o}C), initial metal ion concentration (0.1M), and adsorbent dose (0.5g) constant and the results are displayed in Fig (2).
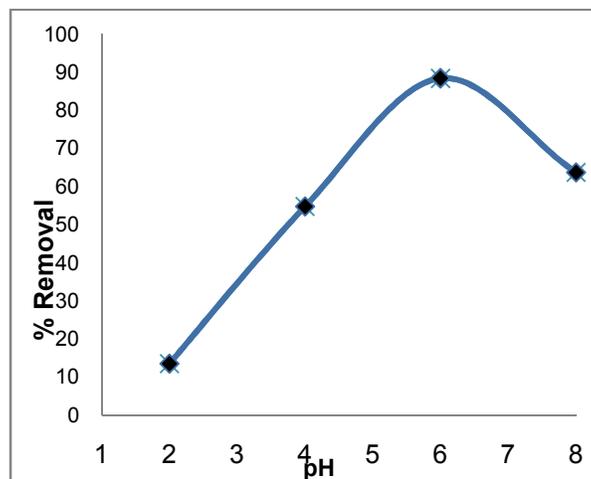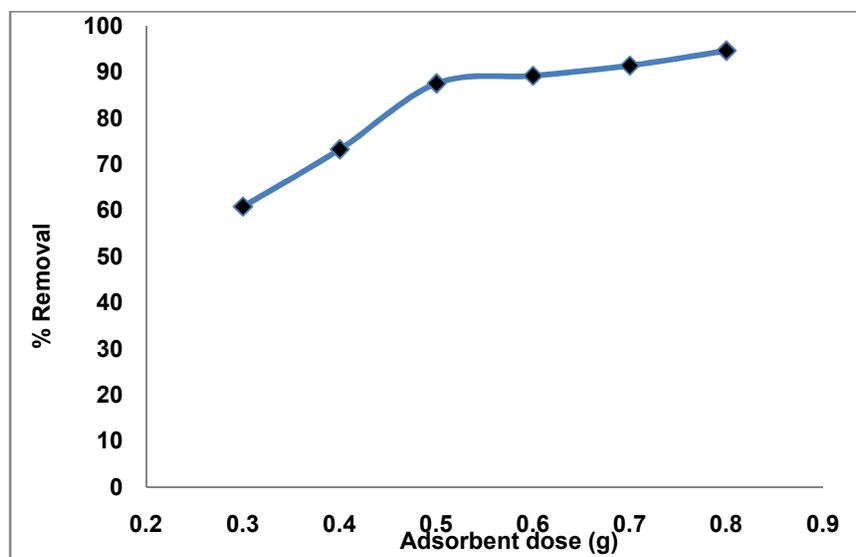

Figure 2. Effect of pH on adsorption of Cu

Results infer that pH has huge impact on the removal efficiency of copperions. The results showed that initially Cu (II) removal increases with increasing pH after that decreases on increasing pH. The removal of Cu (II) using MLAC was maximum of about 88.3% at optimum pH of 6. The reason for the variation was, at pH less than or equal to 6, the predominant species of copper was free Cu(II) ions which involves mainly adsorption process. At pH greater than 6, copper ions began to precipitate as Cu $(OH)_2$, which was confirmed by Ramya et al [18] and Al Subu et al [19]. The removal of metal ion initially increases with increase in pH was due to the decrease in competition between metal cations and proton for same functional groups and by decrease in positive surface charge, which in turn reduces the electrostatic repulsion between surface and metal ions. At higher pH (> pH 6), decrease in adsorption is because of the formation of soluble hydroxy complexes [19, 20].

3.3 Effect of adsorbent dose on Cu (II) adsorption

The effect of adsorbent dose on the adsorption of Cu ions using HLAC was observed by varying the amount of adsorbent from 0.3 to 0.8g keeping other parameters pH (7), metal ion concentration (0.1M), temperature (35 ^{o}C), and contact time (50 min) constant and the results are depicted in Fig (3).

Figure 3. Effect of adsorbent dose on adsorption of Cu

Fig (3) reveals that copper removal efficiency improved with increasing dose of adsorbent. The fact behind that was due to the huge availability of adsorption sites on high adsorbent dose. From the values it is known that adsorption increases rapidly upto the adsorbent dose of 0.5g and after that there was only slight increase in adsorption on increased adsorbent dose. The Cu (II) was removed to the maximum of 90.7% at dosage of 0.8g. It was also inferred that the equilibrium conditions was reached after a certain dose of adsorbent, therefore the amount of free ions in the solution and the amount of ions bound to the adsorbent remain unchanged on further addition of adsorbent. Hussein et al [21] results matches well with this finding.

3.4 Effect of temperature on Cu (II) adsorption

The influence of temperature on copper ion removal using MLAC was analyzed in the temperature range of 35 to 60 ^{0}C and keeping other parameters such as dose of adsorbent (0.5g), pH (7), metal ion concentration (0.1M), contact time (50 min) and pH (7) of solution were kept constant. The results are given in Figure (4). Several thermodynamic parameters are known from the temperature dependence of the adsorption process.
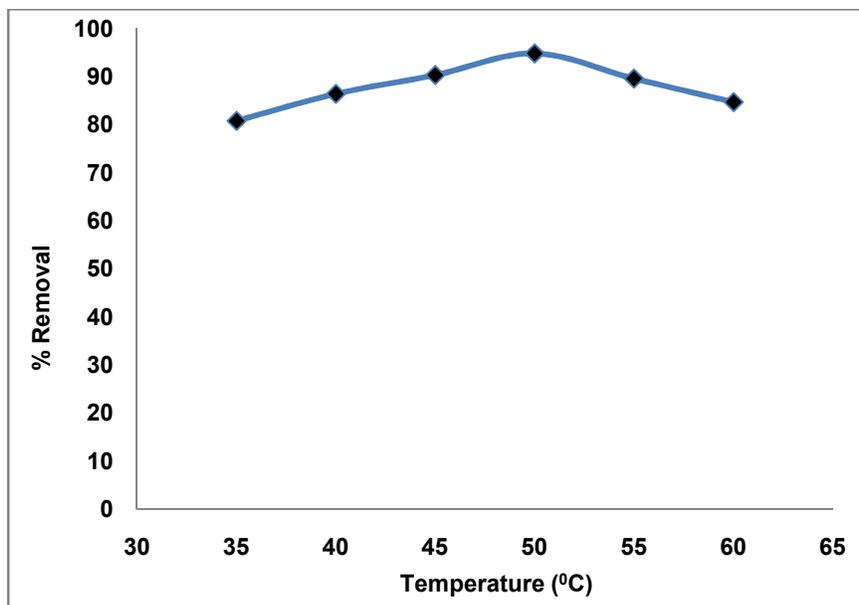
Figure 4. Effect of temperature on adsorption of Cu

The adsorption of copper using MLAC initially increases with increase in temperature but after the optimum temperature, adsorption decreases. On increasing the temperature from 35 to 50 ^{0}C copper ion removal was increased from 80.8 to 94.8% thereafter decreases with further increase in temperature. From the study it is known that the low temperature favours the adsorption of copper ion. The reason may be the copper ions tend to move towards the bulk phase from the solid phase on increasing the temperature of the solution. The results also inform that adsorption of copper is purely physical in nature involving electrostatic interaction between adsorbate and adsorbent, accompanied with low heat of adsorption. This indicates that the adsorption was an exothermic phenomenon. Other researchers are also reported the similar findings [22, 23]

3.5 Effect of initial metal ion concentration on Cu (II) adsorption

The effect of initial copper concentration on the copper adsorption rate was studied by varying the metal concentration in the range of 0.06-0.16M (variation of 0.02M) at pH 7, temperature   35 ºC, 0.5g of adsorbent and 50 min contact time. The results obtained are given in fig (5).
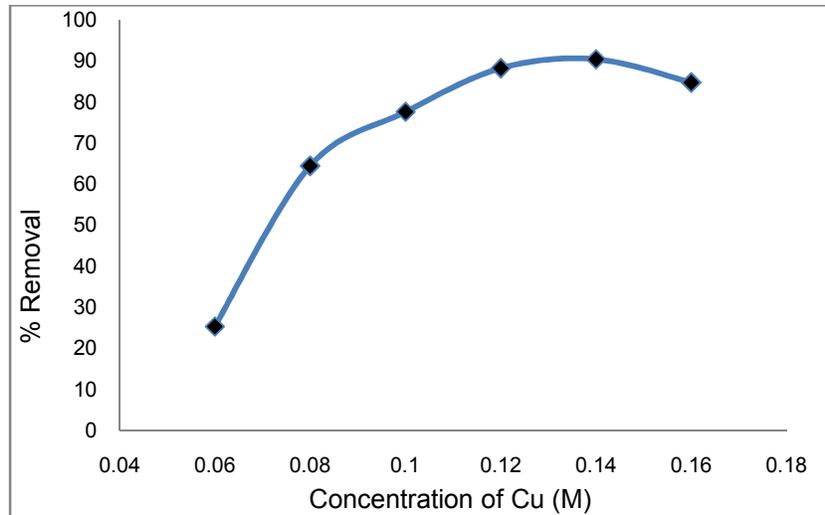
Figure 5. Effect of initial metal ion concentration on adsorption of Cu

Fig (5) indicates that the copper removal decreases with increase in its concentration. From the results it is evident that the copper adsorption was dependent on the initial metal concentration. The poorer adsorption at higher metal concentration was may be due to the increased ratio of initial number of moles of copper to the available vacant sites. The total number of adsorbent sites available was fixed for a given adsorbent dose thus adsorbing almost the equal amount of adsorbate, thereafter leads to desorption, with increase in initial copper concentration. Several researchers reported the similar results [24, 25, 26].

3.6 Adsorption isotherms

The correlation between the amount of Cu (II) ion and its equilibrium concentrations are illustrated using the Freundlich and Langmuir models and the plots are depicted in Figs (6 and 7). From a plot of $1/q_e$ against $1/C_e$ Langmuir isotherm constants were found out while the plot of $\ln q_e$ against $\ln C_e$ gives the Freundlich isotherm constants and are given in Table (1).
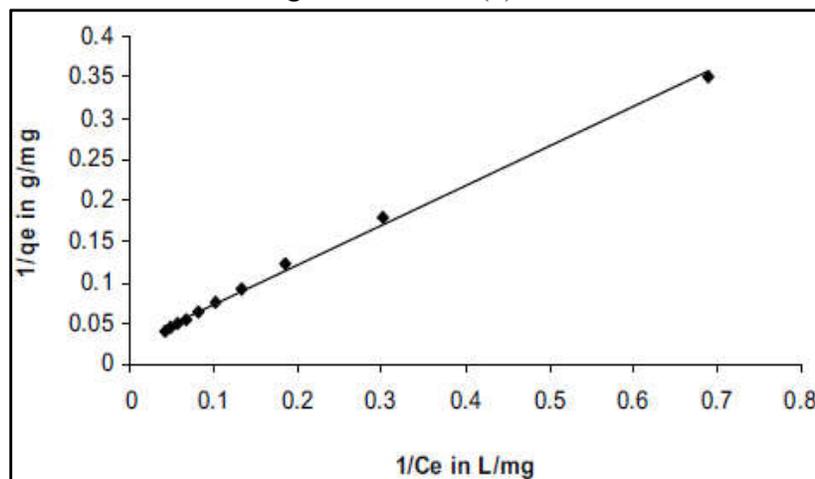
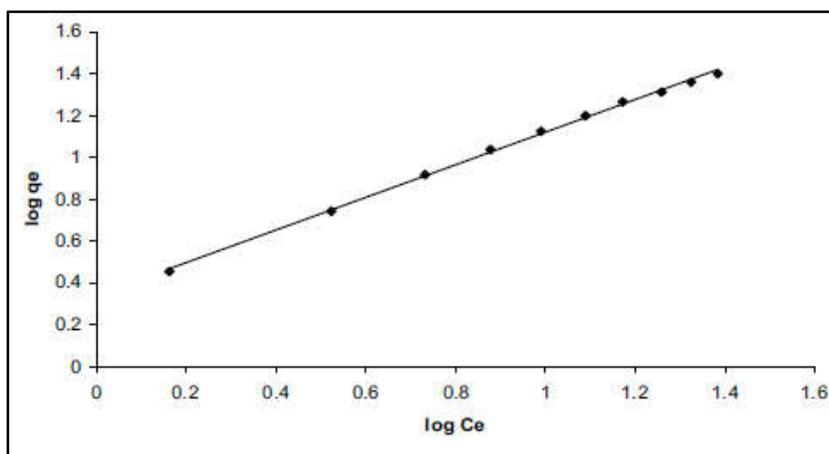**Figure 6. Langmuir adsorption isotherm for Cu adsorption**

Figure 7.Freundlich adsorption isotherm for Cu adsorption

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	0.051		40.259	0.996	
Freundlich		2.195		0.954	1.284

The isotherm correlation coefficient (R^2) of Langmuir and Freundlich model equations was 0.996 and 0.954 respectively for the adsorption of Cu (II) ion on MLAC. The obtained results infer that Langmuir biosorption model best fits the biosorption of Cu (II) ion with MLAC demonstrating a physical biosorption.

A partial list of adsorptive removal of copper ions using biomass carbon is specified in table (2) and it was found that the Cu removal efficiency of MLAC is comparable with the other biomass carbon.

Table(2). Efficiency of biomass carbon on copper adsorption

Biomass	% removal
Date stone [27]	37
Rice hull[28]	98
Palm kernel shell[29]	86
Saffron leaf[30]	76
SorgumVulcaris dust[31]	95
Coir pith[32]	73
Couroupitaguianensis[33]	98
Eichhorniacrassipes root [34]	48
palm kernel shell [35]	82
Banana leaves[36]	95

Hibiscus leaf [37]	91
Pongamia leaves [38]	85
Thumbai leaves [39]	86
Morinda leaf (present work)	95

4. CONCLUSION

Our work is based on take waste, make products and utilize them to remove waste. Green method to free from waste, which is the need of the hour, is also stressed in this work. Thus the work describes the effective usage of biomass carbon from Morindacitrifolia leaf as a potential adsorbent for copper removal from waste water. Results of adsorption data conclude that MLAC was the excellent adsorbent for copper removal from industrial waste water.

ACKNOWLEDGMENT

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