Potential Adsorption of Copper (II) From Wastewater by Hibiscus Leaf (Hibiscus Rosa-Sinensis) Derived Carbon

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Abstract—The contamination of wastewater by toxic heavy metals is worldwide environmental problem. Withered out and waste leaves are affordable adsorbents for the removal of heavy metals from aqueous solutions. In this research, the use of activated biomass carbon derived from Hibiscus rosasinensis leaves (as an eco-friendly and low cost adsorbent) having the ability to remove toxic copper ions (Cu (II)) from aqueous solutions has been investigated. 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, 0.8g adsorbent dose, 35 °C, 0.1M Cu and pH 4 for copper removal. The maximum Cu adsorption capacity was found to be 90.7 on using activated hibiscus leaf derived carbon. Equilibrium data were well represented by the Freundlich Langmuir isotherm model for all tested adsorption systems. The results revealed that the Hibiscus rosa-Sinensis leaves activated with zinc chloride could be an effective, low cost, easily available and renewable biological adsorbent for the removal of copper from aqueous solution.

Keywords—biomass carbon; adsorption; copper (II); hibiscus leaf; adsorbent

I. INTRODUCTION

The contamination of wastewater by toxic heavy metals is worldwide environmental problem. The term heavy metal is applied to a group of elements having atomic density value of more than 6 g/cm³[1]. Heavy metals like arsenic (As), copper (Cu), cadmium (Cd), chromium (Cr), nickel(Ni), zinc (Zn), lead (Pb), mercury (Hg) and manganese (Mn) are major pollutants of freshwater reserves [2] because of their toxic, non-biodegradable and persistent nature. Most of the metals are carcinogenic, teratogenic and pose severe health problems like organ damage, reduced growth and development, nervous system impairments and oxidative stress [3]. The increasing industrial growth is the major source of heavy metals introduction into different segments of the environment including air [4], water, soil and biosphere. These industrial sources include mining, smelting, surface finishing, electroplating, electrolysis, electric appliances and electric boards/circuits manufacturing industries as well as agriculture sector including fertilizers, pesticides [5].

Copper is an important trace element required by humans for its role in enzyme synthesis, tissues and bones development [6]. However, the divalent copper (Cu²⁺) is toxic and carcinogenic when consumed in excess through ingestion. The excessive Cu²⁺ consumption leads to its deposition in liver and subsequent vomiting, headache, nausea, respiratory problems, abdominal pain, liver and kidney failure and finally gastrointestinal bleeding [6]. It has known detrimental deleterious effects on the soil biota and damages to many plant species including some of the endemic Australian native plant species (Acacia holosericea and Eucalyptus crebra) [7]. The excessive amounts of Cu²⁺ in fresh water resources and aquatic ecosystem damage the osmoregulatory mechanism of the freshwater animals [8] and cause mutagenesis in humans [9]. Large quantities of Cu²⁺ are released by the disposal of untreated industrial waste [7]. United State Environmental Protection Agency has set its Cu²⁺ permissible limits as 1.3 mg/L in industrial effluents [9]. World Health Organization (WHO) defines the Cu²⁺ permissible limit of 1.5 mg/L in drinking water [10]. Copper (Cu²⁺) containing
wastewaters are extensively released from different industries and its excessive entry into food chains results in serious health impairments, carcinogenicity and mutagenesis in various living systems. An array of technologies is in use to remediate Cu$^{2+}$ from wastewaters.

A large number of technologies have been adapted and practiced so far to ensure the environmental safety against Cu$^{2+}$ in the industrial effluents. Each technology has its own merits and demerits. Adsorption is a recognized method for the removal of heavy metals from wastewater having low concentration of heavy metal. The adsorption process offers flexibility in design and operation and in many cases produce high-quality treated effluent. Besides this, adsorption is reversible and adsorbents can be regenerated by suitable desorption techniques. Adsorption is the most attractive option due to the availability of cost effective, sustainable and eco-friendly bioadsorbents. Bioadsorption is a relatively newly devised method for an efficient copper removal from the wastewater and still various bioadsorbents are under testing phase for the removal of heavy metals.

Many low cost adsorbents have been developed and tested for heavy metal ion removal so far, which reflect varying adsorption efficiencies depending upon the type of adsorbents used. Irish Peat moss [11], pine cone powder [12], kenaffiber [13], sugar beet pulp [14], tea [15] and many others have been tested for Cu$^{2+}$ removal.

Activated carbon (AC) with micropores and mesopores along with high surface area are the main features of AC which claim higher removal efficiency of heavy metals from wastewater. The current research have explored the activated carbon from Hibiscus rosasinensis leaves for the Cu$^{2+}$ removal with special emphasis on the utility of biomass carbon derived from waste biomasses.

The purpose of the present work was to investigate the possibility of AC derived from Hibiscus rosasinensis leaves which is locally available, free of cost all over India as an adsorbent for removal of copper and the results have been presented in a simplified and systematic way. The effects of various operating parameters on adsorption such as pH, initial concentration of cu ions, adsorbent dosage, temperature and contact time were studied.

II. EXPERIMENTAL

2.1 Preparation of Hibiscus Leaf Activated Carbon (HLAC)

Hibiscus 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 ZnCl$_2$ in the weight ratio of 1:1 biomass: ZnCl$_2$. The contents are stirred well in a magnetic stirrer at 60 $^\circ$C for two days and dried in an air oven. The dried mass was finally heat treated in a furnace at 350 $^\circ$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 AgNO$_3$ 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 Hibiscus Leaf Activated Carbon (HLAC).

2.2 Preparation of adsorbate solution

The wastewater was prepared in lab artificially. The copper stock solution (0.5M) was prepared using analytical grades of CuSO$_4$·5H$_2$O. The test solutions were prepared by dilution to the desired
concentrations of copper solution. The pH of the solution was adjusted using a 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 35 °C 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:

\[ q_e = (C_i - C_e)V/M \]

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 performed in triplicate and the mean value taken for each parameter.

III. RESULTS AND DISCUSSION

3.1 EFFECT OF CONTACT TIME ON Cu (II) ADSORPTION

The effect of contact time on the adsorption of Cu ions using HLAC was studied and the results are shown in figure 1.

![Figure 1: Effect of contact time on adsorption of Cu](image)

From the results, it was observed that there is a rapid initial adsorption in the first 10 min, followed by a longer period of much slower sorption until about 30 minutes when equilibrium was reached, after which there was no significance increase in Cu (II) ion uptake. Initially Cu (II) ion uptake was rapid because there are plenty of readily available sites for adsorption to occur. Subsequently, biosorption increased in the second phase but with a much slower rate until 30 minutes when equilibrium was reached. From figure 1, it is noted that metal ions removal was increased with an increase in contact time before equilibrium was reached. All parameters such as dose of adsorbent, temperature, initial metal ion concentration and pH of solution were kept constant.

The results indicated that on increasing the contact time from 10 to 30 minutes Cu (II) removal was increased from 60% to 86% on using HLAC as adsorbent. From 30 to 60 minutes, the
percentage removal of Cu (II) using HLAC starts decreasing which showed that equilibrium was reached at 30 minutes itself. Thus the results illustrated that after 30 minutes desorption predominates over the adsorption which infers that the optimum contact time for maximum removal of Cu (II) ions using HLAC was 30 minutes. This result is important because equilibrium time is one of the important parameters for an economical wastewater treatment. Recent researches have shown that adsorption equilibrium is dependent on the type of biomass and not on the method of preparation of biomass carbon. Rengaraj et al [16] and Alinnor and Nwachukwu [17] reported equilibrium time of 2 hours for the adsorption of phenol onto palm seed coat activated carbon and sorption analysis of nitrophenol onto fly ash.

3.2 EFFECT OF pH ON Cu (II) ADSORPTION

The effect of pH on the adsorption of Cu ions using HLAC was studied and the results are represented in figure 2.

From the results it is illustrated that pH obviously influences the removal efficiency of the copper ions in the aqueous solution. The results indicated that Cu (II) removal was increased to maximum and then decreased with pH variation from 2 to 12 on keeping all other parameters like contact time, temperature, metal ion concentration and adsorbent dose constant. The maximum % removal of Cu (II) was about 80.6% at pH 4 for HLAC. This is because the dominant species of copper was free Cu(II) and was mainly involved in the adsorption process when the pH was lower than 4. When the pH greater than 4, copper ions started to precipitate as Cu (OH)\(_2\), and this had been confirmed by Ramya et al [18] and Al Subu et al [19]. Increases 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. Decrease in adsorption at higher pH (> pH 4) is due to formation of soluble hydroxy complexes [19, 20]. The adsorption of Cu (II) ion was found mainly to be influenced by solution pH.

3.3 EFFECT OF ADSORBENT DOSE ON CU (II) ADSORPTION

The effect of adsorbent dose on the adsorption of Cu ions using HLAC was studied and the results are shown in figure 3.
Adsorption efficiency of Cu (II) adsorption was studied by varying the amount of adsorbent from 0.3 to 0.8g keeping other parameters (pH, metal ion concentration, temperature and contact time) constant. This shows that removal efficiency of the copper usually improved on increasing adsorbent doses. This may occur due to the fact that the higher dose of adsorbents in the solution provides the greater availability of exchangeable sites for the ions. From the figure it is clear that only slight increase in adsorption after a certain amount of adsorbent was added (0.5g). The maximum % removal of Cu (II) was about 90.7% for HLAC at dosage of 0.8g. 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 findings are in good support with Hussein et al [21].

3.4 EFFECT OF TEMPERATURE ON CU (II) ADSORPTION

The effect of temperature on removal of copper ion using HLAC was studied within the range of 35 to 60 °C and the results are represented in figure 4. 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.
74.1% for HLAC. 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]

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 in the range of 0.06-0.16M (variation of 0.02M) at pH 7, temperature 30 ºC, 0.5g of adsorbent and 0.1M metal ion concentration and 30 min contact time. The results obtained are represented in figure 5.

From the figure 5 it was observed that the percentage of 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. Similar results have been also reported by several researchers [24, 25, 26].

3.6 Adsorption Isotherms

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 Figures 6 and 7. Langmuir isotherm constants were determined from a plot of Ce/qe against Ce while that of Freundlich isotherm constants were determined from the plot of In qe against In Ce as shown in Table 1. The isotherm correlation coefficient (R²) of Langmuir and Freundlich model equations for the adsorption of Cu (II) ion HLAC was 0.998 and 0.964 respectively. The results obtained showed that Langmuir biosorption model was the best fit for the biosorption of Cu (II) ion using HLAC indicating a physical biosorption.
To summarize, we have described how biomass carbon powder from HIBISCUS LEAF can be produced and attempted to evaluate its potential as an adsorbent for removal of copper from waste water.

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

<table>
<thead>
<tr>
<th>Adsorption Models</th>
<th>$K_L$</th>
<th>$K_F$</th>
<th>$q_m$(mg/g)</th>
<th>$R^2$</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>1.322</td>
<td></td>
<td>0.6901</td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td>1.099</td>
<td></td>
<td>0.964</td>
<td>13.389</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

The present investigation is carried out to study the suitability of a novel indigenous adsorbent, hibiscus leaf derived activated carbon (HLAC) for the removal of heavy metal such as copper from the 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 4.
3. Within the scope of the experimental investigation the optimum temperature was found to be 40°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.

Thus, from the results of adsorption data, it was concluded that the HLAC was found to be excellent adsorbent for the adsorption of copper from industrial waste

ACKNOWLEDGMENT

The authors thank The Management and The Principal of V.V.Vanniaperumal College for Women, Virudhunagar. The authors sincerely thank the reviewers for the critical evaluation of the MS.

REFERENCES


