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THE ROLE OF BIOCARBON ON THE REMOVAL OF Cu (II) IONS FROM SYNTHETIC WASTE WATER

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ABSTRACT

Most of the heavy metals are toxic in nature. It may contribute variety of adverse environmental and human health effects due to their acute and chronic exposure through air, water and food chain. They are released into the aquatic environment from many industrial activities. Particularly cadmium, lead, chromium, nickel and copper are the most toxic metals of widespread in industrial wastewater. Hence, treatment water and wastewater and possible removal of toxic pollutants are very essential before discharge into receiving environmental systems. There are number of adsorbents are used in water treatment process. Most of the conventional treatment methods of metal removal are often limited by their operational cost and ineffectiveness at low concentrations. In this respect, a new search is in progress to identify cheap materials which may have potential adsorption capacity for the removal of pollutants in water. The use of activated biocarbon as adsorbents offers an attractive alternative to the conventional chemical materials used in water and wastewater treatment. In the current investigation, a new biocarbon material is introduced, which are produced from a medicinal plant for the metal removal. In a model trial, 2.5g/100mL of biocarbon is used as adsorbent to the removal of Cu (II) ions with the initial concentration of 100mg/L. At the equilibrium time of 180min, at the working pH of 5.0, it is noticed that 96.30% removal of Cu (II) ions are observed. The removal process of selected heavy metal ion on the biocarbon matrix is an ion-exchange mechanism and also mainly depends on the physical characteristics of the materials.

Keywords: Biocarbon, toxic pollutants, copper, material characterization.

INTRODUCTION

Water pollution by heavy metals has received wide spread attention for many decades and has been a major cause of concern due to generation of a high toxicological risk for human health, ecosystem, and agriculture. Most of heavy metals are toxic and due to their non- biodegradability and persistence, they tend to accumulate in living organisms causing various diseases and disorders.

Copper is one of the transition element exhibits malleable and ductile properties. It has wide applications in electrical wiring, utensils, pipes, building materials, alloys, electroplating, petroleum refining, and the azo dye manufacturing process [1]. Copper compounds are also used in fungicides, insecticides, and in fertilizers as a nutrient to support growth. Copper is essential for proper functioning of enzymes such as superoxide dismutase, ceruloplasmin, cytochrome-c oxidase, tyrosinase, monoamine oxidase. Copper is found in various parts of the body such as the lungs, liver, kidney, and brain [2]. Adsorption of copper occurs in the upper gastrointestinal tract. Copper is removed from the body through bile, sweat, and urine [3]. Copper enters into humans through food, water and air. Food and water are the major source of copper ingestion into the body. The lethal dose of copper lies between 4 and 400 mg of copper (II) per kg body weight [4]. Copper exposure can lead to headaches, diarrhoea, nausea and vomiting at low doses. Increased doses of copper can result in gastrointestinal bleeding, hepatocellular toxicity, renal failure and oligouria [5].

Copper exists in both free-state and in hydroxyl forms. Among all the forms free copper (II) ion and monohydroxy copper (II) are considered to be highly toxic. The particulate copper is not toxic unless it is solubilized in water or within the fluids of organism [6].

Treatment of wastewater by economical and effective method is very crucial in the era of development and technological advancements. Various organic and inorganic pollutants present in the effluent calls for specific and effective treatment technique. Adsorption is very promising method for removal of various pollutants from wastewater. Low cost of adsorbents, simplicity and high removal efficiency are few advantages of the method. In order to make this method more environment friendly and economical, regeneration of adsorbent is very important aspect. The main aim of the present research work is to use a novel biomaterial for the removal of copper metal from synthetic wastewater. The biomaterial is *Lantana camara*. The elected biomaterial is widely available in agricultural fields.

MATERIALS AND METHODS

Lantana camara, also known as wild sage, is a thorny multi-stemmed, deciduous shrub with an average height of 2m (6ft). *Lantana camara*'s widespread and diverse distribution is a reflection of its wide ecological tolerances. The species occurs in varied habitats ranging from open unshaded regions which include wastelands, rainforest edges, beachfronts, and forests disturbed by activities such as fire or logging [7]. The species also thrive well in disturbed areas which include roadside, railway tracks and canals [8 – 10]. Anthropogenic activity further aggravates the invasion and allows it to spread [11]. The two principal ingredients for successful establishment are its growth under varied climatic conditions and no cap on temperature or rainfall limit. The legendary plant species present in Figure 1.

Preparation of *Lantana camara* biocarbon (LCBC)

Lantana camara plant leaves are collected and washed several times with distilled water to remove adhered impurities from its surface. The biomass was air dried for 48 hours. The dried leaves are grounded in ball mills and the screened homogeneous powder was used for the preparation of biocarbon. The biocarbon was prepared by treating the leaves powder with the concentrated sulphuric acid (Sg 1.84) in a weight ratio of 1:1.8 (biomaterial: acid). The resulting black product was kept in an oven maintained at 150 ± 2°C for 6 hours and washing with distilled water. The obtained carbon was washed with distilled water and then dried in oven at 120 ± 2°C for 4 – 6 hours. The particle size of activated carbon between 90 and 125 μm was used. The resulting biocarbon was preserved and used as an adsorbent.

Batch adsorption studies

Biocarbon is used as adsorbent in this study. In eight numbers of stoppered 250mL capacity bottles 0.5g to 4.0g of adsorbent dose is introduced with the initial concentration 100mg/L of copper metal ions. The suspensions were shaken at room temperature (28 ± 2°C) using a mechanical shaker for a prescribed time at 250 rpm. The solutions were filtered through Whatman 42 filter paper, and the residual concentration of copper metal ion was determined by AAS method. The amount of metal adsorbed (q_e) by biocarbon was calculated from the difference between metal quantity added to the biomass and metal content of the supernatant using

$$q_e = \left(\frac{C_o - C_e}{w} \right) \times V \qquad (1)$$

Where q_e is the metal uptake (mg metal adsorbed per g adsorbent), C_o and C_e is the initial and equilibrium metal concentration in solution (mg/L), V is the volume of the solution (mL), and M is the weight of activated carbon (g).

The percentage of removal of Cu (II) ions was evaluated from the equation:

$$\%\ \text{Removal} = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \qquad (2)$$

The analytical data were analysed and standard deviations of the statistical tests were carried out using programme of analysis of variance (ANOVA) by using SPSS program.

RESULTS AND DISCUSSION

The characterization of biocarbon is very much essential to ascertain the adsorption capacity of adsorbents. The physic-chemical results of the biocarbon are presented in Table1. Characterization of biocarbon is also very important in order to classify for specific uses. The biocarbon produced in this work from the *Lantana camara* plant leaves sample had acceptable properties.

The surface morphology of the biocarbon was studied before and after removal of Cu (II) ions by SEM photographs. Figure.2a and 2b show the SEM of pure LCBC and LCBC (Cu) respectively, in which the surface morphology has been changed appreciably. It confirmed the presence of chemical interactions on the surface of the adsorbent. The micrographs clearly show a number of macro-pores and well defined crystals structures in biocarbon samples. The SEM of LCBC (Cu) showed speciously isolated and irregularly distributed pores, which are thought to be formed due to the increase of effective diffusion surface area resulting from pore formation. It facilitates the adsorption of metal ions [12, 13].

The FTIR spectrum of biocarbon before and after removal of Cu (II) ions are shown in the Figure 3. The vibrating signals in both cases of adsorption of Cu (II) ions were just similar. The adsorption band at 3414 – 3417 cm^{-1} is due to banded –OH groups. The strong band at 2860 – 2925 cm^{-1} could be assigned to the aliphatic C – H group [14]. The adsorption band at 1629 – 1710 cm^{-1} are attributed to C=O and C=C strong stretching vibrations. The peak observed at 1114 – 1161 cm^{-1} corresponds to C–O group present in biocarbon matrix. When compared the two spectra which shows that there was no shift in wavelength. This indicates that, –OH, –CH and C=O groups are likely to participate in Cu (II) ions adsorption. The ion exchange process may be the mechanism involved in the biocarbon and Cu (II) ions interaction. It also suggests that, the biocarbon matrix is not damaged or altered and can be reused with simple washings.

The effect of pH on the removal of Cu (II) ions from synthetic wastewater was investigated by varying the pH of metal solution in the range of 3 – 8 (Figure 4). The adsorption of Cu (II) depends on the pH value of the aqueous solution. It is noticed that, there is a gradual enhancement of the Cu (II) adsorption with the increase of pH from 3 to 5. The Cu (II) removal efficiency increased from 60 to 96.30%. At low pH values, Cu (II) removal were inhibited possibly due to a competition between protons and copper ions on the sorption sites. As the pH value was increased, the negative charge density on LCBC surface increased due to deprotonation of the metal binding sites resulting in an increase of the adsorption of metal ions. The high dependence on the pH for Cu (II) adsorption could be explained on the basis of surface charge density of biocarbon and O – H groups.

The effects of contact time for the sorption of Cu (II) ions onto the surface of LCBC. The kinetics of copper removal by biocarbon presents a shape characterized by a strong increase of the amount of copper sorbed during the first minutes of contact solution (Figure 5). A rapid sorption rate was observed during 120 min of the sorption process and then a considerable increase in the uptake capacity of the biosorbent for Cu (II) ions continued up to 180 min. Thereafter, it remained nearly constant. As an approximation, the removal of copper ions can be said to take place in two distinct steps: a relatively fast followed by a slower rate. This rapid initial uptake is similar to previous reports on the biosorption of heavy metals by different biosorbents [15].

The effect of the adsorbent dose on the equilibrium adsorption of Cu (II) ions from synthetic wastewater onto LCBC was studied and the results are shown in Figure 6. From the results, it is observed that, the adsorption of Cu (II) increased from 45.5 to 96.30% with an increase of the adsorbent dose from 0.5 to 3.5g. This can be described by the more accessibility of surface sites with the increase of the adsorbent dose. Jung et al., [16] attributed the similar behaviour to the fact that the surface complexation is the major mechanism in the sorption process. It is also noted that, further increase of the LCBC dose didn't lead to any significant change of the Cu (II) adsorption. However, the adsorption density decreased is mainly due to the unsaturation of adsorption sites. It could be also endorsed to the accumulation of adsorbent particle, resulted from high sorbent concentration, which would lead to a decrease in the total surface area of the adsorbent and an increase in diffusional path [17].

The influence of initial copper ion concentration to the removal rate was shown in Figure 7. With the increasing concentration from 10 to 100mg/L, removal rate of copper ion was increased to 96.30%. At the level of 75 and 100mg/L, the removal rate is significantly stable. This may be attributed to that sufficient adsorption sites are available at lower concentration, which facilitates the Cu (II) interaction with adsorption sites. However, in the case of higher concentration, adsorption sites of biocarbon are saturated, leading to the stability in the adsorption efficiency [18].

Table 1. Characterization of the *Lantana camara* biocarbon (LCBC).

Sl.No	Parameters	Values
1.	pH	**6.40**
2.	Bulk density (g/mL)	**0.67**
3.	Apparent density (Kg/m^3)	**0.85**
4.	Moisture (%)	**5.92**
5.	Ash (%)	**0.85**
6.	Volatile matter (%)	**12.5**
7.	Yield of biocarbon (%)	**87.5**
8.	Fixed carbon content (%)	**92.5**
9.	Phenol number (mg/g)	**74.5**
10.	Iodine number (mg/g)	**65.0**

11.	Methylene blue index (mL/g)	**40.0**
12.	Surface area (m^2/g)	**328.0**

Figure 1. *Lantana camara* plant.

Figure 2(a). SEM photograph of *Lantana Camara* biocarbon.

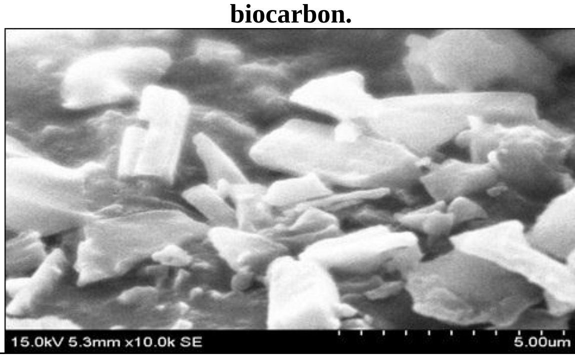


Figure 2(b). SEM photograph of *Lantana Camara* biocarbon after Cu (II) ions removal.

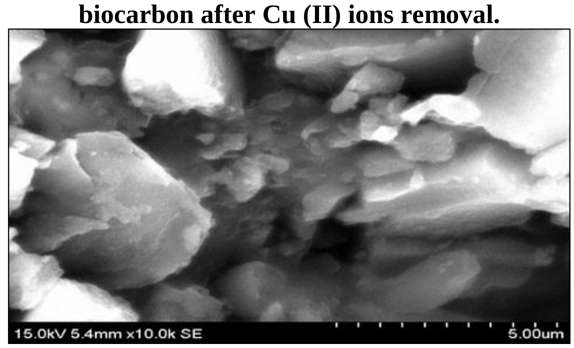


Figure 3. FT – IR spectrum of pure LCBC (A) and (B) is after Cu (II) ions removal.

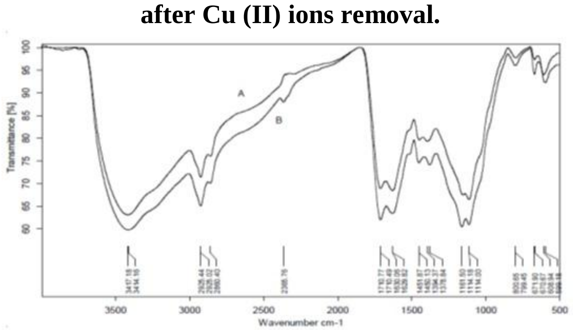


Figure 4. Effect of pH on the removal of Cu (II) ions on LCBC.

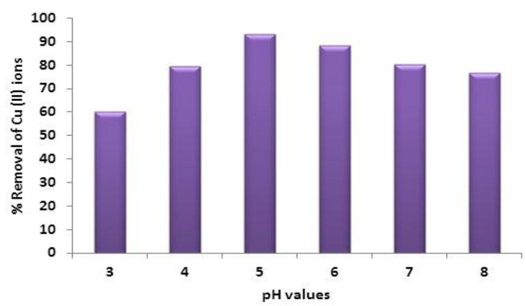


Figure 5. Effect of contact time on the removal of Cu (II) ions.

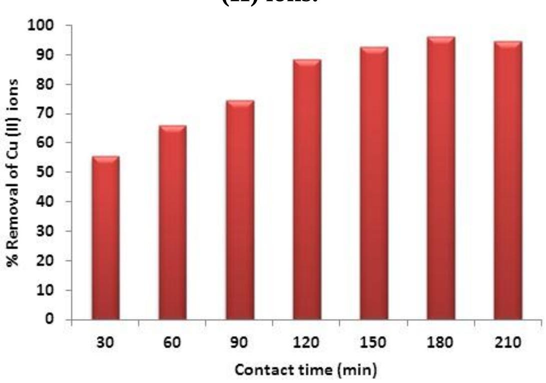


Figure 6. Effect of biocarbon dose on the removal of Cu (II) ions.

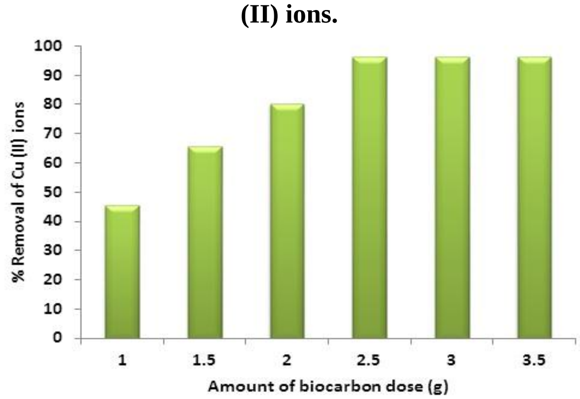
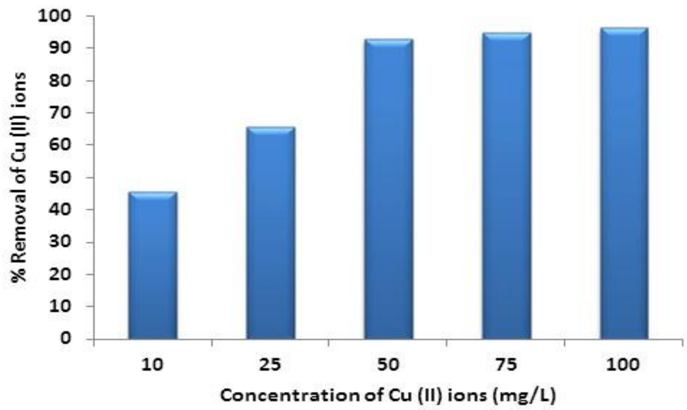


Figure 7. Effect of initial concentration on the removal of Cu (II) ions.



CONCLUSION

Lantana camara biocarbon can be used as an efficient and eco-friendly sorbent for the removal of Cu (II) ions from synthetic wastewater. The sorption capacity of the adsorbent depends upon the pH of the solution, amount of biocarbon dose, concentration of metal ions and contact time. The results from sorption process showed that the maximum adsorption rate was obtained at the initial concentration of 100mg/L Cu (II) ions. The maximum uptake of Cu (II) ions was 96.30% at the biocarbon dose rate of 2.5g/100mL. The optimized contact time was 180min and the operational pH of the solution was 5.0. Hence the adsorbent can be potentially used for removal of Cu (II) from their aqueous solutions.

It could be concluded that biocarbon prepared from the leaves of *Lantana camara* plant in the present study is promising in terms of both economic and environmental aspects and could improve the adsorption economy for the removal of toxic heavy metals like Cu (II) and other hazardous materials from industrial effluents.

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