

REMOVAL OF DIVALENT CALCIUM FROM THE AQUEOUS SOLUTIONS USING EUCALYPTUS CITRIODORA TREE BARK AS A LOW COST BIO-SORBENT

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ABSTRACT

The use of Eucalyptus citriodora Tree Bark (ECTB) as the low-cost biosorbents was examined as a substitute for contemporary costly techniques of removing copper ions from aqueous solutions. Batch adsorption studies were conducted to examine the effects of physico-chemical key parameters such as the stirring rate, initial metal ion concentration, pH, agitation time, and adsorbent dosage on the adsorption of Cu(II) by activated carbon prepared from Eucalyptus citriodora Tree Bark (ECTB) . The optimum results were determined at an initial metal ion concentration of 40 (mg L⁻¹), Stirring Rate = 200 rpm pH=4, Agitation Time – 150 min, and an Adsorbent Dose (3000 mg/100 ml).

Keywords: *Biomaterial, Bioadsorption*

I. INTRODUCTION

Heavy metal pollutions often are generated from many types of industry, such as electroplating, metal plating, batteries, mining, pigments, stabilizers, alloy industries, and sewage sludge, where the main constituents include copper, lead, nickel, chromium, and so on. Adsorption with activated carbon is one of the most effective techniques for the treatment of such heavy metal containing wastewater. International growing demand of this adsorbent, mainly due to their usages in environmental mitigation applications, has led to a search for new, available low-cost feedstock with renewable character.

unlike organic pollutants, heavy metals are non-biodegradable materials and hence are accumulated in living organisms by food chains. Some metals such as Cd, Hg, Ag and Pb can become extremely toxic for the cycle of living beings. The others such as Cu, Zn, Mn, Fe, Ni and Co are essential for plant and animals in little quantities but when present in excess concentrations above certain limits, can be very harmful to living organisms [1]. The main sources of copper pollution are metal cleaning and plating baths, pulp, paper board mills, wood pulp production, the fertilizer industry, etc. The World Health Organization (WHO) recommended a maximum acceptable concentration of Cu(II) in drinking water of 1.5 mg L⁻¹[2]. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. Briefly, any processing or container using copper material may contaminate the product such as food, water or drink [3].

Conventional methods for removing dissolved heavy metal ions include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology and evaporation recovery. However, these technology processes have considerable disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring system, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal [4,5]. Adsorption, an alternative technology for conventional wastewater treatment, has received considerable attention for the development of an efficient, clean and cheap technology. In this study, widely available Delonix *regia* fruit pod is used for the biosorption of Cu(II) ions which is known to be major contaminant at many sites around the world.

II. MATERIALS AND METHODS

2.1 Preparation of activated carbons

The raw material was collected, crushed into small pieces, washed with water and dried under sunlight for two days. Here carbonization is done at 400°C for 3 hours, followed by cooling at room temperature. After that the carbons were washed with double-distilled water to remove the excess acid and dried at 150°C for 12h. These activated carbons which are prepared from tree bark of *Eucalyptus citriodora*

2.2 Preparation of Cu(II) solution Adsorbate

A standard stock solution of cupric sulfate pentahydrate, each milliliter of which contained 4 mg of copper, was made by dissolving 15.7160 grams of the salt in distilled water, adding 1 ml of concentrated sulphuric acid, and accurately diluting to 1 liter. To produce color system varying volumes of the standard copper solution in a 100 ml volumetric flask were just neutralized with 13 M ammonium hydroxide, diluted to the mark with 3M ammonium hydroxide, and thoroughly shaken [6].

2.3 Chemicals and Equipment

All reagents used were of AR grade. Deionized double distilled water was used throughout the experimental studies. ACS reagent grade HCl, NaOH and buffer solutions (E. Merck) were used to adjust the solution pH. An Elico (LI-129) pH meter was used for pH measurements. The pH meter was calibrated using buffer standard solutions of pH 4.0, 7.0 and 9.2. Fourier transform infrared spectrophotometer (multinuclear FT NMR Spectrometer model Avance-II (Bruker)) was used to analyze the organic functional groups of the biosorbent. The metal concentrations in the samples were determined using spectrophotometer. Wide angle X-ray diffraction (WAXD) patterns of powder ECTB sample was recorded on an X-ray diffractometer (Panalytical's X'Pert Pro), by using Cu K α radiation ($\lambda=1.54060 \text{ \AA}$) at 45 kV and 4 mA. Scanning Electron Microscopy (JEOL/EO) was used to study the surface morphology of the biosorbent.

2.4 Batch adsorption experiments

Batch adsorption experiments were carried out by agitating 2 g of the ECTB samples with 100 ml of Copper(II) solutions of desired concentrations at room temperature using an orbital shaker operating at 150 rpm. The effect of initial metal ion concentrations was carried out by shaking 100 ml Copper(II) solutions of desired concentrations (2.00, 4.00, 8.00, 16.00, 24.00, 32.00, 40.00 mg/l) with 2 g of the adsorbent. The sample was then filtered using Whatman No. 42 filter paper and analyzed for the concentration of metal ions remaining in the solution using spectrophotometer.

All the investigations were carried out in duplicate to avoid any discrepancy in experimental results and metal solution controls were kept throughout the experiment to maintain quality control. The percentage of metal and the amount of metal adsorbed by the biomaterial was computed using the equation:

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$\text{Amount adsorbed } (q_e) = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

Where, C_0 = initial concentration of metal solution in mg/l

C_e = equilibrium concentration of metal in mg/l

m = mass of the adsorbent in grams

V = volume of test solution in liters

III. RESULT AND DISCUSSION

3.1. Characterization of the biosorbent

Scanning electron microscope Scanning electron microscope has been widely used to study the morphological features of the biosorbent. Study of the SEM micrographs of ECTB showed in Fig. 1 indicated the presence of asymmetric pores and open pore structure, which may provide high internal surface area and a rough structure on the surface of ECTB, which is favorable for biosorption of Cu(II) from aqua solutions.

3.2 X-ray diffraction

XRD pattern of the ECTB shown in Fig. 2 illustrates the presence of a significant amount of amorphous material due to lignin and tannin in the sample.

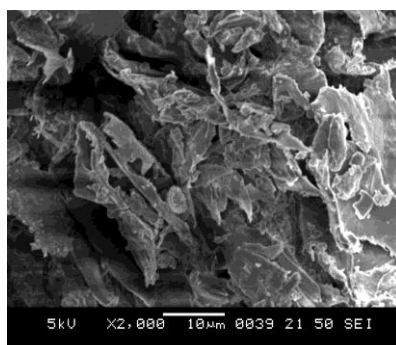
3.3 Infrared spectroscopy

The FTIR spectra of ECTB Fig. 3, showed the presence of many functional groups, indicating the complex nature of ECTB as biosorbent

3.4 Influence of PH

It is well known that pH of the medium is most important factors that influence the biosorption process [3]. The pH level affects the network of negative charge on the surface of the biosorbing cell walls, as well as physicochemistry and hydrolysis of the metal. Percentage removal of the metal ion as a function of pH is shown in the Fig: 4. It has been observed that under highly acidic conditions ($\text{pH} \approx 2.0$) the amount of metal removal was small, while the sorption had been increased with the increase in pH from 3, then decreased in the range 4.0 to 5.0. The lower removal efficiency at low pH is apparently due to the presence of higher concentration of H^+ in the solution which competes with metal ions for the adsorption sites of the biosorbents. With increase in pH, the H^+ concentration decreases leading to increased metal uptake.

Fig 1



3.5 Effect of biosorbent dose

Biosorption of Cu(II) onto ECTB was studied by changing the quantity of sorbent from 0.1 to 5g in the test solution while maintaining the initial concentration 40 mg/ml and contact time 2 h constant. Biosorption of Cu(II) as a function of biomass shown in Fig. 5, indicates the effect of sorbent dose on the Cu(II) biosorption by ECTB. Obviously, the biosorption efficiency increased as the sorbent dose increased, but it remained almost constant when the sorbent dose reached 2g. This may be explained by the following analysis. When sorbent ratio is small, the active sites for binding metal ions on the adsorbent surface is less, so the adsorption efficiency is low; when biosorbent dose increased more metal ions were adsorbed. Thus it results in the increment of adsorption efficiency until saturation.

Fig 2

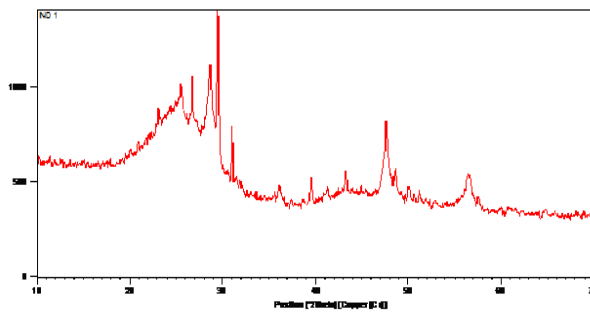


Fig 3

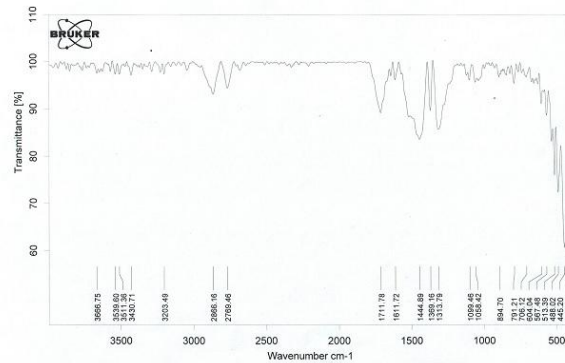


Fig: 4

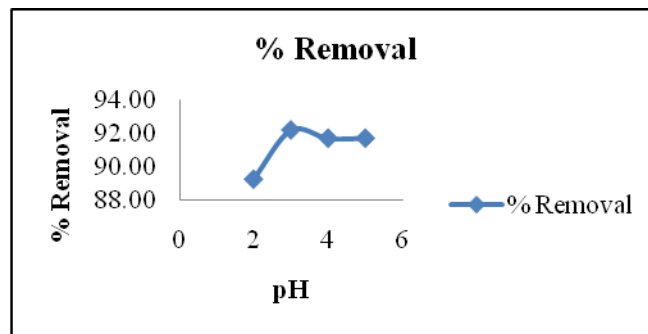
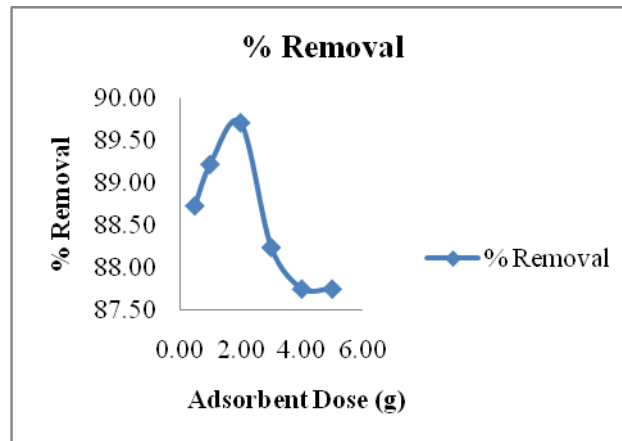


Fig. 5



IV. CONCLUSION

The experimental investigation concluded that ECTB could be used as potential sorbent, for the removal of Cu(II) from aqueous solution. The batch study parameters; pH of solution, biomass concentration were found to be effective on the biosorption processes. The maximum biosorption capacity of Cu(II) was 7.216 mg/g by ECTB. The ECTB biomass can be used as alternative biosorbent for treatment of waste waters containing Cu(II) ions.

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