

Efficient Abatement of Cu (II) ion by Use of A Newly Derived Adsorbent from the Bark of *Diospyros Melanoxylon*

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Abstract

Wide-range application of heavy metals in industrial, medical, agricultural, and domestic places. The pollution of water by heavy metals is a worldwide environmental issue. Overall, of the toxic metal ions, Cu (II) ion is the most toxic metal ion present in industrial wastewater. The adsorption capacity of activated carbon developed from the bark of *Diospyros Melanoxylon* for the removal of Cu (II) ion from the aqueous solution has been investigated. The batch experiment was performed at different parameters such as contact time, pH of adsorbate solution, adsorbent dose, and initial metal ion concentration, which were changes in order to get optimal conditions for Cu (II) ion removal. The result showed that activated carbon developed from *Diospyros Melanoxylon* was an efficient adsorbent for Cu (II) ion removal. The optimum pH was found to be 5 and optimal contact time is established at 80 min with 89% removal of Cu (II) ions from wastewater. Overall findings of experiments suggest that activated carbon developed from *Diospyros Melanoxylon* can be employed as a cost-effective and promising adsorbent for the removal of Cu (II) ions from wastewater.

Keywords: Activated Carbon, Adsorption, bark of *Diospyros Melanoxylon*, Cu (II) ions

1. Introduction

In the recent era, the contamination of natural water bodies with various hazardous wastes containing heavy metal compounds has become a serious environmental issue and a threat to the well-being of living and non-living organisms [1, 2]. Heavy metals like Cu, Cd, Pb, Cr, Ni, Zn and Fe are present in industrial wastewater such as electroplating, metal finishing, and chemical manufacturing [3]. These heavy metals in the industrial wastewater are not

biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which leads to many health issues in animals, plants, and human beings such as cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure and damage in the stomach of the rodent [4, 5, 6]. Therefore, the removal of heavy metals from water and wastewater is very necessary to protect the environment as well as living and non-living things [7]. One of the most toxic heavy metals is copper, and it is used in various areas such as plastics, metal processing industries, building constructions, electric and electronic products, etc. [8]. The contamination of copper in water can be caused by natural sources such as forest fires, eruptions, and windblown dust or man-made sources like mining, metal production, domestic waste, etc. [9, 10]. According to the United States Environmental Protection Agency (USEPA) and World Health Organization (WHO), in drinking water, the exceed limit for the copper concentration should not exceed 1.3 mg/L and 2.0 mg/L, respectively [11, 12].

Various technologies based on physical, chemical and biological processes such as chemical precipitation [13], membrane filtration [14], ion exchange [15], electrolysis [16], adsorption [17] phytoremediation [18] have been used for the removal of Cu(II) ions from wastewater. Among all these technologies, the adsorption technique is a widely used and effective method for the treatment of wastewater [19]. Activated carbon is one of the most widely used nonpolar adsorbents for the adsorption of heavy metal ions from wastewater because of its high porosity, high surface area, and strong adsorption capacity [20, 21].

2. Materials and Methodology

Preparation of adsorbent from bark of *Diospyros melanoxylon*.

Diospyros melanoxylon bark was collected from the nearby local forest area of Chandrapur (M.S.) and it was cut into tiny particles. It was washed with tap water to remove adhering dust, soil, sand and other surface impurities before drying process. It was cleansed with distilled water and dried in sunlight to remove

moisture. Then it was reacted with formalin solution (10%) to prevent the liberation of colour by bark into the solution during the adsorption process. After drying the treated bark was carbonized by using muffle Furnace at about 650-750°C for 5 to 6 hrs to obtained char material. The activation of char material was performed with ZnCl₂ solution. The obtained carbon material was crushed and filtered in 100 mesh sieves. The newly obtained activated carbon material was kept in airtight bottle. It is noted as DMBAC

Characterization of DMBAC

Characterization of DMBAC was performed by SEM (Fig 1) and FTIR (Fig 2)

Adsorption studies

Standard solution was prepared by dilution of stock Cu (II) ion solution. Eradication of Cooper (II) ions using DMBAC was performed using Batch adsorption method. The effect of different parameters like impact of pH, contact time, dose of adsorbent and starting concentration Cu⁺² ion were studied at room temperature taking 50mg/L of initial copper (II) concentration and 6g/l of adsorbent dose. The impact of adsorbent material was examined by varying them 1 to 10g/l. and also concentration was varying from 10 to 100mg/l to examine the effect of initial metal ion concentration with fixed dose of adsorbent of 6g/l at room temperature. The residual concentration of Cu (II) was measured in Atomic Absorption Spectrophotometer (AAS).

Batch Adsorption studies:

Batch Adsorption were performed to investigate the effect of initial adsorbate concentration on the adsorption of Cu (II) ions by activated carbon. Copper ion solutions were prepared by dissolving copper nitrate in double distilled water to obtain a stock solution which was diluted to the required concentrations (50-150mg/l). A known volume (50ml) of Cu (II) ion solution with known concentration (Co) was put in a series of conical flasks with addition of adsorbent. The pH was varied by with dil. HCl solution. The flasks were agitated in a shaker at 100 rpm for 24 Hrs. to attain adsorption equilibrium. After the Contact period the suspensions were filtered using what man

filter paper No. 40. The residual Cu (II) Concentration (Ct) in the filtrate was calculated by using spectrophotometer. The adsorption capacity at any time interval (t) was calculated by using,

Where; C_0 = initial Cu (II) Concentration (mg L^{-1})

C_t = Cu (II) Concentration at time t (mg L^{-1})

V = Volume of Solution (L)

M_s = Mass of adsorbent (g)

The removal percentage was calculated by using

$$\% \text{ Removal} = \frac{C_0 - (C_t) \times V}{M_s} \times 100$$

The adsorbent dosage was maintained at 4 g L^{-1}

3. Results and Discussion

SEM images of DMBAC is shown in fig: 1

Fig.1 represents surface morphology of DMBAC by SEM at a magnification of $10,000\times$ (scale bar $1\mu\text{m}$) at 20kV which shows heterogeneous and rough surface composed of irregularly shaped particles with noticeable agglomeration. The microstructure was characterized by fine granular features and abundant inter particle pores which provides a high surface area for adsorption. The rough and uneven surface provides a large number of potential active surface sites for metal ion adsorption. The bearing of several cavities, cracks, and interconnected pores distributed over the carbon

surface enhancing the adsorption efficiency. Thus the observed morphology confirms that the activated carbon possesses well developed surface suitable for adsorption of Copper (II) metal ion.

FTIR Analysis:

Fig.2 represents FTIR of DMBAC. The broad peak at 3457.44 cm^{-1} is represented to the stretching oscillation of hydroxyl ($-\text{OH}$) groups, indicating the presence of phenolic and alcoholic functional groups as well as adsorbed moisture on the activated carbon surface. These hydroxyl groups play an important role in the Cu (II) ions adsorption through hydrogen bonding and surface interaction. The broad peak 1637.05 cm^{-1} indicate to the stretching oscillation of $-\text{C}=\text{O}$ bonds, suggesting the existence of Carbonyl containing group and aromatic $\text{C}=\text{C}$ bonds which suggest the presence of oxygenated functional group that facilitate heavy metal adsorption. The peak at 1119.11 cm^{-1} is indicate to $\text{C}-\text{O}$ stretching vibrations of alcohol, phenolic, or ether groups. A weak band at 618.76 cm^{-1} is associated with aromatic $\text{C}-\text{H}$ out-of-plane bending or metal-oxygen vibrations. Overall, the FTIR analysis confirms oxygen-containing functional groups, including hydroxyl, carbonyl, phenolic, and ether groups, on the surface of the activated carbon. These functional groups provide active adsorption sites and significantly enhance Copper (II) ions adsorption through electrostatic force of attraction, exchange of ions, and surface complexation process.

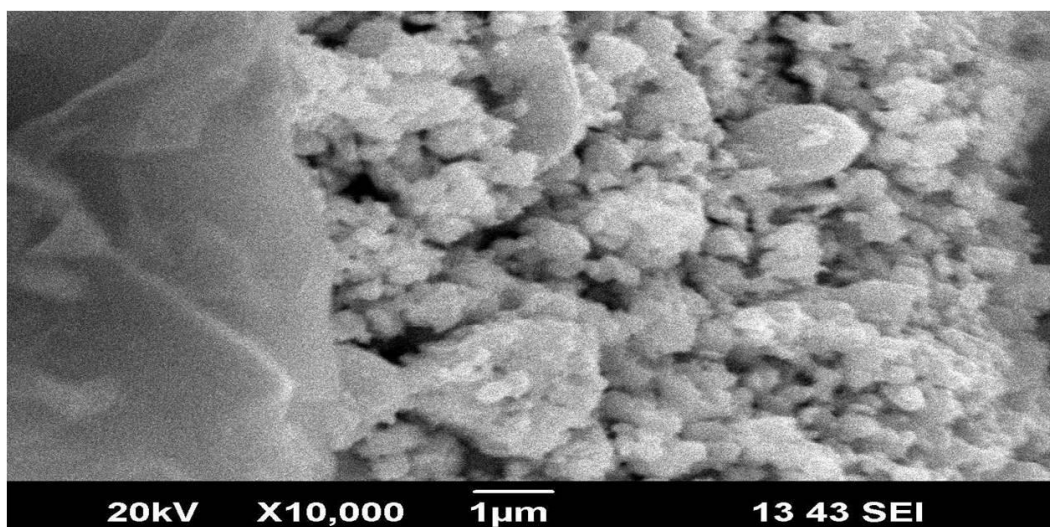


Fig 1: Scanning electron micrographs (SEM) of DMBAC at $10,000\times$

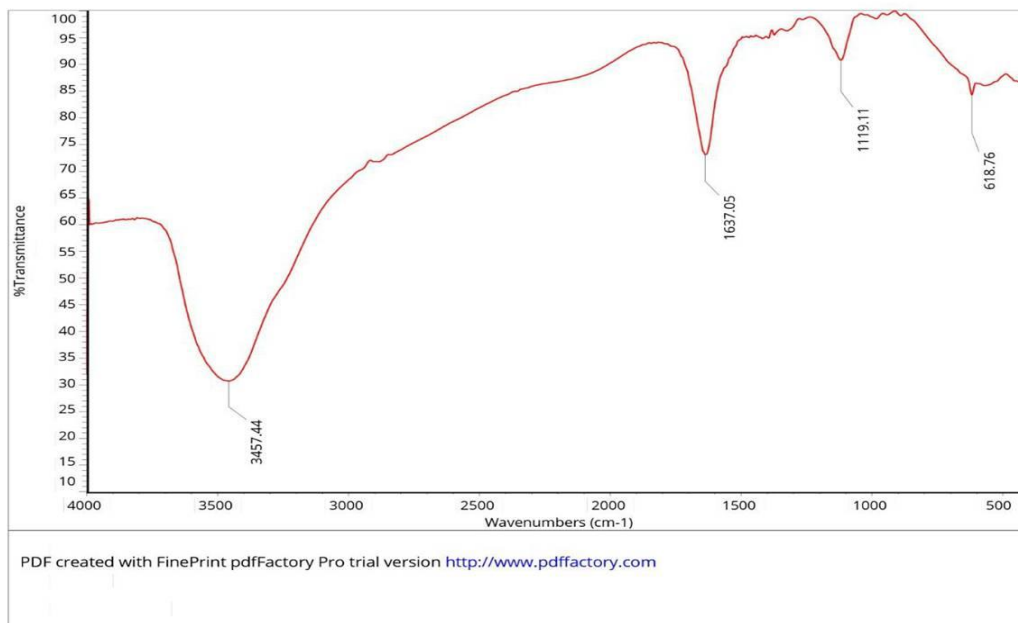


Fig 2: FT-IR spectrum of activated carbon of *Diospyros melanoxylon* bark (DMBAC)

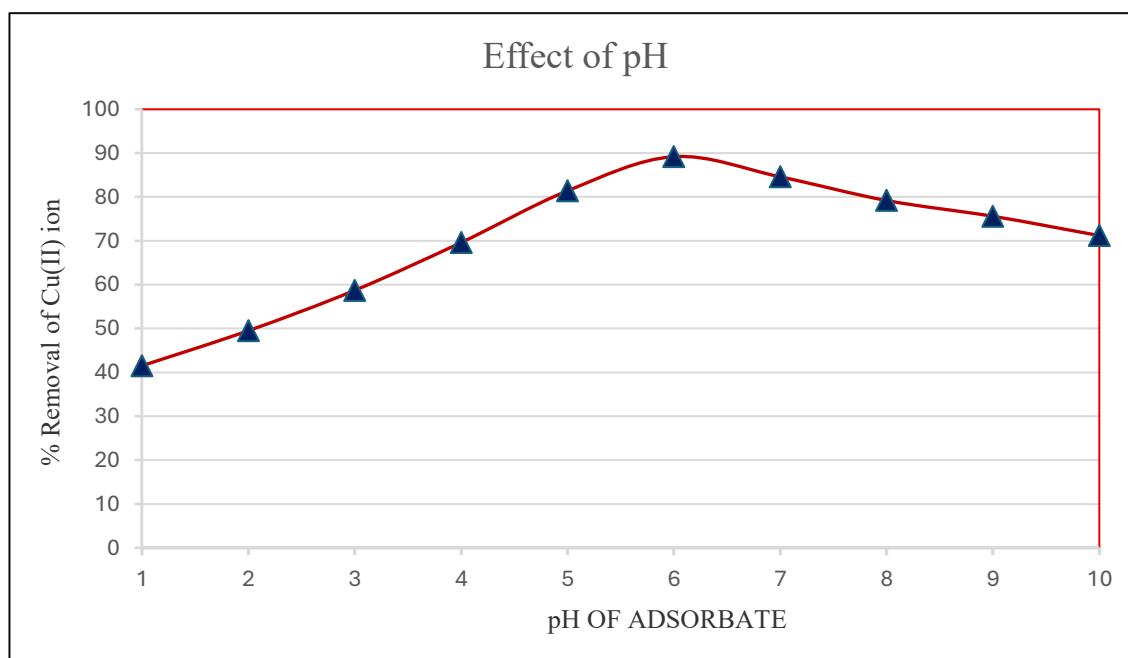


Fig.3. pH effect on Cu(II) adsorption

Effect of pH: The pH impact on excision of Cu (II) ions was studied by changing pH from 1 to 10 at 50mg/l concentration of solution with time 80 min. and 6 g/L DMBAC material is shown in Fig.3. The figure 3 show that % removal of Cu (II) ions increased with the rising of pH from 1.0 to 6.0 and reaching a highest removal 89% at pH 6.0. At lower pH values, the high

concentration of H^+ ion competes with Cu^{2+} ion for the active adsorption sites on surface of DMBAC, which results lower adsorption efficiency. Above pH 6, formation of copper hydroxide causes the adsorption efficiency showed little improvement. Hence at pH 6 was identified as the maximum pH for Cu^{2+} ion removal by DMBAC material.

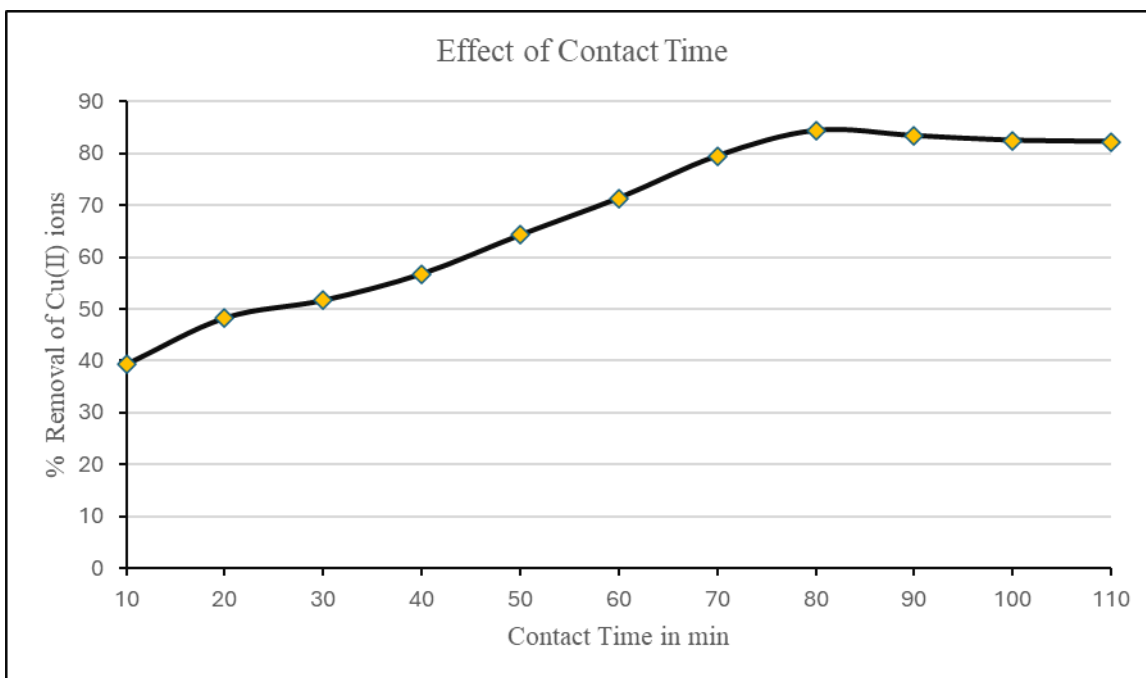


Fig.4. Effect of Contact Time in min on Cu(II) adsorption

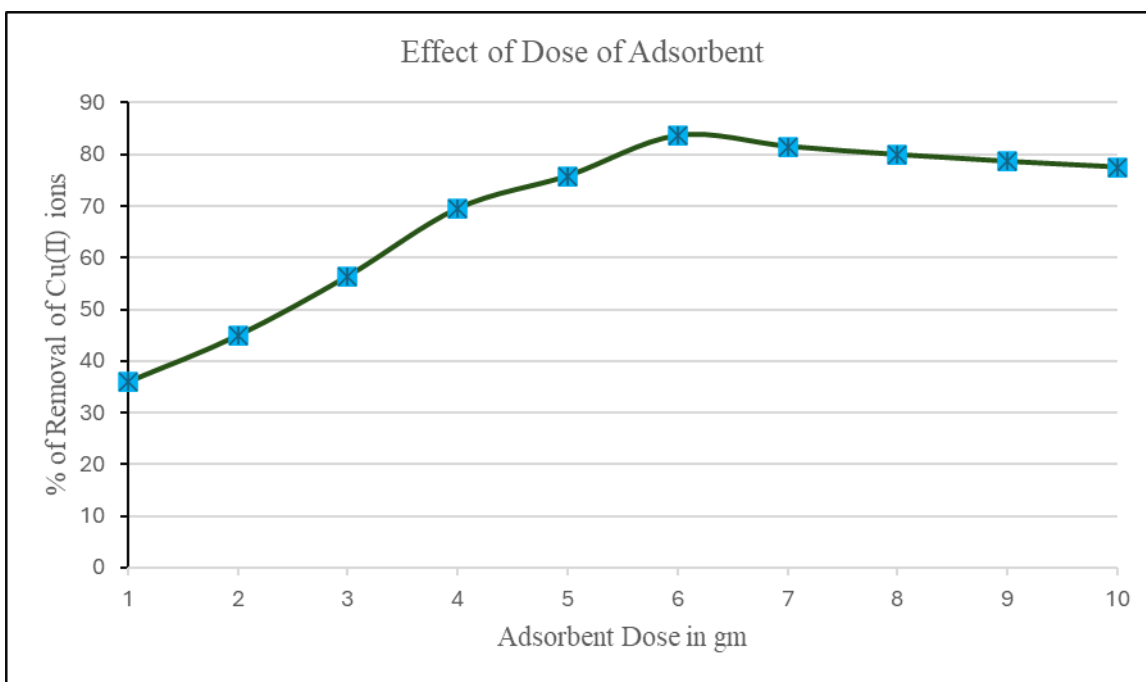


Fig.5. Effect of Dose of Adsorbent on Cu(II) adsorption

Effect of contact time: In treatment of wastewater, the most crucial factor is equilibrium time. The contact time affect on the adsorption of Cu (II) ion on the DMBAC was studied by changing time 10-110 min with the pH 6.0, concentration of adsorbate 50mg/L and 6 gm of DMBAC represented in Fig.4. The Fig. 4 indicates that the abatement rate continuously raise with increasing

the contact time and reached equilibrium after 80 min. achieving a highest value 84.0%. At equilibrium position, most active surface sites are saturated and no increase in metal ions occurs with further increase in contact time. Therefore, an equilibrium contact time of 80 min was found as the optimum value for excision of Copper (II) by DMBAC adsorbent.

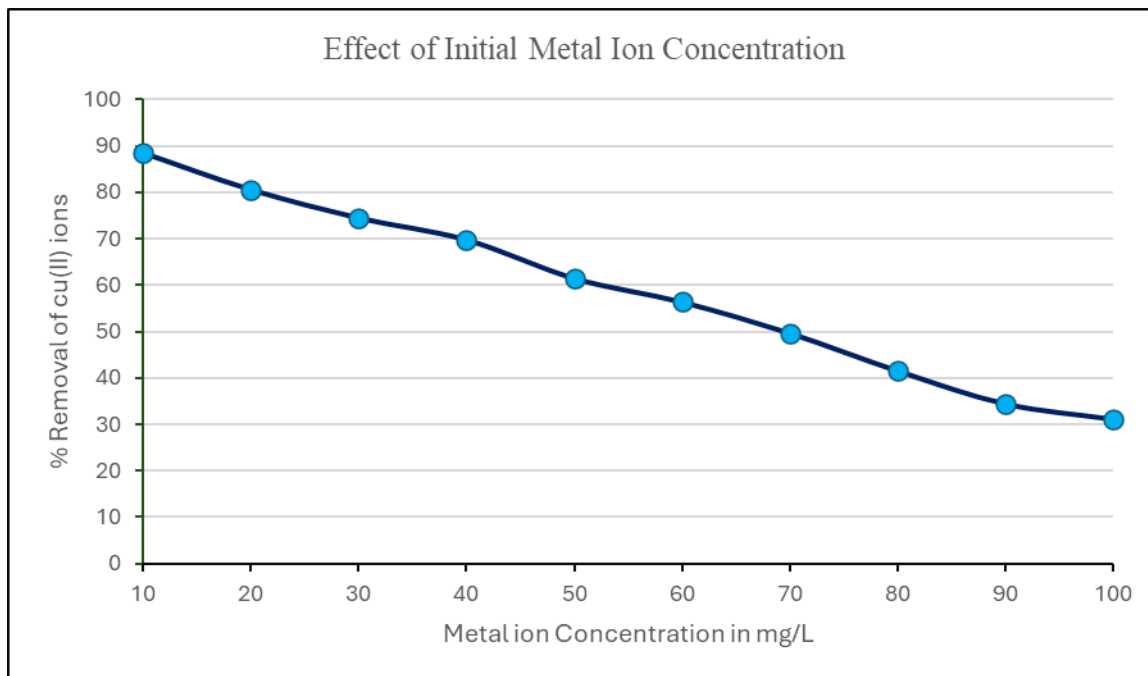


Fig.6. Effect of Initial Cu(II) ion solution

Effect of Adsorbent Dosage: To decide the maximum quantity of sorbent used for maximum elimination of Cu (II), the dose of adsorbent was found out by changing the quantity of DMBAC from 1 to 10 g/L with pH 6, metal ion concentration of 50mg/L, at 100 min explorer time represented in Fig.5. It is indicated that the removal of Copper (II) ions increased significantly with increasing adsorbent dosage from 1 to 6 gL⁻¹, which can show that increase accessible active centres and larger surface area for higher amount of adsorbent. The highest Cu²⁺ ions removal 83.5% was achieved at a sorbent amount of 6 gl⁻¹. This may happen due to aggregation and overlapping of adsorption particles at higher dosages. Therefore, the optimum dosage was found at 6g for elimination of Cu (II) ions.

Effect of initial Concentration: The impact of Cu²⁺ ion concentrations on the efficiency was studied with the altering the concentration from 10 to 100 mg/L; quantity of DMBAC (6 g/L), explorer time (80 min) and pH (6) remain constant as indicated in fig.6. Figure 6 observed that the percentage of adsorption of Cu (II) decreased with raised of initial Cu²⁺ ion concentration. The removal efficiency from 88.5% to 31.8% as the

concentration of Cu (II) raised from 10 to 50 mgL⁻¹. At lower Cu (II) concentration, most Cu (II) ions might bind on the adsorbent solutions as the starting copper (II) ion concentration increased the magnitude relation of unoccupied binding site is obtaining smaller whereas the lower elimination of Cu (II) at high concentration could also presence of the active site on the surface of DMFSAC.

Conclusion:

The activated carbon was synthesized successfully from bark of *Diospyros melanoxylon* and characterized by using FTIR and SEM studies. The newly developed modified activated carbon has highly porous structure and excellent surface area. At pH 6, DMBAC was most effective for removal of Cu (II) with 89% adsorption. This indicates that adsorption was found to be dependent of pH value. Above pH level 6 decreases in Cu (II) ion removal were noticed. With the rise in dose of adsorbent and contact time, the percent removal capacity for Cu (II) ion was also increasing. The maximum percentage removal is 83.5% for 6.0g/L dose and at contact time 80 min.

The newly synthesized activated carbon is successfully developed and can be effectively applied for Cu (II) ion remediation in pollutant accumulation water and utilized for waste water purification.

Conflicts of interest: The authors stated that no conflicts of interest.

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