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Kaolinite-based biochar nano composite material derived from Roystonea Regia for the removal of Copper (Cu^{2+}) from effluent

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ABSTRACT

The growth of industry in recent years has led to a gradual increase in concerns about heavy metal poisoning in water and soil, which, if ignored, might seriously endanger human health. Although copper (Cu) is a naturally occurring element that is widely distributed, exposure to high concentrations can have harmful effects on the body due to bioaccumulation and toxicity. With the help of biochar, an adsorbent made from the Roystonea Regia plant, batch adsorption experiments were utilized in this study to remove copper from aqueous solutions. Bentonite clay modifies the adsorbents surface to boost its reactivity, For Cu the percentage removal efficiency was 72.62%. The equilibrium isotherms were defined by analyzing the experimental data with the help of Thomson model and Yoon Nelson. To ascertain the elemental composition and surface modification of the produced biochars, the surface area was assessed using SEM, EDAX and FTIR techniques both before and after the adsorption. The results of the study demonstrated that surface-modified biochar produced by Roystonea Regia performed effectively as an adsorbent to eliminate Cu^{2+} ions from effluent.

Keywords: Copper; Adsorption; Biochar modification; Adsorption isotherm.

1. INTRODUCTION

Extraction of hazardous heavy metals from streams of industrial waste and water and soil ecosystems has recently attracted significant interest. Because heavy metals are very soluble in water, they can readily infiltrate the food chain. These non-biodegradable species are known to be dangerous and have been linked to a variety of illnesses, disorders, and health issues [1]. Mining activities, metal-plating facilities, power generation facilities, electronic device manufacturing units, and tanneries are frequently found to contain these hazardous metal ions. One of the most widely utilized heavy metals, copper (Cu^{2+}), is extracted from the earth and employed in a variety of industrial processes [2]. Copper (Cu^{2+}) is a key contaminant in printed circuit boards (PCBs), electronic component manufacture, metal plating and printing, paints, and pigments. These are the main industrial processes [3]. When PCB-containing electronic trash (E-waste) is dumped in a landfill, it creates leachate that is highly concentrated in heavy metals, particularly Cu^{2+}. Experimental evidence has demonstrated that heavy metal intoxication can cause fatal consequences for human health, such as impairment of the liver, kidneys, and central nervous system. Furthermore, these hazardous compounds have the potential to cause ecotoxicity and bioaccumulation in the food chain when they are discharged into the environment [4]. The adsorption process is perhaps one of the more often used methods for extracting Cu^{2+} metal ions from aqueous solutions due to its simplicity, low cost, and high removal efficiency. As such, emphasis has been placed on using low-cost materials as sorbents for this purpose. Since they are affordable and effective at removing trace amounts of heavy metal ions from aqueous solutions, As an alternative to more costly treatment techniques, low-cost biosorbents like as biomass, clay materials, agricultural wastes, and wastes from seafood processing could be used [5]. The functional groups of the biochar adsorbent can provide binding sites for the removal of metal ions from aqueous solutions. Biochar made from plant materials is an emerging and environmentally friendly method of removing heavy metal ions from aqueous solutions. The adsorption process is accelerated when synthetic materials are used

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to modify the adsorbent surface, increasing the adsorption capacity [6]. In order to determine the adsorption capacity of biochar as an adsorbent, synthetic chemicals are used to make nano composites. These nanoparticles displayed better adsorption adeptness, particularly their larger apparent range and more vigorous positions for interface with metallic sorts. Adsorbents with certain efficient clusters included have been developed to improve adsorption capacity [7]. The purpose of the current work is to prepare kaolinite nanoparticles and surface-modified biochar from Roystonea Regia for use as adsorbent surfaces. Because of its significant adsorption capability, distinct structural features, chemical and mechanical stability, and abundance in nature, kaolinite is an excellent support material for the removal of Cu^{2+} ions. Furthermore, kaolinite has been investigated as an adsorbent, photocatalyst, and catalyst supporting material [8]. One starts by increasing the adsorption capacity of the adsorbent by looking at its surface area. We examined the investigative statistics and determined the equilibrium kinetics by Yoon Nelson and Thomas models. The surface area of the adsorbent should be examined using the SEM (scanning electron microscope), EDAX (energy dispersive X-ray analysis) and FTIR (Fourier-transform infrared spectroscopy) techniques in order to identify the presence of Cu^{2+} and surface modification.

2. MATERIALS AND METHODS

2.1. Preparation of adsorption capacity biochar

This Roystonea Regia is burned for 3 hours at 560°C, and the resulting powdered biochar is milled to a size of 0.6–2.5 mm. Sieve analysis is used to determine the final size of the Roystonea Regia biochar particle particles. Because Roystonea Regia produces biochar with high carbon (C) content and low hydrogen to carbon (H/C) ratio [9], Better adsorption capacities are possessed by the Roystonea Regia adsorption when it comes to the electrostatic adsorption process's removal of Cu^{2+}. The highest amount of phosphate removed from aqueous solution is also found in digested Roystonea Regia because of the large amount of colloidal and nano-sized periclase on its surface area [10]. After the biochar product naturally cooled down to the point where the entire sample passed through a 150-mesh sieve, it was retained on a 100-mesh filter and then ground into powder. Techniques for treating acidic soils further altered Roystonea Regia chemically. First, for around 24 hours, a single amount of biochar and two sections of HCl were combined in a china dish [11]. After the allotted time, the biochar is mixed 1:1 with kaolin and dried for 3hr at 70°C in a hot air oven.

2.2. Synthetic Cu^{2+} preparation

Analytical grade compounds were all that were used. Distilled water was used to dissolve analytical grade Copper (II) sulfate in order to produce stock solutions with 500 mg/L of metal ions [12]. This was made by dissolving 2.5g of copper (II) sulfate in distilled water, it was mixed with kaolinite materials in the ratio of 1:4 and shaken for three hours to ensure that the copper (II) solution was distributed evenly.

2.3. Spectrophotometry analysis

Weighed volumes of the adsorbent were swirled in 50 ml of Cu^{2+} at suitable pH, contact time, starting concentration, and adsorbent dose for Cu^{2+} solution for 6 hours at a speed of 300 rpm in order to perform the batch adsorption experiments at room temperature [13]. Several 500 ml flasks were used for these studies. The amount of adsorbent that was first added to each flask was calculated. After shaking, samples were taken and filtered through membrane filter paper with a 100 µm pore size. Using a UV-visible spectrophotometer the Cu^{2+} concentration of the solutions was ascertained. The pH of the solution was adjusted using H_2SO_4 solutions. In each experiment, this was conducted twice [14]. The following formula was used to determine how much dye was adsorbed per unit mass of resin.

$$qe = (F0 - Fe)V/(m) \tag{1}$$

Where, V (ml) was the volume of solution and m(g) was the weight of adsorbent.

Fo, and Fe (mg/L) were the initial and equilibrium, qe (mg/g) was the adsorbent capacity.

2.4. Equilibrium study

2.4.1. Thomson model

Using the Thomson model, the relationship between the progress of internal and exterior adsorption was discovered. The Thomson model can be stated using an equation.

$$\ln\left\{\frac{fo}{ft}-1\right\}=\frac{qTH\ pe\ W-kTH\ \mathrm{Co}\ t}{Q} \tag{2}$$

kTH-interception point and slope of the plot, Co-inlet concentration, t-ion concentration at time (mg/L), W- mass of the adsorbent (g), pe-adsorption capacity, Q is the inlet flow rate (ml/min), qTH-Thomson rate constant (ml/min.mg), Squeezing ln (fo/ft–1) and Co/Ct is the ratio of intake and outflow against time yielded the values respectively.

2.4.2. Yoon Nelson model

The Yoon-Nelson Model is less complicated and doesn't need strong proof of the adsorbate. The shortest time needed for a 50% adsorbate breakthrough is revealed by this model, This also shows how the likelihood of the adsorbate and the potential for adsorbate revolution on the adsorbent are related to the chance of adsorption decreasing for each adsorbate component [15]. The linearized equation of the model, represented as Eq:, is typical for a system with a single element.

$$\ln\frac{ct}{Co-Ct}=\mathrm{Kyt}-\tau\mathrm{ky} \tag{3}$$

kyt (min^{-1}) at rate constant, and linear plot ky, 50% adsorbate breakthrough, intercept and slope of the ln [ct/c0-ct].

2.5. Material characterization

An electron microscope equipped with an APEXTM and EDS software was used to perform SEM analysis. The image illustrates how the presence of particles with varying sizes and a homogeneous shape describe this sample. The SEM apparatus was used to determine the elemental composition of Na-MNC [16]. Before being put through the SEM testing, every sample was coated in gold and placed on an aluminum stub. FTIR of the Jasco FTIR-6600 was used to identify the type of surface species. The detector used to study the adsorption the DLaTGS detector was used. After mixing the samples with Cu and drying them at 150°C, infrared light was applied. As soon as the pellets were prepared, they were examined in the mid-infrared band in natural illumination [17]. The spectra were generated by averaging 50 photos at wavelengths ranging from 5000 to 700 cm^{-1}. A nitrogen adsorption device was used to measure the adsorption-desorption isotherms at a liquid nitrogen temperature of 90°C.

3. RESULT AND DISCUSSION

3.1. Adsorption study

The relationship between the initial concentrations of Cu^{2+}, the concentration of the adsorbent as shown in Figure 1, and the % removal capability has been studied. At various starting Cu^{2+} concentrations (fi) of 110.60 mg/L, the adsorption of Cu^{2+} was conducted; the contact period was 70 minutes, and the pH was 7. At a concentration of 65.28 mg/L, the initial adsorbent concentration of 10 mg/L had a percentage removal

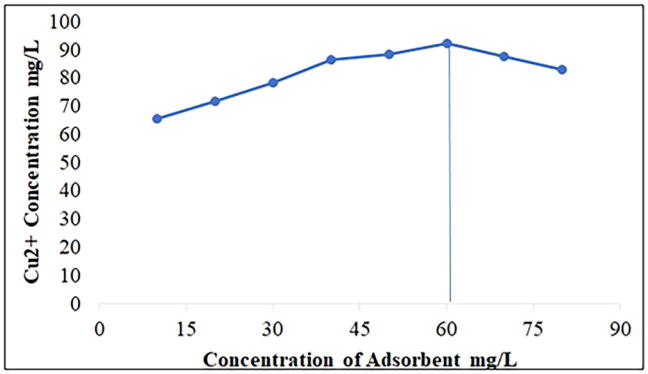

Figure 1: Adsorption study of Cu^{2+} concentrations.

Table 1: Adsorption study of Cu^{2+} concentrations.

CONCENTRATION OF ADSORBENT MG/L	F_0 MG/L	F_E MG/L	REMOVAL EFFICIENCY %
10	110.60	65.28	59.02
20	110.60	71.54	64.68
30	110.60	78.32	70.81
40	110.60	86.55	78.25
50	110.60	88.27	79.81
60	110.60	92.11	83.28
70	110.60	87.63	79.23
80	110.60	82.81	74.87

Table 2: pH difference study in Cu^{2+} removal adsorption.

PH	F_0 MG/L	F_E MG/L	REMOVAL EFFICIENCY %
6	110.60	89.26	80.70
7	110.60	92.03	83.20
8	110.60	91.14	82.40
9	110.60	88.37	79.90

efficacy of 59.02%. At 71.54 mg/L and 78.32 mg/L of adsorbent, the removal percentage was 64.68% and 70.81%, respectively, for the ensuing adsorbent attentiveness of 20 mg/L. The next adsorbent had a elimination of 78.25% in the range of 40 mg/L with a concentration of 86.55 mg/L; in the range of 50 mg/L and 60 mg/L, it reached maximum optimum level of 79.81 and 83.28% with concentrations of 88.27 mg/L and 92.11 mg/L; in the range of 70 mg/L and 80 mg/L adsorbent, the concentration was dragged to 87.63 and 82.81 mg/L with percentages of 79.23 and 74.87. This study established that raising the meditation at the idyllic adsorbent level enhanced the removal efficiency [18], as indicated in Table 1.

3.2. pH variation study

In this method, the correlation between pH and Cu^{2+} removal efficiency was examined. The sample concentration was 110.60 mg/L, the pH was changed to 6, and the absorbance showed an 80.70% removal efficiency percentage at 89.26 mg/L. The HCl used to adjust the pH. The elimination efficiency for pH 7 had an abrupt drop of roughly 83.20%, which is the optimal concentration of 92.03 mg/L. The pH 8 reached 82.40% removal efficiency in the following level, with a meditation of 91.14 mg/L; the pH 9 range reached 79.90% removal percentage in the range of 88.37 mg/L in the fourth level [19]. The full pH variation investigation showed that the Cu^{2+} effectiveness, as shown in the Table 2, decreased with increasing pH and changing techniques.

3.3. Kinetic study

3.3.1. Thomson model

The Thomson model is used to calibrate the titration of adsorbent from 10 mg/L to 80 mg/L in the experimental inquiry. It was observed that the inflow concentration (fi) was consistently kept at 110.60 mg/L. The kTH value was influenced by the removal efficiency, and the Thomson rate constant also contributed to variations in the kTH. From 0.136 to 0.510 mL/min.mg, the kTH decreased. The fluctuation in the range was seen even while the qe remained within the range of 1.172 to 1.151 mg/g. This could be due to the inflow concentration's stronger driving force [20]. Table 3 provides an explanation of R^2 values of 0.903 and 0.986, respectively.

3.3.2. Yoon Nelson model

The compatibility of the Yoon-Nelson model with variations in adsorbent concentration was verified using the regression coefficient values. With an R^2 value of 0.9674 for 60 mg/L, 0.9137 for 10 mg/L, 0.9371 for 20 mg/L, 0.9390 for 30 mg/L, and 0.9512 for 40 mg/L of adsorbent, results indicated that Cu^{2+} had a stronger adsorption break through. The rate constant value, which peaked at 60 mg/L, fell within the range of 3.24. The value of

Table 3: Thomson model of adsorption study.

ADSORBENT CONCENTRATION (mg/L)	10	20	30	40	50	60	70	80
qe (mg/g)	1.172	1.024	0.953	0.641	1.324	1.417	1.002	1.151
k_{TH} (mL/min.mg)	0.136	0.007	0.521	0.583	0.591	0.604	0.573	0.510
R^2	0.903	0.931	0.948	0.950	0.963	0.986	0.975	0.951

Table 4: Yoon Nelson model of adsorption study.

ADSORBENT CONCENTRATION (mg/L)	F_0 MG/L	KY(MIN^{-1})	τ(HR)	R^2
10	110.60	0.414	2.04	0.9137
20	110.60	0.427	2.11	0.9371
30	110.60	0.491	2.36	0.9390
40	110.60	0.530	2.53	0.9512
50	110.60	0.542	3.01	0.9601
60	110.60	0.577	3.24	0.9674
70	110.60	0.542	2.96	0.9593
80	110.60	0.506	2.90	0.9017

Ky(min^{-1}) peaks at 60 mg/L within the range of 0.577. This stated that the kinetic values of Cu^{2+} adsorption in various adsorbent ranges [21], which were described in Table 4, correspondingly, largely determined the experimental results.

3.4. Characterisation

3.4.1. SEM analysis

The surface structure of the bioadsorbent in terms of adsorbing the Cu^{2+} ion has been determined using SEM measurements. Figure 2 (Before adsorption) provides modest superficial characteristics about raw Cu^{2+} retention, with relatively smooth pits and fissures with slight irregularities. According to the SEM analysis, the pyrolysis process caused pore production on Roystonea Regia, which was demonstrated by the expected surface of the adsorbent modified by Kaolinite. Huge porous structure with enhanced surface characteristics Figure 2 (after adsorption), However, the SEM analysis of the biochar adsorbent revealed relatively poor structural elucidation, which limited its ability to adsorb Cu^{2+} ions due to less activation by the reagent [22]. The Roystonea Regia adsorbent sample that had been chemically treated showed significant pore development and expansion in the SEM analysis. This was caused by the activation of HCL acid and the evaporation of the adsorbent. SEM reports indicate that Roystonea Regia adsorbents have a strong surface at tributes, suggesting that Cu^{2+} ions are a good fit for them.

3.4.2. FTIR analysis

The FTIR pictures of the adsorbent nanoparticles made of Roystonea Regia Biochar are shown in Figure 3. The Cu^{2+} ion nanoparticles have a porous surface and spherical form, as illustrated in Figure 3. The generated surface area exhibited short nanorods in its shape. Figure 3's FTIR spectra of the Cu^{2+} adsorbent demonstrated the appearance of the surface-modified adsorbent in vibrational modes in the relevant to presence in a polymer matrix and verifies the findings of FTIR pictures. The faint absorption peaks at 2881.65 and 1049.28 cm, respectively, indicate broadening and winding vibrations of the OH-bond and show that coordinated water and a few adsorptions can exist simultaneously [23]. The adsorbent peak at 727 cm may be associated with the H−O, whilst the bands at 528 cm and 437 cm are thought to be associated with the distortion vibration and the C=C widening quivering. The C−O bond is indicated by the broad band between 1049.28 and 2881.65 that is induced by vibrational stretch.

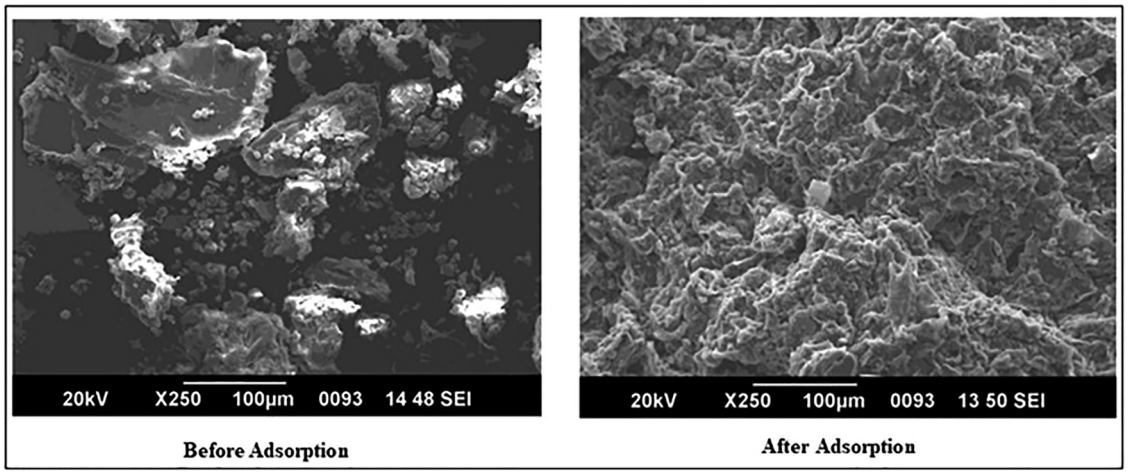

Figure 2: SEM Analysis of Roystonea Regia before and after adsorption.

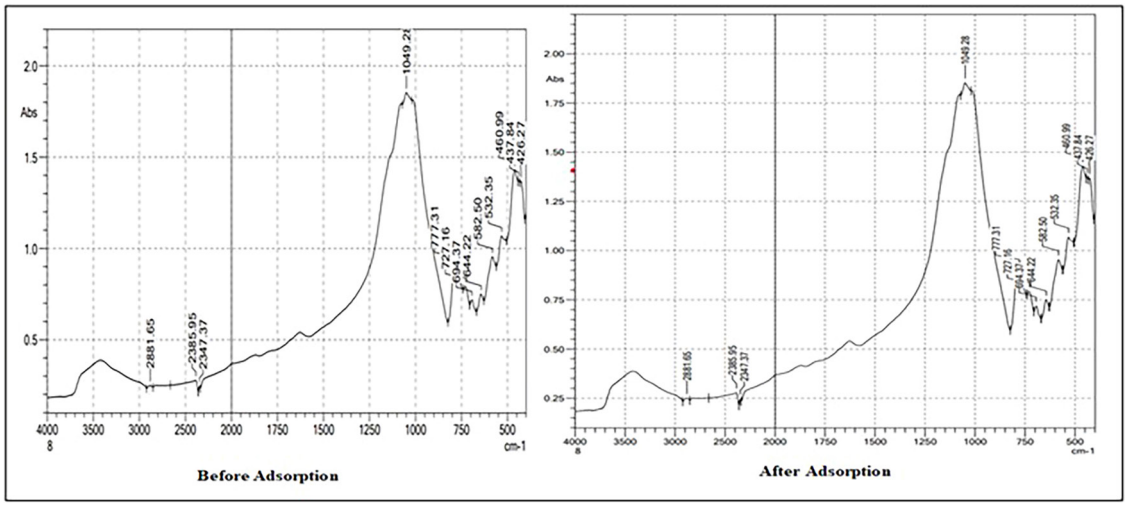

Figure 3: FTIR study of roystonea regia before and after adsorption.

4. CONCLUSION

According to this research, utilizing the Roystonea Regia surface coated with kaolin to remove Cu^{2+} from synthetic effluent was an effective method. This work evaluated a low-cost alternative adsorbent for the removal of Cu^{2+} from aqueous solution: bio-char, a by-product. As amount of adsorbent is increased, the removal percentage rises as well. However, once the adsorption capacity of the biochar adsorbent reaches its optimal level of maximum 79.81% and 83.28%, it begins to decline. Adsorption isotherm results indicate that the Cu^{2+} adsorption profile was best modeled by both Yoon Nelson and Thomson models. For a concentration of 60 mg/L, the Thomson model's R^2 was 0.986, nearly matching the Yoon-Nelson model's regression value of 0.9674. The kinetic test shows that the biosorption equilibrium for Cu^{2+} was attained between 50 and 60 mg/L. These models also did the greatest job of describing the adsorption behavior of Cu^{2+} ions. The sorption capacity of the adsorbent was characterized by SEM and FTIR analysis, and the outcomes showed that the synthetic surface area had a flat absorbing surface area. In order to trap the Cu^{2+} ions, the surface-modified adsorbent manifested in vibrational modes. According to the findings, Roystonea Regia is regarded as a low-cost, efficient, and environmentally safe technique for eliminating Cu^{2+} metal ions from aqueous effluent.

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