From Waste to Resource: Assessing the Biosorption Efficiency of Citric Acid-Modified Activated Carbon from Corn (*Zea Mays*) Husks in Aqueous Copper (II) Ion Solutions

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ABSTRACT

The global focus on cost-effective and sustainable adsorbents, specifically activated carbon from corn husk wastes, addresses environmental waste disposal issues. This economical solution efficiently removes heavy metal ions and promotes the use of agricultural biomass residue in wastewater treatment. In this study, unmodified and modified activated carbon produced from corn husk waste was investigated for the removal of Cu (II) ions in an aqueous solution. The activated carbon was modified with citric acid, resulting in citric acid corn husk activated carbon (CA-CHAC). Several batch adsorption experiments were carried out for both adsorbents to examine the influences of various factors, including pH, adsorbent dose, and contact time. Additionally, the adsorption system was fitted to isotherm and kinetic adsorption models to characterize its adsorption behavior. Results from adsorption studies showed that both the unmodified (CHAC) and citric acid-modified activated carbon (CA-CHAC) adsorbents achieve their optimum adsorption for Cu(II) at pH=7, with a dosage of 5 mg, and contact times of 45 minutes for CHAC and 30 minutes for CA-CHAC. The outcomes additionally demonstrated that the fundamental mechanism of both adsorbents is most effectively described by both the Langmuir isotherm model and the pseudo-second-order model, signifying that the adsorption system adheres to chemisorption. Maximum removal of Cu (II) ions using CHAC and CA-CHAC was obtained with 69.52% and 82.22% average removal, respectively. Additionally, the maximum adsorption capacities recorded were 77.58 mg/g for CHAC and 88.10 mg/g for CA-CHAC. The findings of this study indicate that corn husk-activated carbon modified with citric acid (CA-CHAC) has the potential to effectively adsorb Cu (II) ions.

Keywords: Activated carbon, adsorption, citric acid modification, copper, *Zea mays* husks

INTRODUCTION

In recent years, industrial and agricultural operations have grown increasingly as a result of the rising demand for food and other basic resources from a growing population. Industries based on agriculture produce a significant amount of waste due to ineffective or inconsistently used disposal, utilization, and management practices. Improper disposal of agricultural wastes not only results in environmental pollution but also wastes a significant amount of biomass resources. The most common significant staple crop that produces a large amount of agricultural waste is corn. In any part of the country, tremendous amounts of corn husk waste are generated after harvest. These kinds of lignocellulosic materials currently have no established commercial value and are often simply considered as agricultural waste [1].

In addition to the significant increase in agricultural waste, the rapid development of society and the economy exposes waters to severe contamination. These contaminants mostly refer to harmful heavy metals that are persistent, tend to bio-accumulate, and are toxic substances. Heavy metals can enter into water bodies through agricultural runoff, industrial effluents, household uses, and commercial applications [2]. According to the World Health Organization (WHO) [3], ten metal ions are identified as a major public health concern including arsenic (As), mercury (Hg), cadmium (Cd), lead (Pb), and copper (Cu). Copper is found in many parts of the world. Copper can enter the environment through discharges from the mining of copper and other metals, as well as from industries that produce or utilize copper metal or copper compounds. Long-term

exposure to copper dust can irritate the eyes, nose, and mouth, as well as result in headaches, nausea, and diarrhea.

Recent studies have focused on a particular method for heavy metal ions removal, such as electrocoagulation (EC), adsorption using synthetic and natural adsorbents, magnetic field implementation, advanced oxidation processes, and membranes [4]. Among these methods, adsorption is the most efficient as the other techniques have inherent limitations such as the generation of a large amount of sludge, low efficiency, sensitive operating conditions, and costly disposal [5]. The adsorption method is emerging as a potentially preferred alternative for the removal of heavy metals because it provides flexibility in design, high-quality treated effluent, and is reversible and the adsorbent can be regenerated [6].

Several adsorbents such as activated carbon, silica, and graphene can be used in the purification of water [7]. Activated carbon is an efficient adsorbent for the removal of a wide variety of organic and inorganic contaminants present in the aquatic environment. From agricultural wastes, activated carbon can be produced from a variety of plant parts, including root, stem, bark, flower, leaf, and fruit peel, husk, shell, and stone. The surface chemistry of activated carbon derived from biomass shows its potential as a natural sorbent for a wide range of chemical compounds and ions due to its porous structure and effective specific surface area. Several studies were able to investigate the adsorption capacity of activated carbon in removing dyes [8]-[10], organic and inorganic pollutants [11]-[13], oil from spills [14], and heavy metal ions [15]-[17].

Several studies have been conducted and are being conducted in order to enhance the adsorption capabilities of activated carbon. Chemical surface modification procedures have been reported and used as a successful way for producing effective adsorbent to remove various contaminants in order to increase the adsorption capacity of an adsorbent. The surface functional groups of activated carbon are modified by chemical treatments which also increase the material's capacity and selectivity for adsorption. Furthermore, acid treatment improves chelation ability with heavy metal species and increases acidic surface morphology. In general, chemically modified activated carbon offers greater adsorption capabilities than its unmodified form due to poor adsorption capacity and the tendency of desorption of contaminants during its sorption process [18].

In this study, corn husks were used as the precursor material for the production of activated carbon. The corn husk was then subjected to surface modification with the use of a chelating agent such as citric acid. The general aim of this study was to assess the biosorption efficiency of Citric acid-modified activated carbon (CA-CHAC) produced from corn husks for the removal of Cu (II) ions. Specifically, this study is guided with the following specific objectives, to wit: (1) synthesize activated carbon from corn husk wastes; (2) modify the synthesized corn husk activated carbon (CHAC) with citric acid for the surface modification; (3) characterize the citric acid-modified corn husk activated carbon (CA-CHAC) via Fourier transform infrared (FT-IR) analysis; (4) determine optimum parameters such as pH effect, adsorbent dosage, and contact time for efficient adsorption of Cu (II) ions; (5) determine the % removal of Cu (II) ions using the unmodified (CHAC) and citric-acid modified activated carbon (CA-CHAC) as adsorbents to remove Cu (II) ions at optimum conditions; (6) describe the adsorption behavior of CHAC and CA-CHAC using adsorption studies, in particular kinetics and isotherms for the removal of Cu (II) ions using UV/Vis spectrophotometry analysis after various adsorption experiments.

METHODOLOGY

Preparation of Corn Husk Activated Carbon (CHAC)

Corn husk samples were freshly collected in the sampling area via purposive sampling during its harvesting period. The samples were placed in a clean and dry sack to prevent contamination before analysis. Plant samples were initially surface-cleaned using tap water and were further cleaned using distilled water. The sample husks were initially air-dried at ambient temperature and were further oven-dried. The dried corn husk samples were cut into smaller pieces, homogenized, labeled, and stored in a plastic container. Through chemical activation and carbonization, the biomass from the corn husk was converted into activated carbon through the procedure reported by Kalavathy & Miranda (2010) [19]. Dried corn husk was mixed with the phosphoric acid at an impregnation ratio of 1:2 (weight of corn husk: weight of phosphoric acid) and soaked for 24 hrs so that the reagents were fully adsorbed onto the raw material. The mixture was dried at 110°C for 1.5 hrs and was

then transferred to a sealed ceramic container. The dried mixture was then activated in a muffle furnace at 400°C for 30 min. carbonization time. After cooling, the carbon was repeatedly washed with DI water until pH neutral and dried at 110°C for 2 hrs. Finally, the produced activated carbon was grounded and sieved to a particle size of less than 0.30 mm. The carbonized corn husk was then stored at room temperature for further adsorption experiments.

Surface Modification of Activated Carbon

Surface modification of the activated carbon was done by following a study conducted by Chen et al., (2003) [20]. The activated carbon was reacted with a 1.0 M citric acid solution at a ratio of 4 g activated carbon to 25 mL citric acid solution. It was then shaken for 30 min before being dried at 50°C overnight. The citric acid-modified activated carbon was washed with DI water until no color change could be observed when a potassium permanganate solution was added to the washed liquid. The modified activated carbon was then dried at 110°C for 2 hrs. The obtained citric acid-treated residue was considered as modified corn husk activated carbon (CA-CHAC) and was used for adsorption studies.

Characterization of the Adsorbents

The CA-CHAC was subjected to characterization and identification of functional groups. For comparison, a sample of the CHAC was also subject to characterization. The samples were examined using a Fourier transform infrared (FT-IR) spectrometer (Shimadzu IR Affinity-1S) using a transmission accessory.

Adsorption Experiments for Cu (II) Adsorption

A solution of 100 ppm Cu(II) ion solution was prepared by dissolving 0.268 g of copper (II) chloride dihydrate (CuCl$_2 \cdot$ 2 H$_2$O) in deionized water. Biosorption conditions were established by batch experiment, adding the adsorbent in the Cu (II) ion solution at different parameters at optimum conditions. These parameters were the effect of pH (3-7), adsorbent dose (2-6 mg), and contact time (15-75 min). Each experiment was carried out in 25 mL Cu (II) ion solution at a known initial concentration of 25 mg/L. The pH adjustments were carried out either by the addition of H$_2$SO$_4$ or NaOH ions. The isotherm and kinetic studies were performed by varying the initial concentration and contact time from 5 mg/L to 45 mg/L and from 15 min to 75 min, respectively.

ANALYTICAL METHODS

After all the batch adsorption experiments, the resulting mixture was filtered using a filter paper (Whatman No.1) and the remaining Cu(II) in the filtrates was added with concentrated 25% v/v Ammonia (NH$_3$) solution to form colored-complex and was then analyzed spectrophotometrically (Biobase BK-D560 Double Beam Scanning UV/VIS Spectrophotometer) at the wavelength λ = 615 nm. The Cu (II) ions adsorption capacity (q$_e$) and removal efficiency (%) were calculated according to the following equations:

$$q_e = \frac{(c_o - c_e)V}{m}$$

$$\%Removal = \frac{(c_o - c_e)}{c_o} x100$$

where C$_0$ is the initial metal concentration (mg L^{-1}), C$_e$ is the final metal concentration (mg L^{-1}), V is the volume of the metal solution (L) and m is the mass of the activated carbon sorbents (g).

The adsorption mechanism of Cu (II) ions onto the surface of the activated carbons was described using two (2) well-known isotherm models, namely the Langmuir and Freundlich isotherm models. The Langmuir isotherm model was initially developed for gas-solid interaction but is also used for various adsorbents. It is an empirical model based on kinetic principles; that is, the surface rates of adsorption and desorption are equal with zero accumulation at equilibrium conditions [21]. The Langmuir equation is mathematically defined in the following linear form:

$$\frac{1}{q_e} = \frac{1}{K_L q_{max}} \cdot \frac{1}{c_e} + \frac{1}{q_{max}}$$

where q_{max} is described as the maximum adsorption capacity (mg/g) and K_L is the energy affinity (L/mg). These two parameters of the Langmuir isotherm can be calculated using the slope and the intercept of the plot $1/q_e$ vs $1/C_e$ from the equation.

The Freundlich isotherm model is an empirical model that can be used for multilayer adsorption on heterogeneous sites. It assumes that the adsorption heat distribution and affinities toward the heterogeneous surface are nonuniform [22]. This describes multilayer adsorption and assumes exponential decay in the energy distribution of adsorbed sites [23]. The linear form of the Freundlich equation can be expressed in the following equation:

$$\log q_e = \log K_F + \frac{1}{n} log c_e$$

where $1/n$ is described as the adsorption intensity and K_F is related to adsorption capacity (L/mg). Moreover, the slope and intercept of the plot $\log q_e$ vs $\log C_e$ from the equation can also be used to calculate both of these parameters.

Moreover, adsorption kinetic data of activated carbon towards the removal of Cu (II) ions was examined by plotting data fit both the pseudo-first-order equation and pseudo-second-order equation. Adsorption kinetics is a curve (or line) that describes the rate of retention or release of a solute from an aqueous environment to a solid phase interface at a given adsorbent dose, temperature, flow rate, and pH [24]. The pseudo-first-order equation is based on the assumption that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time, which is generally applicable over the initial stage of an adsorption process [25]. Pseudo-first-order model can be expressed using a linearized equation:

$$\ln(q_e - q_t) = - k_1 t + \ln q_e$$

where q_e and q_t are the amount of Cu (II) ions adsorbed (mg/g) at the equilibrium and at a time, respectively while k_1 describes the rate constant of the adsorption (min^{-1}).

The pseudo-second-order equation is based on the assumption that the rate-limiting step is chemical sorption or chemisorption and predicts the behavior over the whole range of adsorption. In this condition, the adsorption rate is dependent on adsorption capacity not on the concentration of adsorbate [25]. The linear equation for the pseudo-second-order model is represented as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

still q_e and q_t are the amount of Cu (II) ions adsorbed (mg/g) at the equilibrium and at a time, respectively while k_2 describes the rate constant of the adsorption ($g/mg^{-1}\ min^{-1}$).

RESULTS AND DISCUSSION

Adsorbent Structural Characterization

Fourier transform infrared (FT-IR) spectroscopy was utilized to distinguish between CHAC and CA-CHAC, showcasing the characteristic absorptions of their respective functional groups.

The spectra of the adsorbents were measured in the range of 400–4000 cm^{-1}. The distinctive absorptions of CHAC (highlighted in blue) and CA-CHAC (highlighted in red) are depicted in Figure 1, while Table 1 provides a summary of the significant peaks alongside their corresponding functional groups.
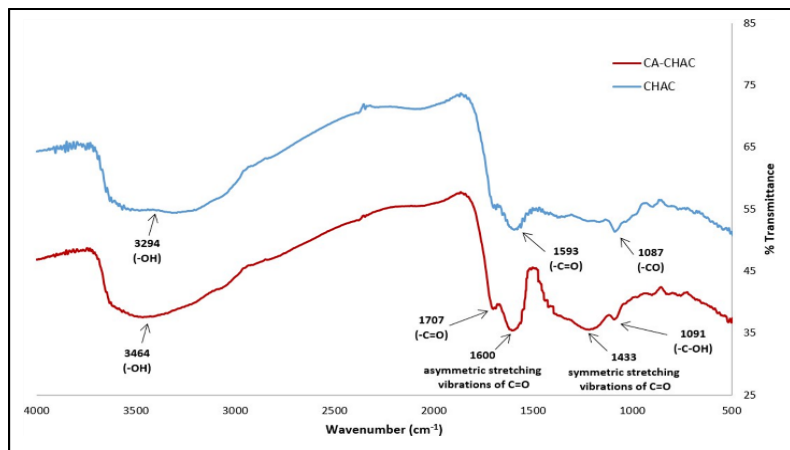

Figure1. Infrared Spectra of Activated Carbon derived from Corn Husk Wastes.

(Blue – CHAC, Red – CA-CHAC)

Table1. Characterization of CHAC and CA-CHAC using FTIR Spectral Data Analysis.

Adsorbent	Band Positions (cm^{-1})	Assigned Functional Group
CHAC	3200-3550	O-H stretching
	1600-1700	C=O stretching
	1087-1124	C-O stretching
CA-CHAC	3200-3550	O-H stretching
	1400-1700	C=O stretching
	1087-1124	C-OH stretching

In Figure 1, it could be observed some increase of stretching vibration of CA-CHAC at wavelength ranges of 1087-1124 cm^{-1}, 1200-1300 cm^{-1}, 1600-1700 cm^{-1}, and 3200-3550 cm^{-1}. The presence of wide broadband at 3464 cm^{-1} in the infrared (IR) spectrum of CA-CHAC is significant as it indicates the occurrence of O–H stretching vibrations. In this context, these vibrations are associated with the cellulose, pectin, hemicellulose, and lignin components found in various natural materials [24]. A wide range of frequencies are observed in the OH stretching vibrations, suggesting the existence of both free hydroxyl groups and bonded OH bands of carboxylic acids [27]. The detected peak at 1707 cm^{-1} corresponds to the stretching vibration of a bond attributed to nonionic carboxyl groups (-COOH, -COOCH$_3$), and it could be associated with carboxylic acids or their respective esters. The peaks observed at 1600 cm^{-1} and 1433 cm^{-1} are a result of the asymmetric and symmetric stretching vibrations of C=O within ionic carboxylic groups (-COO$^-$) respectively. The peaks observed at 1091 cm^{-1} are likely attributed to the stretching vibration of C–OH present in both alcoholic groups and carboxylic acids. Upon comparing the spectra of CHAC and CA-CHAC, noticeable variations in the positions of the absorbance peaks were observed. This suggests that the modification involving citric acid resulted in CA-CHAC exhibiting a broader range of oxygen functional groups on its surface compared to its initial state.

Batch Adsorption Studies

To analyze the adsorption capabilities of both the CHAC and CA-CHAC, three parameters—specifically (1) pH, (2) adsorbent dosage, and (3) contact time—were utilized as experimental parameters in the batch adsorption experiments. All other variables such as temperature (298 K), initial concentration (25 ppm), volume (25 mL), and the rate of mechanical stirring (300 rpm) remain consistent unless specified otherwise.

Effect of pH

The absorption of Cu (II) relies on both the characteristics of the adsorbent surface and the distribution of Cu (II) species within the solution, primarily influenced by the pH level of the system. In this study, pH was varied at a range of 3 to 7. The effect of pH on the adsorption of Cu (II) ions using CHAC and CA-CHAC is shown in Figure 2. The result showed that the percentage removal of Cu (II) using CHAC and CA-CHAC increased at a steady rate as pH increased up to 7, attaining a maximum value of 58.10% and 77.78%, respectively. Moreover, the maximum adsorption capacities achieved were 134.49 mg/g and 180.10 mg/g. At pH>7 adsorption of Cu (II) ions observed was smaller. The removal percentage recorded at pH 8 was 25.71% for CHAC and 44.76% for CA-CHAC, with corresponding maximum adsorption capacities of 78.99 mg/g and 123.57 mg/g, respectively. Increasing pH decreases the concentration of H^+ therefore reducing the competition between metal ions and protons for adsorption sites on the particle surface [28]. Additionally, increasing pH promotes metal ion precipitation from the solution in the form of hydroxides, which is another factor that could improve metal ion adsorption. The formation of soluble hydroxyl complexes causes the decrease in the adsorption which was observed after pH 7. Following pH 7, three species are present: $Cu(OH)^+$, $Cu(OH)_2$, and Cu^{2+} in relatively small amounts which significantly affects the adsorption of metal. Similar findings were demonstrated in prior research that utilized activated carbon for copper ion removal [29], [30].
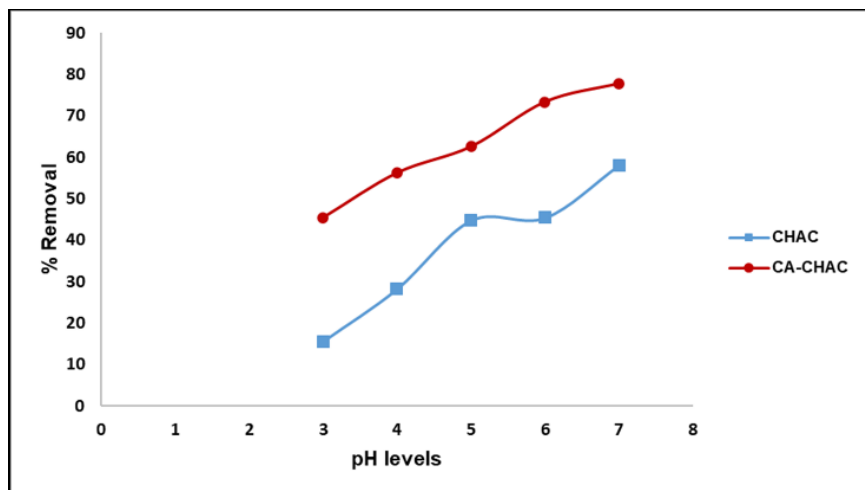

Figure 2. Effect of pH Towards Adsorption of Cu (II) by CHAC and CA-CHAC.

Effect of Adsorbent Dosage

The significance of the adsorbent dosage lies in its direct impact on the effectiveness of adsorption. Varying the amount of adsorbent alters the capacity to capture substances from a solution, thus influencing the overall efficiency of the process. For this study, the effect of activated carbon dosage towards adsorption was varied from 2 mg to 6 mg with 1 mg intervals. Figure 3 shows the effect of adsorbent dosage for both CHAC and CA-CHAC on the Cu (II) removal. Based on the graphical representation, it shows a clear trend where the percentage of copper removal reaches its optimum at an adsorbent dosage of 5 mg. This optimal point is explained by the presence of a limited number of adsorbing species. Adsorbing species are substances capable of attracting and holding onto copper ions. Despite the limited number of these species, there are a relatively larger number of surface sites on the adsorbent material at higher adsorbent dosages. Furthermore, it is reasonable to assume that an increased adsorbent dosage could lead to a higher availability of exchangeable sites for metal ions. Maximum removal of Cu (II) ions using CHAC and CA-CHAC was obtained at 5 mg with 65.08% and 79.68% average removal, respectively. Additionally, the maximum adsorption capacities reached 75.86 mg/g and 96.40 mg/g. However, after 5 mg a decrease in the removal percentage was observed. These results may be due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles [31]. Additionally, this shift indicates a potential point of saturation or an optimal dosage, suggesting that beyond this point, further increases in the adsorbent dosage do not proportionally enhance the removal efficiency, resulting in a decline in the removal percentage.
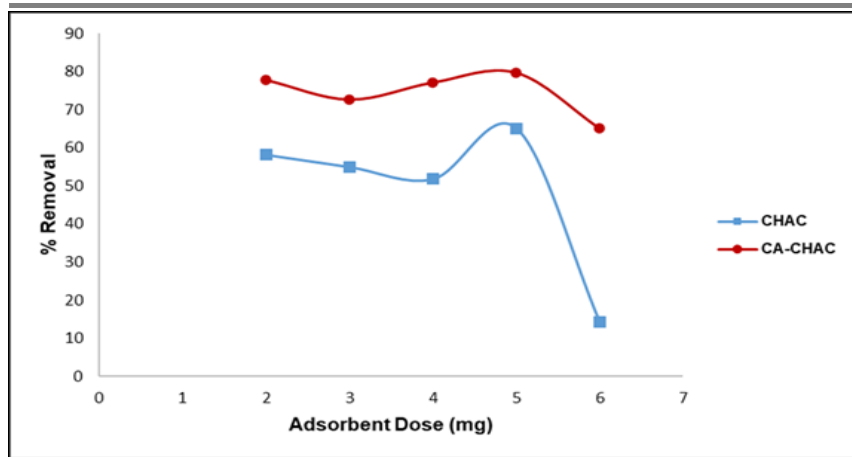
Figure 3. Effect of Adsorbent Dosage towards Adsorption of Cu (II) by CHAC and CA-CHAC.

Effect of Contact Time

To determine the total adsorptive capacity of an activated carbon sample, it needs to reach adsorption equilibrium. In an adsorption system, the duration of contact time significantly influences the adsorption kinetics, regardless of the other experimental parameters. Adsorption time was varied for this study at intervals of 15, 30, 45, 60, and 75 minutes. As shown in Figure 4, in the initial 45 minutes for CHAC and 30 minutes for CA-CHAC, there is a substantial and noticeable rise in the adsorption of Cu (II). This period marks a rapid uptake of copper ions onto the adsorbent material, indicating a significant enhancement in the adsorption process within these specific time frames. During the initial phase of the adsorption process, numerous adsorption sites are accessible, resulting in a higher availability for Cu (II) ions to adhere to these sites. Consequently, this availability facilitates a faster rate of adsorption, as there is less competition among the adsorbate molecules for binding sites on the adsorbent surface. Figure 18 also illustrates a noticeable increase in the percentage removal of Cu (II) for CHAC and CA-CHAC with 69.52% and 82.22% average removal, respectively. Moreover, the maximum adsorption capacities recorded were 77.58 mg/g and 88.10 mg/g. However, as the contact time continues, there is only a marginal increase in copper removal, indicating site saturation and limited capacity for further adsorption.
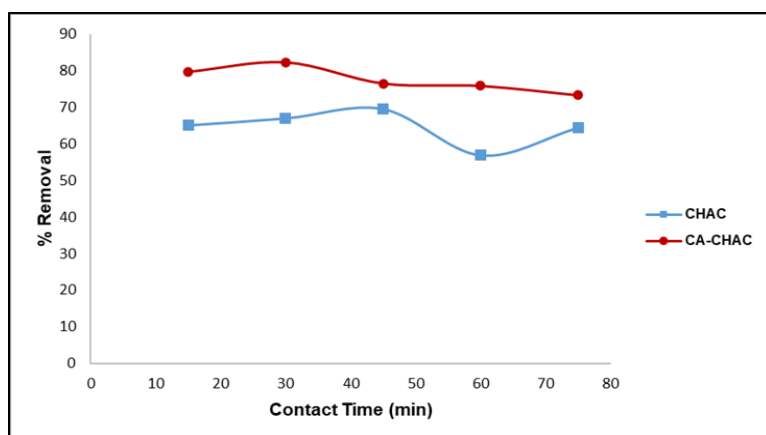

Figure 4. Effect of Contact Time towards Adsorption of Cu (II) by CHAC and CA-CHAC.

Comparative Analysis of Adsorbents

To delve deeper into the collected data concerning the adsorption characteristics of both CHAC and CA-CHAC, the data from the adsorption experiments involving different pH levels, varying adsorbent dosages, and different durations of contact time underwent the following test: Two-way Analysis of Variance (ANOVA) and t-tests at the significance level of 0.05. These tests aimed to compare the adsorption behaviors of CHAC and CA-CHAC. The information obtained from the experiment measuring adsorption performance provided slopes depicting the rate of Cu (II) ion removal under different conditions, allowing for comparative

analysis. Table 2 and Table 3 present the results of the Two-way ANOVA and t-test analysis conducted on both CHAC and CA-CHAC under three different parameters (pH, adsorbent dosage, and contact time). Furthermore, Table 4 illustrates the comparison of percent removal between both adsorbents under optimal conditions.

Table 2. Two-way Analysis of Variance (ANOVA) for CHAC vs CA-CHAC over % Removal of Cu (II) ions.

Conditions of CHAC vs CA-CHAC	F value	F critical
Varying pH	6.225	
Varying Adsorbent dosage	61.43	2.87
Varying Contact Time	6.03	

Table 3. t-Test Analysis for CHAC vs CA-CHAC over % Removal of Cu (II) ions.

Conditions of CHAC vs CA-CHAC	P value	P critical
Varying pH	5.47×10^{-5}	
Varying Adsorbent dosage	1.04×10^{-4}	0.05
Varying Contact Time	1.40×10^{-8}	

Table 4. t-Test Analysis for CHAC vs CA-CHAC over % Removal of Cu (II) ions at optimum conditions.

Conditions of CHAC vs CA-CHAC	P value	P critical
pH	1.34×10^{-3}	
Adsorbent dosage	1.42×10^{-2}	0.05
Contact Time	2.13×10^{-3}	

Table 2 presents the outcomes of the two-way ANOVA analysis, indicating a significant difference observed among the adsorbent types as well as among the pH levels, adsorbent dosages, and various contact times based on the calculated f-values obtained which were greater than the f-critical value, signifying statistical significance. Meanwhile, as shown in Table 3 and Table 4, in all conditions, CA-CHAC showed a significant difference over CHAC (p value < p crit) in terms of percent removal towards Cu(II) ions across varying parameters and under the attained optimal conditions. The statement suggests that the positive P-values obtained from the analysis indicate a significant positive difference between the modified and unmodified forms of activated carbon derived from corn husk concerning the percent removal of Cu (II) ions. These positive differences in the results of the tests imply that the modification process applied to the activated carbon, involving the introduction of functional groups from citric acid, led to an increase in the percentage of Cu (II) ion removal from the aqueous solution via the adsorption process. Moreover, it further reinforces the idea that the addition of these functional groups derived from citric acid has the potential to enhance the adsorption performance of the activated carbon towards the removal of heavy metal ions like Cu (II) from water. This outcome strengthens the evidence supporting the effectiveness of the modification technique in improving the material's capability to adsorb and remove heavy metal contaminants from aqueous solutions.

Adsorption Isotherm and Kinetics

The adsorption behavior of CHAC and CA-CHAC concerning Cu (II) ions were graphically analyzed and fitted to both Langmuir and Freundlich isotherms. This analysis aimed to determine the nature of the interaction between the adsorbent (CHAC and CA-CHAC) and the adsorbate (Cu (II) ions)–whether it follows a chemisorption monolayer adsorption or a multilayer adsorption mechanism. The Langmuir model typically suggests monolayer adsorption where adsorbate molecules form a single layer on the adsorbent surface, while the Freundlich model implies a multilayer adsorption phenomenon where adsorbate molecules form multiple layers or exhibit heterogeneous adsorption behavior. The comparison between these models helps ascertain the most suitable representation of the adsorption behavior in this specific system.

The graphs illustrating the linearized data for Langmuir (Fig. 5a and 5b) and Freundlich (Fig. 5c and 5d) isotherms indicate that the Langmuir isotherm exhibited a better fit compared to the Freundlich isotherm for both CHAC and CA-CHAC. This was supported by the obtained R-squared values of 0.9903 and 0.9888 (Table 5), respectively, suggesting that the Langmuir model more accurately represents the adsorption behavior of these materials than the Freundlich model (Table 6). This implies that the adsorption process likely involves a monolayer of adsorbate molecules forming on the surface of the adsorbent material. Adsorption takes place at specific homogeneous sites on the adsorbent. Once a pollutant occupies a site, no further adsorption can take place in that site. All sites are identical and energetically equivalent [32].

Table 5. Langmuir Parameters of CHAC and CA-CHAC towards the Adsorption of Cu (II) ions.

Adsorbent	Langmuir Parameters			
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2
CHAC	612.52	0.01465	0.7319	0.9903
CA-CHAC	643.92	0.02717	0.5955	0.9888

Table 6. Freundlich Parameters of CHAC and CA-CHAC towards the Adsorption of Cu (II) ions.

Adsorbent	Freundlich Parameters		
	K_f	$1/n$	R^2
CHAC	9.4544	0.8727	0.9652
CA-CHAC	20.176	0.7854	0.9345

Furthermore, the process involved calculating the maximum adsorption capacity and Langmuir constant by analyzing the linear plots obtained from the relationship between $1/C_e$ and $1/q_e$. The maximum monolayer saturation capacity of two materials, CHAC and CA-CHAC, was determined through this analysis. Specifically, it was found to be 612.52 mg/g for CHAC and 643.92 mg/g for CA-CHAC based on theoretical computations. These theoretical calculations revealed that the capacity for adsorbing molecules in a single layer on the surface of CA-CHAC is notably higher compared to CHAC, indicating a greater potential adsorption capability for CA-CHAC. In addition, the equilibrium factor (R_L) of the Langmuir isotherm shows a favorable value (CHAC: 0.7319, CA-CHAC: 0.5955). The value of R_L indicates the type of isotherm to be either unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$), or irreversible ($R_L=0$). When analyzing the R_L values obtained for CHAC (0.7319) and CA-CHAC (0.5955), both values fall well below 1. This indicates that the adsorption behavior for both materials is favorable according to the Langmuir isotherm model. A favorable R_L value ($0 < R_L < 1$) signifies that the adsorption process is favorable and likely to occur efficiently. In this context, lower R_L values (CA-CHAC) suggest a higher favorability of the adsorption process.
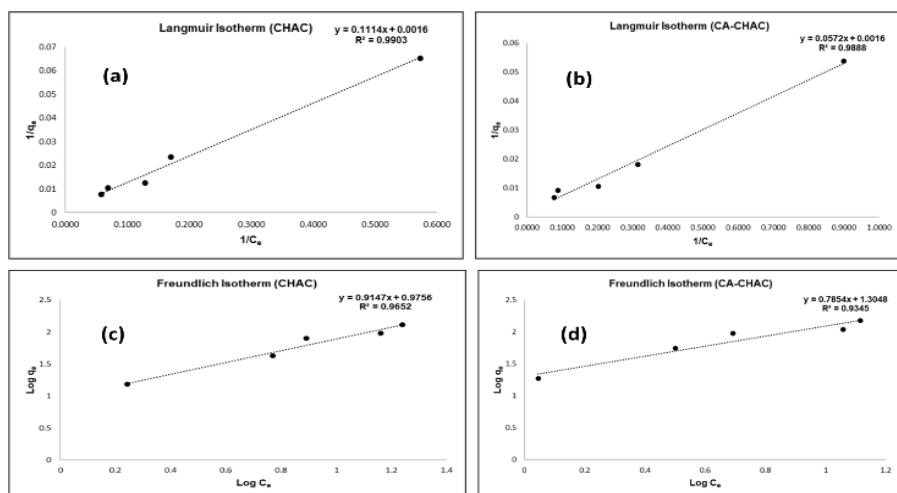

Figure 5. Adsorption isotherm of Cu (II) ions. (a) Langmuir adsorption isotherm using CHAC; (b) Langmuir adsorption isotherm using CA-CHAC; (c) Freundlich adsorption isotherm using CHAC; and (d) Freundlich

adsorption isotherm using CA-CHAC.

The study of adsorption kinetics is important because the rate of adsorption (which is one of the criteria for the efficiency of adsorbent) and also the mechanism of adsorption can be concluded from kinetic studies [33]. The data gathered from variation in contact time was used to investigate the kinetic behavior of CHAC and CA-CHAC towards the removal of Cu (II) ions (Table 7).

Table 7. Comparison of Adsorption Kinetics of Both CHAC and CA-CHAC.

Adsorbent	Pseudo-First Order			Pseudo-Second Order		
	q_1 (mg/g)	K_1	R^2	q_2 (mg/g)	K_2	R^2
CHAC	2.5343	6.09×10^{-5}	0.0294	75.9167	0.1767	0.9894
CA-CHAC	6.8901	8.54×10^{-5}	0.0654	91.9949	0.0142	0.9945

This data was graphed and analyzed by applying linearized forms of both the pseudo-first-order (Fig. 6a and 6b) and pseudo-second-order equations (Fig. 6c and 6d).
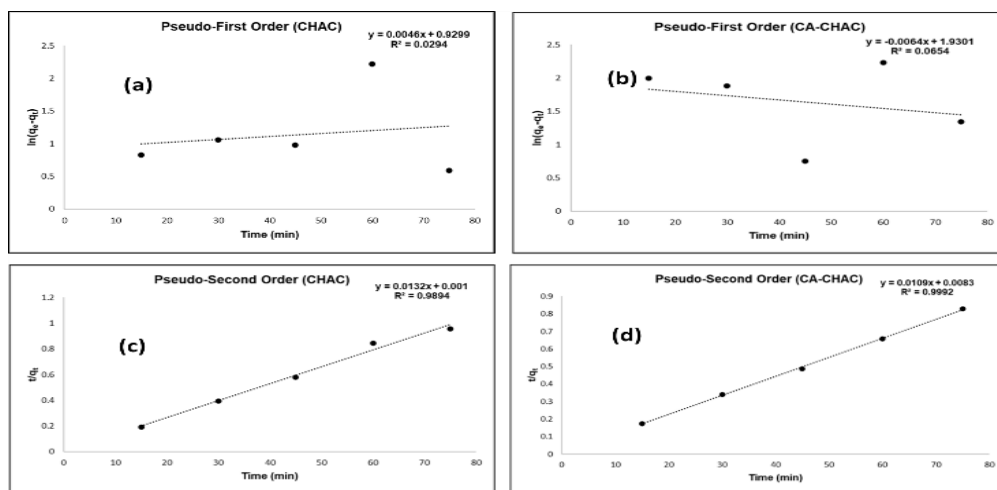

Figure 6. Adsorption kinetics of Cu (II) ions. (a) Pseudo-First order kinetics using CHAC; (b) Pseudo-First order kinetics using CA-CHAC; (c) Pseudo-Second order kinetics using CHAC; and (d) Pseudo-Second order kinetics using CA-CHAC.

The data depicted in the Figures indicate that the R^2 values derived from the pseudo-second-order model (0.9894 for CHAC and 0.9945 for CA-CHAC) were notably higher than those obtained from the pseudo-first-order model. These results suggest that the adsorption kinetics of CHAC and CA-CHAC towards Cu (II) ions are better explained by the pseudo-second-order model, based on the assumption that the rate-limiting step is chemical sorption or chemisorption and predicts the behavior over the whole range of adsorption. In this condition, the adsorption rate is dependent on adsorption capacity not on the concentration of adsorbate [25]. The pseudo-second-order expression has been predominantly observed in various adsorption systems including the removal of heavy metal ions, dyes, oils, and organic compounds from aqueous solutions [34]. Furthermore, the pseudo-second-order kinetics model was observed to fit similar studies using corn husk-activated carbon in the adsorption kinetics of various heavy metals (Cu^{2+}, Zn^{2+}, Fe^{2+}, and Mn^{2+}) [35].

CONCLUSION AND RECOMMENDATIONS

The utilization of activated carbon obtained from corn husk waste was used to investigate the removal of Cu (II) ions from aqueous solutions. Variations in pH, adsorbent dosage, and contact time were observed to significantly influence the removal efficiency of both CHAC and CA-CHAC about Cu (II) ions. The attainment of equilibrium and the saturation of binding sites were identified as limiting factors affecting the removal efficiency of these two adsorbents. The adsorption process of CHAC and CA-CHAC favors a Langmuir isotherm and a pseudo-second-order model. The adsorption isotherm studies indicate that these

adsorbents have a consistent and homogeneous surface structure consistent with the assumptions of a monolayer adsorption process. Meanwhile, the findings from kinetic studies imply that the adsorption mechanism leans significantly towards chemisorption. However, further investigations may be conducted to improve the current findings of the study, to wit: (1) exploring alternative modification methods, such as utilizing different acids and bases to further enhance the adsorption capacity of activated carbon derived from corn husk waste; (2) it is advisable to take into account additional variables, including temperature, initial concentration, and agitation speed in batch adsorption experiments; (3) exploring the potential of CA-CHAC as an adsorbent for various contaminants can also be done by investigating its efficacy in removing additional heavy metal ions, as well as organic and/or inorganic compounds; and (4) assessing the reusability of CA-CHAC is essential to determine its lifespan as an adsorbent. Nevertheless, this study highlights the enhanced efficiency of modified activated carbon over its unmodified form in adsorbing Cu (II) ions from an aqueous solution.

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