

Modification of *Carica papaya* Seeds with NaOH for Copper Removal from Water

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As people work to create a sustainable future, initiatives to improve the state of the environment have recently taken precedence. Due to the persistence of heavy metals in the environment and their nonbiodegradable nature, heavy metal contamination has become a global issue. In conjunction with the Sustainable Development Goals, this study proposes a green method of heavy metal removal by applying *Carica papaya* seeds (CPS) as an environmentally friendly and highly efficient adsorbent to remove copper (Cu) from the environment. To increase its potential in adsorbing copper(II) ions, CPS were treated with sodium hydroxide (NaOH). The effects of the adsorbent mass, pH, initial metal solution concentrations, and contact time were investigated in batch experiments. The optimum pH and contact time for CPS are pH 3–5 and 120 min, respectively, and the highest percentage of removal achieved is 82%. The adsorbent was characterized with scanning electron microscopy (SEM) and Fourier transform-infrared (FT-IR) spectroscopy to analyze the Cu adsorption process. In conclusion, the chemically treated CPS can be utilized as a potential bio-adsorbent for Cu removal from aqueous solutions.

Keywords: *Carica papaya* seeds (CPS); copper (Cu); green adsorbent; heavy metals; water treatment

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Water contamination has become a major concern for society today since water is a basic requirement for life and, therefore, crucial for all living things. Fast-moving sectors, including the metal mining, fertilizer manufacturing, paper, and pesticide industries, have released a variety of pollutants into the environment, particularly in developing nations. Numerous pollutants including heavy metals, notably from industrial effluents and mining and agricultural waste, are continually released into the water system and have a negative ecological impact^{1,2}. Such pollution notably affects the sustainability of clean water, which is concerning considering future generations.

Heavy metals are nonbiodegradable contaminants that are notably difficult to remove from the environment through natural means. When the concentrations of heavy metal elements in the ecosystem exceed acceptable limits, almost all can become hazardous. After entering the food chain, they may begin to accumulate in the body and lead to significant health issues if their concentrations exceed the allowable levels. One of the toxic heavy metals that is frequently

released into effluents or surface water by a variety of sectors, including the mining and metal-plating industries, is copper³. Additionally, over time, copper pipes and fittings used in homes may corrode, releasing the metal's toxic ionic forms into the water stream, which subsequently finds its way into domestic tap water. Copper (Cu), when ingested, may build up in the human body over time and, due to its potential to interfere with DNA replication, may ultimately lead to death if present in significantly high amounts⁴⁻⁷.

Hence, many techniques have been developed and implemented to reduce water contamination at the source. Vacuum evaporation and solvent extraction are two conventional methods for treating such contamination, though they are expensive and exceedingly complex^{8,9}. The demand to develop innovative and affordable water treatment solutions for heavy metal pollutants has increased due to such drawbacks. In addition, the present priority is to achieve the Sustainable Development Goals and create a reusable, low-cost, sustainable solution to address the declining water quality. Hence, adsorbent materials

derived from agricultural waste can be introduced as an alternative to recover harmful metal pollutants as they are simple to operate, environmentally friendly, and affordable^{10,11}. Plant-based adsorbents have the potential for wider application than those derived from animal waste; the former are, thus, favored over the latter, which have faced restrictions due to religious prohibitions. Malaysia produces high numbers of papayas annually; for example, in 2018 alone, its papaya production was estimated at 88,480 metric tons¹². This suggests that a large amount of papaya seeds is generally discarded. As they are abundant and highly accessible, making use of these seeds as a biosorbent can promote the reusability of waste¹³. *Carica papaya* seeds contain cellulose and lignin with a relatively high concentration of hydroxyl functional groups (-OH), which may act as porous binding sites capable of adsorbing metallic ions in water treatment^{5,10,14,15}. However, further modification by NaOH treatment may help increase their efficiency in adsorbing heavy metal cations^{16,17}.

In the present study, we developed a highly efficient and environmentally friendly adsorbent prepared from the NaOH treatment of *Carica papaya* seeds (CPS). The structure and surface morphology of the adsorbent (before and after metal ion adsorption) were characterized by Fourier transform-infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The effects of pH and contact time on the adsorption performance were also investigated.

EXPERIMENTAL

Chemicals and Materials

Copper standard solution, 1000 ± 2 mg/L, potassium bromide (KBr), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were purchased from Merck KGaA (Germany). The metal Cu^{2+} ions were provided as $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, which were purchased from Merck KGaA (Germany). These reagents were of analytical grade and prepared with deionized water.

Adsorbent Preparation

CPS were obtained from a local fruit market (Pahang, Malaysia). Prior to the experiments, the adsorbents were washed once, dried, and chemically treated by soaking them in 0.1 M NaOH solution for 1 h. They were then dried in an oven (Memmert GmbH) at 60 °C for 48 h, finely ground in a Waring blender, and sieved in an automatic sieve (Endecottis Limited, London, UK) to a size of less than 425 μm (ASTM E11:01). Untreated adsorbents were also prepared as a control. The sieved particles were stored for further experimental usage.

Adsorption Experiment

The effects of the operational parameters of pH and contact time on Cu metal ion adsorption were investigated. Batch studies to explore the effect of pH were performed by testing the adsorption of the Cu solution at different pH values (pH 1, 3, 5, 7, and 9) while keeping the contact time constant at 60 min. The pH of the aqueous solutions was adjusted with either 0.1 M NaOH or HCl to the desired value. The treated CPS were mixed into the Cu solutions and agitated at 200 rpm at an ambient temperature of 28 ± 1 °C on a magnetic plate stirrer. In a separate experiment, the effect of the contact time was investigated by performing batch adsorption studies at different contact times (0, 15, 30, 45, 60, 90, and 120 min) while keeping the solution pH constant at pH 5. The adsorbent mass and initial Cu concentration were fixed at 0.3 g and 10 mg/L, respectively, in all the adsorption experiments. The solutions were then filtered (pore size of 11 μm) into a 15-mL Falcon centrifuge tube, and the Cu solution filtrates were analyzed using a PerkinElmer AAnalyst 700 Atomic Absorption Spectrophotometer (AAS; PerkinElmer, Germany) to measure the remaining metal concentration and calculate the percentage of Cu removal, as given in Equation 1:

$$\text{Percentage Removal (\%)} = \frac{C_0 - C_t}{C_0} \quad (1)$$

where C_0 is the initial ($t = 0$ min) liquid-phase concentration of the metal adsorbate solution (mg/L), and C_t is the liquid-phase concentration of the adsorbate solution at any time t (mg/L). The wavelength was set at 324.75 nm. Calibration curves were obtained from the prepared standard copper solutions using a range of concentration. The concentration of copper in the filtrate was derived from the calibration curve.

Characterization Methods

Infrared absorption measurements were performed using an FT-IR spectrophotometer (PerkinElmer, United States). The FT-IR spectra were obtained in the wavenumber range of 400–4000 cm^{-1} using transmission analysis. SEM was used to investigate the morphology of the prepared CPS (adsorbent) before and after NaOH treatment and the adsorption of metal ions. The adsorbent samples were sprinkled on an adhesive tape attached to a knob. Approximately 1–2 mg of the adsorbent samples were then coated with conductive gold by fitting the knob into a sputter coater (Leica Microsystems, Singapore), which was operated in vacuum (10^{-2} – 10^{-1} mbar) for 2 h, followed by a gold-coating process (of 15–20 nm thickness) for 60 s under 45 mA. The coated knob was then analyzed morphologically via SEM (Carl Zeiss Microscopy GmbH, Germany) operating under a voltage of 3 kV for the sample CPS.

RESULTS AND DISCUSSION

Characterization

FT-IR Spectroscopy

As seen in Figure 1, the peaks in the range of 3,500–3,200 cm^{-1} indicate the presence of -OH functional groups. Peaks within the 3,000–2,800 cm^{-1} range can be assigned to C-H stretching; 1,750–1,730 cm^{-1} , C=O stretching; 1,680–1,600 cm^{-1} , C=C alkenes; and 1,300–1,000 cm^{-1} , C-O stretching. Some wavenumber shifts were observed between the untreated and NaOH-treated CPS. The strong peak at 3,412 cm^{-1} , which can be assigned to -OH groups (alcohols, carboxylic acids, and phenols), in the untreated CPS (Figure 1a) shifted to 3,409 cm^{-1} in the treated CPS (Figure 1b). Meanwhile, the peaks for C-O stretching at 1,157 and 1,099 cm^{-1} shifted to 1,160 and 1,105 cm^{-1} , respectively. These visible shifts indicate the interactions of the NaOH solution with the functional groups on the adsorbent surface, where the hydroxyl groups of the CPS are

deprotonated after treatment. This observation is aligned with the results of another study, where a shift in the hydroxyl group wavenumber was noted after the treatment of wheat straw with NaOH¹⁸. The intensity of the hydroxyl group peak also decreases post treatment, indicating that NaOH successfully deprotonates the hydroxyl groups¹⁹.

The sites at which the metal ions interact are indicated through the wavenumber shifts of the adsorbent, before (Figure 1b) and after (Figure 1c) metal adsorption. The Cu(II) ions interact with the -OH groups on the adsorbent, as demonstrated by the wavenumber shift from 3,409 cm^{-1} (before adsorption) to 3,375 cm^{-1} . Other visible shifts occur in the C=O stretching and C=C alkene regions, where the peaks shift from 1,744 and 1,651 cm^{-1} before adsorption to 1,742 and 1,653 cm^{-1} after metal adsorption, respectively. Furthermore, the peak at 1,380 cm^{-1} (before adsorption) shifts to 1,382 cm^{-1} (after the adsorption of Cu ions), which indicates the C-O stretching region.

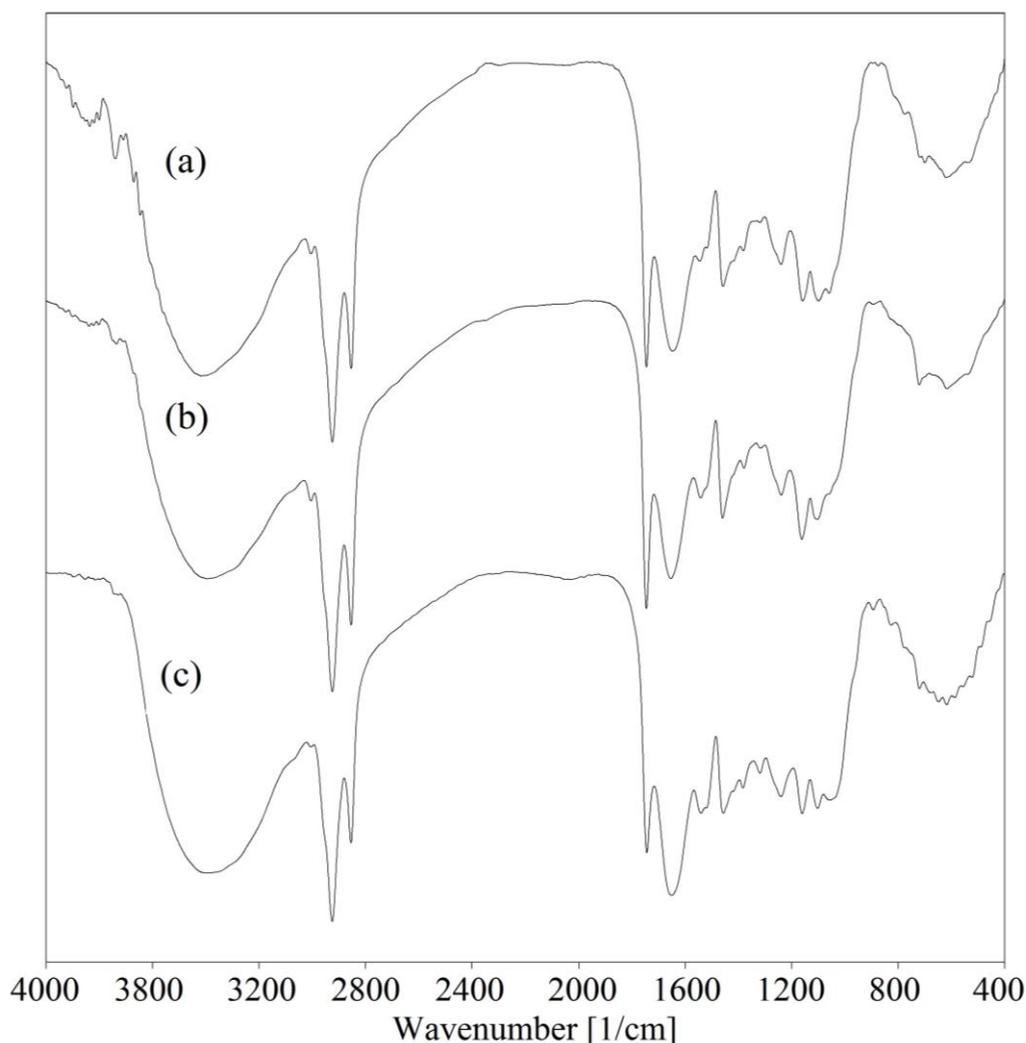


Figure 1. FT-IR spectra of (a) untreated adsorbents, (b) NaOH-treated adsorbents, and (c) Cu-loaded adsorbents.

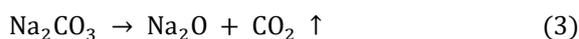
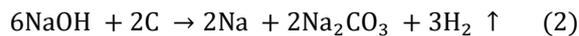
According to the existing literature, the shifts in the FT-IR spectra arise due to interactions between the donor and acceptor groups, resulting in the formation of metal–ligand complexes^{20,21}. The wavenumbers shift to lower values if the electron densities of the functional groups (C=O, OH, and C=C) decrease following the formation of the metal–ligand complexes. Based on the interactions in this study, one can assume that the adsorbent and Cu²⁺ interact to produce metal–ligand complexes through the functional groups of OH, C=O, and C=C.

These conclusions are supported by studies revealing that lignin and cellulose generally form the main components of CPS and are embedded with polar functional groups, such as alcohols (-OH-), aldehydes (-CHO), ketones [-RC(=O)R'-], carboxylic acids (-COOH-), and ethers (-R-O-R'-)^{8,22,23,24}. They also contain prominent carotenoids (such as lycopene), which are capable of binding to toxic heavy metal ions by donating electron pairs, forming metal–ligand complexes. In addition, the fatty oil of CPS is composed of various saturated acids (palmitic, stearic, and arachidic) and unsaturated acids (oleic and linoleic). These support the assumption that the carboxyl group (in carboxylic acids) is the major functional group present in CPS, which is responsible for cation adsorption²⁵.

Scanning Electron Microscopy (SEM)

The surface structure of the NaOH-treated adsorbents, exhibited in Figure 3, appears to have porous cavities,

in contrast to the untreated adsorbents shown in Figure 2, with no porous cavities. Earlier studies have also noted the porous structure of NaOH-treated adsorbents²⁵⁻²⁷. The adsorbent is activated by NaOH, increasing the pore sizes on the surface due to reductive and oxidative changes²⁸. The reaction between active intermediates of the NaOH solution and the carbon surface of the adsorbent leads to the formation of the gases H₂, CO₂, and CO, giving rise to the development of pores. The possible reactions are given in Equations 2, 3, and 4²⁸.



The micrograph of the CPS after the adsorption of Cu ions is depicted in Figure 4, indicating that Cu forms bonds within the porous structure, filling in the pores and, consequently, producing a nonporous, smooth surface. The increased specific surface area from the porous cavities makes the surface functional groups more accessible to metal adsorbates, boosting the adsorption density²⁹. Additionally, compared to non-porous structures, these porous architectures offer more ligands for metal-ion binding. Thus, the adsorbents can be activated with alkalis to increase cationic adsorption via hydrolysis of the surface functional groups to carboxylate (-COO) and alcohol (-OH) groups²⁹.

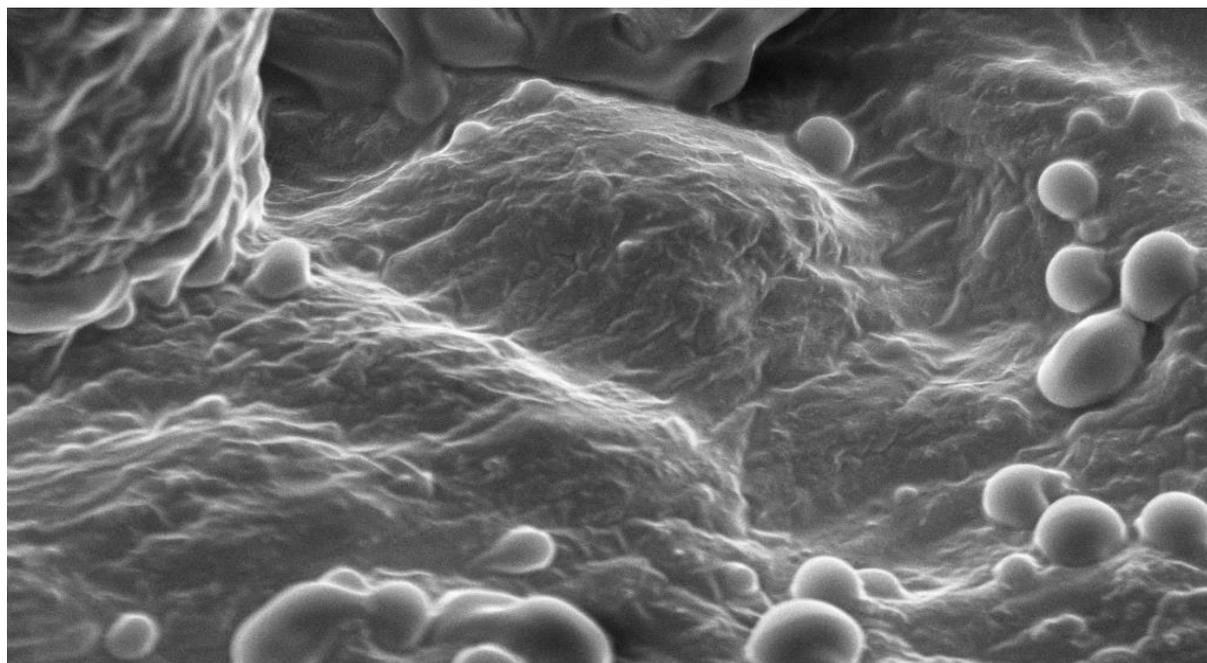


Figure 2. SEM micrograph of a) untreated *Carica papaya* adsorbent seeds at 2000× magnification (operating at 10 kV).

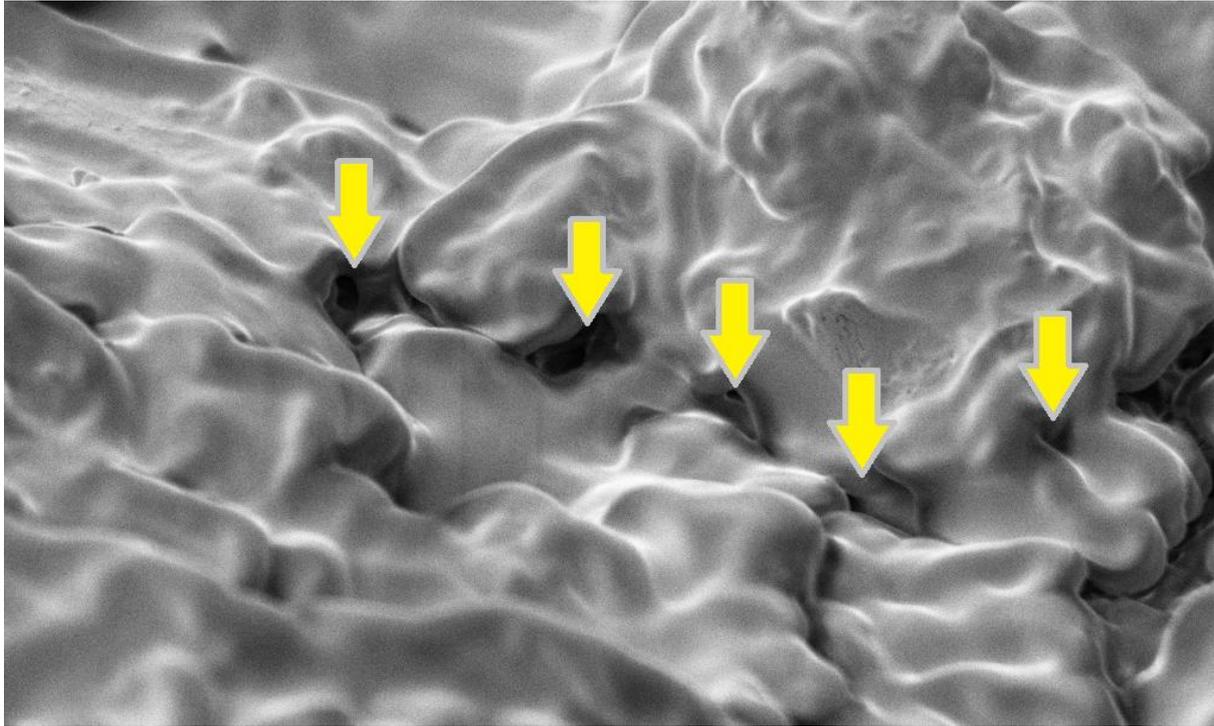


Figure 3. SEM micrograph of treated *Carica papaya* seeds adsorbents at 3500 \times magnification (operating at 10 kV). The arrows show the appearance of pores on the surface structure of the treated adsorbents.

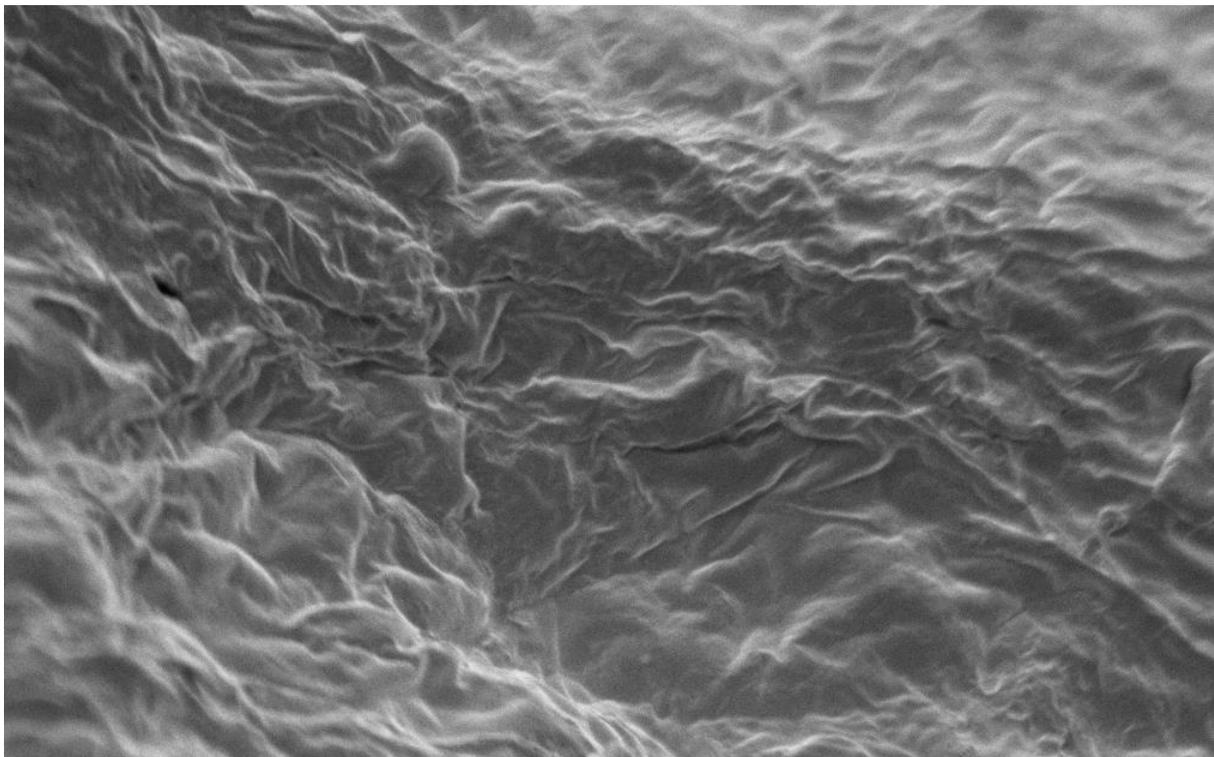
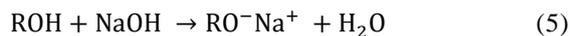


Figure 4. SEM micrograph of treated *Carica papaya* adsorbents seeds with adsorbed Cu ions at 2000 \times magnifications (operating at 10 kV). The circle shows the presence of Cu ions on the surface structure of the adsorbents.

Adsorption Studies

Effect of NaOH Modification on Adsorbent

Considering the percentage removal of Cu metal from the aqueous solutions, the untreated and treated CPS were compared and evaluated. We discovered that in comparison to the untreated adsorbent, treating the adsorbent with NaOH increases its adsorption from 45 to 49% at a mass of 0.9 g of the adsorbent. In addition to increasing the solubility and degree of ionization of the metal ions, the introduction of a strong base (such as NaOH) to the adsorbents alters the surface characteristics of the adsorbent and increases its adsorption capacity¹⁰. The hydroxyl ions in the NaOH solution contribute significantly to the overall negative surface charge of an adsorbent, which promotes the adsorptive attachment of positively charged metal ions, such as Cu^{2+} ¹⁴. Equations 5 and 6 represent the reactions of NaOH with the functional groups on the adsorbent³⁰.



Where R and M are the functional groups on the adsorbent surface and the metal ions in the aqueous solution, respectively.

Effect of pH of Solution

The percentage of Cu metal removed from the aqueous solutions by the CPS at different pH values is shown in Figure 5; it is the lowest (7%) at pH 1, demonstrating that the most ineffective rate of adsorption occurs at this pH^{8,10,15}. The pH level affects how Cu(II) interacts with the surface functional groups of the adsorbent, including the carboxyl and hydroxyl groups. In strongly acidic media, the adsorption sites (carboxyl or phenolic hydroxyl groups) tend to be protonated by hydrogen ions and become positively charged as $-\text{COOH}_2^+/-\text{OH}_2^+$, leading to electrostatic repulsion between the metal (Cu^{2+}) ions and the adsorbent and preventing the adsorption of the former³¹.

The trend in the percentage of Cu removal shows a rapid surge from pH 1 to 3, reaching the maximum removal at pH 5, and then falling significantly with further increases in the pH. The increased percentage of removal as the pH increases from 1 to 5 is due to the deprotonation of the functional groups on the adsorbent. As a result, the negative charge of the functional groups ($-\text{COO}^-/-\text{O}^-$) increases, which subsequently bind the Cu^{2+} cations via electrostatic attractive forces^{22,32}. This could also be explained by a decrease in competition for the adsorption sites between metal and hydrogen ions as the pH increases. The adsorption of Cu^{2+} by the CPS is the most efficient/optimal at pH 5, as indicated by the highest percentage removal of 84%.

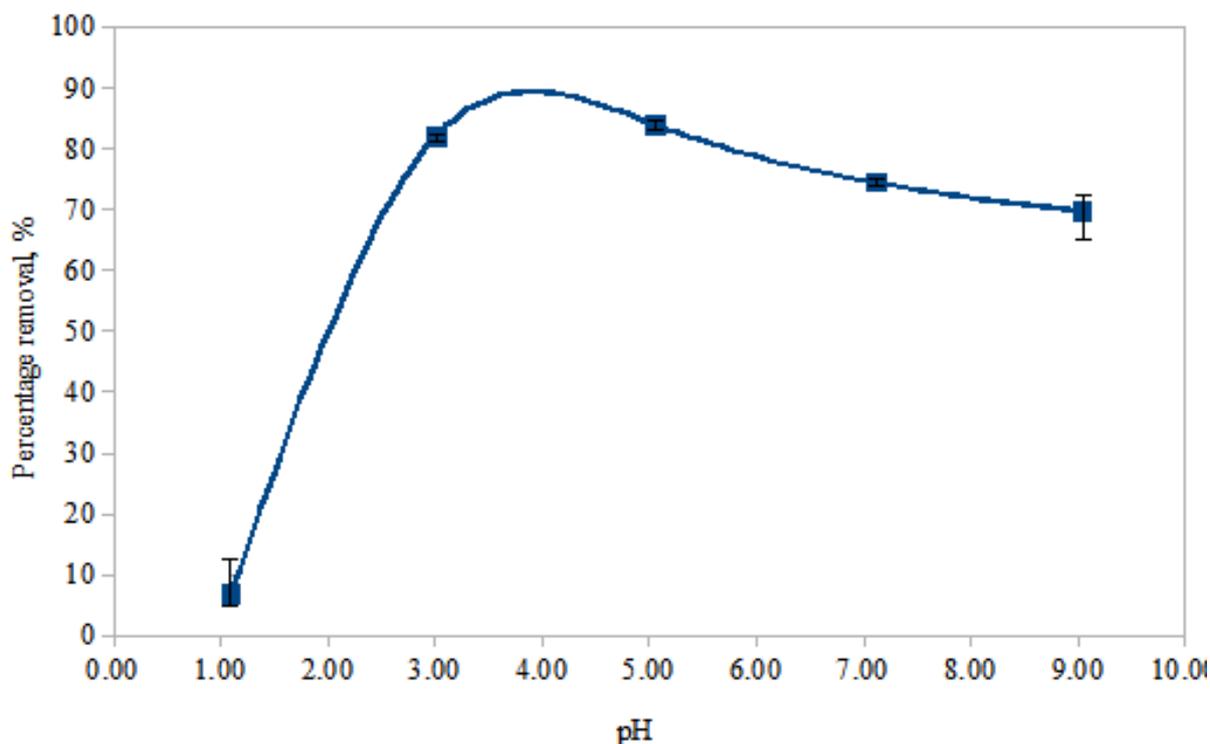


Figure 5. Percentage removal of Cu in the aqueous solution (10 mg/L, 100 mL) by varying the pH of the solution (pH 1–9, 200 rpm, 1 hr) using 0.3 g of NaOH-treated CPS.

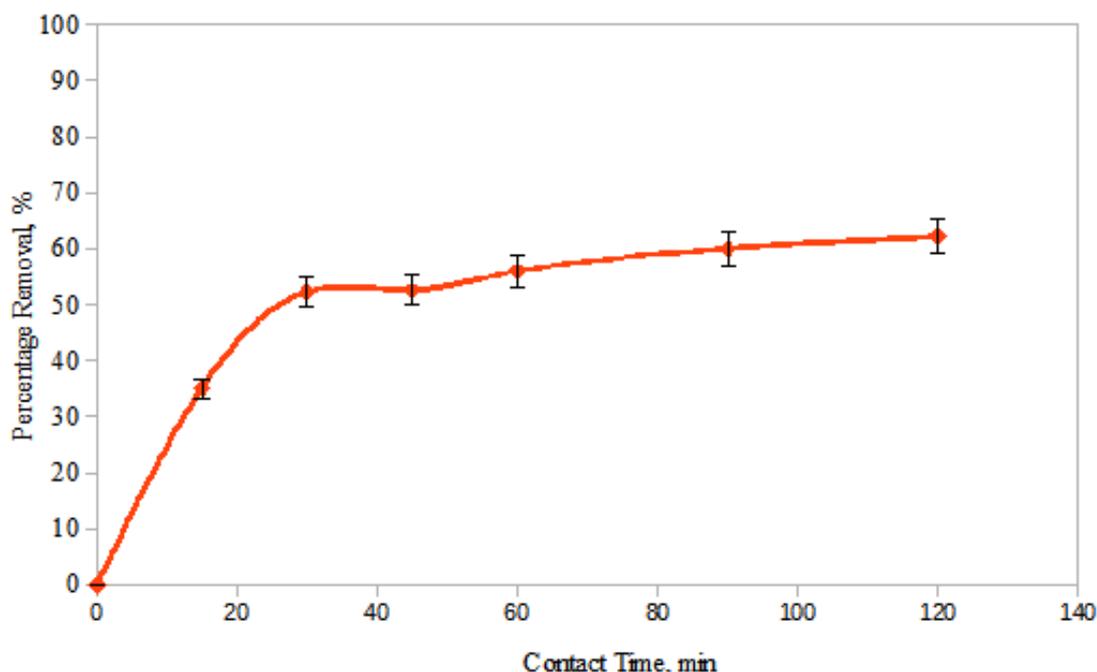
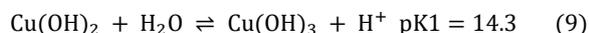
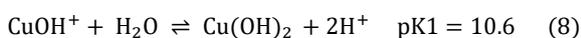
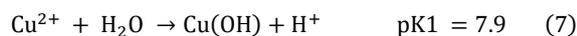


Figure 6. Percentage removal of Cu in the aqueous solution (100 mL) at various contact time intervals using 0.3 g of NaOH-treated CPS (pH 5, 200 rpm).

Aside from affecting the surface charge of the adsorbent, the pH also has an impact on the adsorbate's degree of ionization, which could affect the adsorption process⁸. Research has revealed that divalent ions can exist in various forms (anions, cations, or neutral) upon dissolution in water^{34,35}. Although the deprotonation of the adsorption sites increases the attraction of metal cations to them, the increase in hydroxyl ion concentration at higher pH values may alter the degree to which the metal ions are ionized, making the adherence of the metal cations to the adsorption sites difficult^{35,36}. Equations 7, 8, and 9 show the hydrolysis of Cu^{2+} ions in solutions of different pH values³³.



This leads to the decrease in the percentage of Cu removal after the peak pH values. The most prevalent species below pH 6.0, which represents true adsorption, is Cu^{2+} ³⁷. Cu^{2+} ions are among the metal ions that are hydrolyzed in aqueous solution between pH values of 6 to 8, resulting in the formation of the metal hydroxides CuOH^+ and $\text{Cu}(\text{OH})_2$ at higher pH³⁸. According to earlier research, CuOH^+ formation starts between pH 4 and 5, and $\text{Cu}(\text{OH})_2$ precipitates at pH levels higher than 6, implying that Cu is not entirely removed by adsorption²². That is, the hydroxyl ions interact with the metal ions to yield the precipitation of hydroxylated species, which causes both the hydrolysis and reduction of free metal ions⁸⁻¹⁰. The slight increment in the percentage of Cu removal at pH 9 is assumed to be mainly due to metal precipitation

rather than adsorption. This is because the AAS can only measure free-moving metal ion concentrations as opposed to precipitated Cu.

The solubility of the adsorbate ions, the surface charge of the adsorbent, and the degree of ionization of the adsorbate ions (ionic speciation) during the adsorption process are all influenced by the solution pH, the raising of which may facilitate metal hydrolysis. The pH of the solution also affects the adsorption mechanism, which can involve electrostatic interactions, metal complexation, or the formation of hydrogen bonds on the adsorbent surface²⁸. Further, the adsorption sites may be protonated or deprotonated depending on the pH level. Since pH has a significant impact on adsorption, accurate comparative research necessitates collecting data at the same pH level.

Effect of Contact Time

Figure 6 illustrates the increase in the percentage of Cu removal with increases in the contact time. During the first 30 min of the experiment, a sharp rise in the percentage removal of Cu, up to 52%, is observed; this is explained by the greater surface area of the adsorbents available for the adsorption of metal ions in the initial stages of the process⁹. The adsorption behavior ultimately plateaus to achieve equilibrium after 45 min, after which no significant removal is observed. At an equilibrium time of 120 min, the maximum percentage (up to 62%) of Cu is removed. The adsorption and desorption rates are equal at equilibrium. When the adsorption sites become saturated with adsorbates over time, desorption is forced to occur, leading to an adsorption equilibrium. One can explain the higher percentage of removal at later contact

times by noting that when the solution is agitated over time, the Cu ions are more effectively adsorbed onto the functional groups on the adsorbents due to the frequent contact with the adsorbent. Previous literature has also noted a pattern comparable to this result⁸.

CONCLUSION

Carica papaya seeds are effective in strongly adsorbing Cu, where pretreating the adsorbents with NaOH results in a notable improvement in Cu removal. For the highest percentage of Cu metal removal, the ideal pH and contact duration are pH 5 and 120 min. The adsorption equilibrium was achieved at 120 min contact time. The occurrence of metal adsorption and the changes brought about by NaOH chemical treatment on the adsorbents are confirmed by the SEM micrographs and FT-IR spectra of the adsorbents.

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