MALAYSIAN JOURNAL OF ANALYTICAL SCIENCES
Published by The Malaysian Analytical Sciences Society
ISSN
1394 - 2506

ADSORPTION STUDY ON THE REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTION USING SODIUM HYDROXIDE-MODIFIED *Carica papaya* PEELS

(Kajian Penjerapan Dalam Penyingkiran Ion Kuprum Dari Larutan Akueus Menggunakan Kulit *Carica papaya* Yang Dimodifikasikan Dengan Sodium Hidroksida)

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Received: 1 August 2018; Accepted: 10 November 2019

Abstract

Recently, environment contamination by heavy metals has gained much attention due to the significant impact on public health. Heavy metals such as copper are non-biodegradable pollutants and they are very difficult to eliminate naturally from the environment. Therefore, this study was conducted to deal with the removal copper from an aqueous solution using a highly efficient, environmentally friendly adsorbent from *Carica papaya* peels (CPP) prepared by chemical treatment of NaOH modification. The effects of adsorbent mass, pH of the aqueous solution, and contact time were studied in batch experiments. The optimum parameters for the removal of copper (79%) are 0.9 g, pH = 3, and 45 minutes. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) were employed to validate the efficiencies of the adsorbents towards copper. FT-IR analysis showed that carboxyl and hydroxyl functional groups were involved in the adsorption of copper ions. As a conclusion, the chemical-treated CPP can be utilized as a potential biosorbent for copper removal from aqueous solutions.

Keywords: *Carica papaya* peels, adsorbent, heavy metal

Abstrak

Sejak kebelakangan ini, pencemaran alam sekitar berpunca dari logam berat telah mendapat banyak perhatian berikutan kesannya yang signifikan terhadap kesihatan awam. Logam berat seperti kuprum adalah bahan pencemar tidak boleh diurai dan ianya sangat sukar untuk disingkirkan secara semula jadi dari alam sekitar. Oleh itu, kajian ini dijalankan untuk menangani penyingkiran tembaga daripada larutan akueus menggunakan penjerap yang berkesan dan mesra alam dari kulit *Carica papaya* (CPP) yang dihasilkan melalui pengolahan secara kimia menggunakan NaOH. Kesan jisim penjerap, pH larutan akueus, dan masa hubungan dikaji dalam eksperimen ini. Parameter optima keberkesanan penjerap untuk menyingkirkan kuprum (79%) adalah pada 0.9 g jisim penjerap, pH = 3, dan 45 minit masa pengeraman. Pengimbas mikroskop elektron (SEM) dan Fourier spektroskopi inframerah Fourier (FT-IR) digunakan untuk mengesahkan kecekapan penjerap untuk menjerap kuprum. Analisis FT-IR menunjukkan bahawa kumpulan berfungsi karboksil dan hidroksil adalah terlibat dalam penjerapan ion kuprum. Sebagai kesimpulan, CPP yang dirawat dengan kimia boleh digunakan sebagai penjerap yang berpotensi untuk penyingkiran kuprum daripada larutan akueus.

Kata kunci: kulit *Carica papaya*, penjerap, dan logam berat

Introduction

Wastewater discharged by industrialization and urbanization into the water stream is a great concern to the world as it is detrimental to living organisms. This is because wastewater contains toxic metals (poisonous soluble metal ions) that may be fatal at high concentration and cannot be degraded easily [1, 2]. Copper (Cu) is one example of a toxic metal that could be discharged from electrical, construction, and household pipes. The two oxidation states of Cu, cuprous (Cu^+) and cupric (Cu^{2+}) ions, can form complexes with oxygen-containing ligands and partial covalent bonding with nitrogen- and sulphur-containing cores that can affect the structure and function of biomolecules, to which long-term overexposure can cause health problems [3].

Thus, a safe and effective treatment of wastewater containing toxic metal ions is always a challenge to industrialists and environmentalists. Previously, conventional technologies (ion exchange, chemical precipitation, reverse osmosis, and membrane separation) have been employed to remediate toxic metals pollution [4, 5] However, these are limited by technical (high level of expertise and generation of noxious chemical sludge) and economic (high capital and operational cost) issues [6, 7]. Furthermore, conventional adsorbents have low adsorption capacity and cannot be reused. Therefore, nowadays researchers are looking for other potential and effective materials for toxic metals' removal. Currently, agricultural by-products adsorbents have gained wide attention because of their abundant availability, low cost, renewability, biodegradability, higher efficiency and good reusability [8]. Furthermore, they have a large number of hydroxyl functional groups and a porous structure that are important to bind and complex with the toxic metal ions [3, 9, 10].

In this study, we developed a highly efficient and environmentally friendly adsorbent prepared by chemical modification of *Carica papaya* peels with sodium hydroxide (NaOH). *Carica papaya* was chosen because it is rich with hydroxyl functional groups [11, 12] and easily available in Malaysia (ranked second in the world for exported *Carica papaya*) [13]. The optimization of parameters, namely adsorbent mass, pH, and contact time for adsorption of Cu, was carried out using atomic absorption spectroscopy (AAS). Characterization was performed using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) to understand further the physical and chemical properties, respectively.

Materials and Methods

Reagents

Sodium hydroxide (NaOH, ≥98%,), hydrochloric acid (HCl, 35-37%) and copper standard solution (1000 mg/L) were purchased from Sigma-Aldrich (Missouri, USA). Potassium bromide (KBr) was purchased from Merck KGaA (Germany). All reagents were of analytical grade. All experiments were done using ultrapure deionized distilled water (Sartorius Stedim, France).

Preparations of adsorbents

Carica papaya peels (CPP) used were obtained from the local fruit market (Malaysia). Prior to the experiments, the adsorbents were washed, dried, and chemically-treated by soaking completely in 0.1 M NaOH solution in stirred at an ambient temperature of 28 ± 1 °C for 1 hour. Adsorbents were dried in an oven (Memmert GmbH, Germany), at 60 °C for 48 hours. Dried adsorbents were finely ground in a Waring blender and sieved in an automatic siever (Endecotts Limited, London) of size No. 40 (ASTM E11:01) for uniformity in particle size and total surface area across the adsorbents. Untreated adsorbents were also prepared as a control.

Procedures for adsorption of Cu^{2+}

The adsorption of metal ions on the adsorbents was studied by mixing a known mass of adsorbent into 200 mL of 10 mg/L metal adsorbate solution and agitating at 200 rpm speed, at an ambient temperature of 28 ± 1 °C for 1 hour on a magnetic plate stirrer (Wisd Laboratory Instruments, Germany). The experiments were conducted for Cu ions with various parameters such as the adsorbent mass (0.1, 0.3, 0.5, 0.7 and 0.9 g), the pH of the aqueous solution (pH 1, 3, 5, 7 and 9) and the contact time of adsorption (0, 15, 30, 45 and 60 minutes). The pH of the aqueous solutions was adjusted with either 0.1 M NaOH or HCl. The solution was then filtered using Whatman filter paper, Grade 1 (GE Healthcare, Illinois, USA), into a 15 mL Falcon centrifuge tube to filter off solid adsorbents from the metal adsorbate solution. The metal adsorbate solution filtrate was analysed using AAS (PerkinElmer, Germany) to measure the remaining metal adsorbate concentration and calculate the percentage removal as in Eq. (1).

$$\text{Percentage removal } (\%) = \frac{(C_0 - C_t)}{C_0} \times 100\,, \tag{1}$$

where C_0 is the initial (t = 0 min) liquid-phase concentration of metal adsorbate solution (mg/L) and C_t is the liquid-phase concentration of adsorbate solution at any time t (mg/L).

Characterisation of adsorbents

The surface morphology of the adsorbents between the NaOH-treated and untreated CPP, as well as after the adsorption of copper was analysed using a scanning electron microscope (SEM) (Carl Zeiss Microscopy GmbH, Germany). About 1–2 mg of adsorbent samples were sprinkled on an adhesive tape attached on a knob, and then coated with conductive gold by fitting the knobs into the sputter coater (Leica Microsystems, Singapore) operated in vacuum (10^{-2}–10^{-1} mbar) for 2 hours, followed by a gold-coating process (of thickness 15–20 nm) for 60 s at 45 mA. The samples were then analysed with SEM operated at 10 kV. The functional groups present in these adsorbents were characterised using Fourier Transform Infrared Spectroscopy (FT-IR) (PerkinElmer, Germany) in the mid-infra-red region, 400–4000 cm^{-1}. A blank KBr disc was prepared from KBr powder as the background control. Then, 1–2 mg of the adsorbent powders was mixed together with 300–350 mg KBr powder to produce the sample disc using a hydraulic press for analysis.

Results and Discussion

The effect of adsorbent mass

CPP was ground and sieved to a size of less than 425 μm (No. 40 by ASTM E11:01) for uniformity in particle size and total surface area across the adsorbents. It was established that the smaller the size of the adsorbents, the higher the percentage removal of metal adsorbates [5, 14, 15]. The relationship between adsorbent size and percentage removal is explained by the shell adsorption mechanism which explains the preference of natural organic matter to adsorb on the exterior surface of the adsorbent particles instead of penetrating through it [16]. The increase in the percentage removal is due to the increase in the effective total surface area of the same mass of adsorbents and shortened diffusion path as the size of the adsorbents gets smaller [15, 17]. The smaller adsorbent size also makes the internal pore structure more accessible to the penetration of adsorbates and the large effective surface area provides an increasing number of binding sites [15, 17].

Figure 1 shows the percentage removal of Cu metal ions in aqueous solution between untreated and treated adsorbents. The results show that the sorption is initially fast and then slowed until equilibrium was reached. Cu percentage removal was constant at 0.7 g of untreated adsorbent but for treated adsorbents did not reach a constant value. The increase in percentage removal was due to the enhancement of mass of adsorbents, which increases the total surface area that is exposed to the adsorbate solution, generally allowing more metal adsorbate to be adsorbed onto the adsorbent surface. When the percentage removal graph was horizontal at equilibrium, this shows that all of the binding sites had been taken, leaving behind adsorbates that were impossible or difficult to interact with the adsorption sites (which explains the remaining percentage of unremoved metal adsorbate).

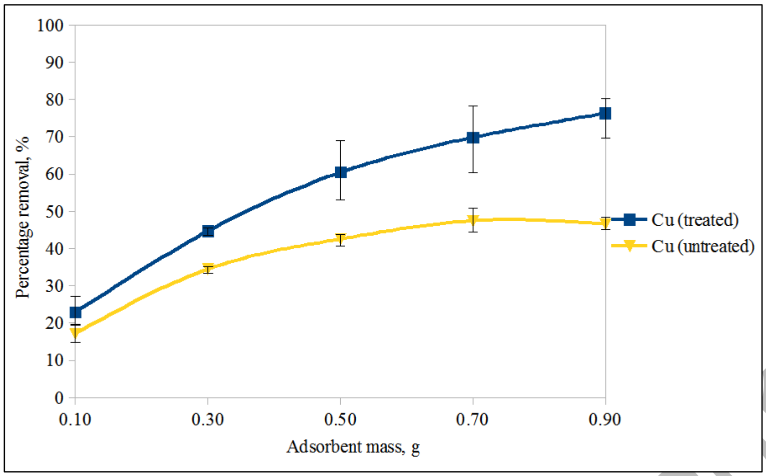

Figure 1. Percentage removal of Cu in aqueous solution (10 mg/L, 200 mL) by varying adsorbent mass of treated and untreated CPP adsorbent (0.1-0.9 g, 200 rpm)

Distinctively, treated adsorbents showed improved percentage removal over untreated adsorbents for Cu removal throughout the adsorbent mass range. Cu adsorbates' adsorption was enhanced from 47% using untreated adsorbents to 76% using the NaOH-treated adsorbents (at a mass of 0.9 g). Ong et al. reported that the introduction of a strong base (such as NaOH in this experiment) to the adsorbents modifies the surface properties of the adsorbent, besides enhancing the solubility and the ionization degree of the metal ions, which would improve the adsorption density [18]. As used in this study, Chong and Thoe reported that 0.1 M NaOH concentration is the optimum concentration that gives the best adsorption of heavy metals onto the adsorbents [19]. This is attributed to the partial solubilisation of lignin and soluble organic components in the adsorbents that have exposed more adsorption sites for the binding of heavy metals [19]. NaOH also removes tannins and de-esterifies, resulting in more active binding sites, which increases the adsorbents' capacity to adsorb metal adsorbates [5]. The 0.1 M NaOH concentration was also utilised in various previous studies [21–24]. In NaOH-treated adsorbents, the total surface negative charge is increased significantly (contributed by the hydroxyl ions in the NaOH solution) and thus encouraging positively charged metal ions such as Cu^{2+} to be adsorbed on the adsorbent [8]. NaOH solution reacts with the functional groups on the adsorbent as characterised by Eq. (2) and Eq. (3) [20]. Therefore, NaOH chemical-modification treatment on the adsorbents was chosen for this experiment to be compared with the untreated adsorbents.

$$ROH + NaOH = RO^{-}Na^{+} + H_2O \tag{2}$$

$$2RO^{-}Na^{+} + M^{2+} = R_2O_2M + 2Na^{+} \tag{3}$$

where R is the functional group on the adsorbent surface and M^{2+} is the metal ion in aqueous solution.

Effect of pH

Figure 2 illustrates the percentage removal of Cu ions in aqueous solution using treated adsorbents by varying the pH of the aqueous solution. The pH can affect both the surface charge of the adsorbents and solubility of metal ions. The point of zero charge (pH_{pzc}) of the functional groups on an adsorbent is the pH at which the groups have no net potential charge (zero charge). The zero charge of the adsorbents may be influenced by the pH of the solution. If the pH of the solution is below pH_{pzc} of a functional group, the group will be protonated by H^{+} ions; in contrast, if the pH is above the pH_{pzc}, the group will be deprotonated instead [7, 11]. For effective adsorption of metal ions, the ionic state of the functional groups on the adsorbents that are involved in adsorption should be in an anionic state (negatively charged) because the metal ions are cations (positively charged) and hence an interaction between them can occur. The change in the charges of the functional groups due to the change of surrounding pH can be generalised by Eq. (4), where R is the functional group on the adsorbent surface.

In general, the percentage removal of Cu was the lowest at pH 1, at 17%. This shows that at pH 1, adsorption on the surface of the adsorbent materials occurs at the most inefficient rate [6, 10, 18]. At lower pH, the carboxyl and phenolic hydroxyl functional groups of the adsorbents exist as their neutral or protonated conformations. The neutral structures, –COOH and –OH, respectively, have no net charge and thus prevent adsorption of any Cu^{2+} ions. These functional groups may also exist in the protonated state of $–CO_2H_2^+$ and $–OH_2^+$, respectively, which repulses same-charged species [25, 26]. Besides, Cu^{2+} ions have to compete with the free excess H^+ ions at low pH for any available adsorption sites. As the pH value increases, the carboxylic group on the adsorbent surface will be deprotonated to become $–COO^-$ followed by deprotonation of phenolic hydroxyl to $–O^-$. Deprotonation of various functional groups on the CPP surface, each with its own pH_{pzc}, formed negatively charged groups that encourage binding to the metal ions. The percentage removal trend showed a sharp increase from pH 1 to reaching the peak at pH between 3 and 5, followed by a sharp decline at higher pH. The deprotonated carboxylic and phenolic hydroxyl groups which are polar functional groups help in metal binding [5]. The percentage removal of Cu was at its highest value, 75%, at pH 3. This is characterised in Eq. (5) as the hydrolysis of Cu^{2+} ions.

$$–RH_2^+ \ (<pH_{pzc}) \rightleftharpoons –RH \ (pH_{pzc}) \rightleftharpoons –R^- \ (>pH_{pzc}) \qquad (4)$$

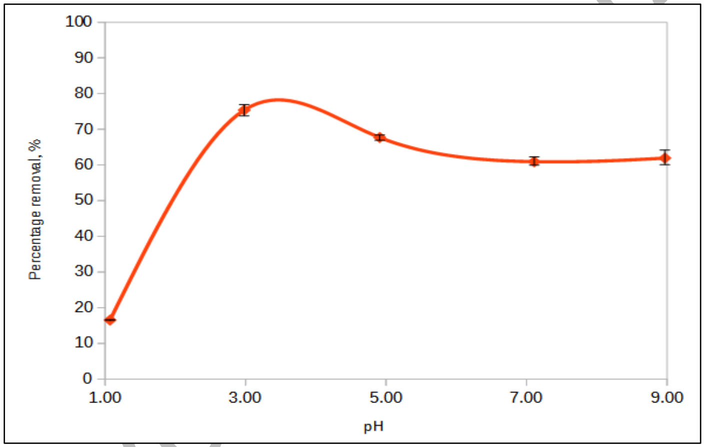

Figure 2. Percentage removal of Cu in aqueous solution (10 mg/L, 100 mL) by varying the pH of the aqueous solution (pH 1-9, 200 rpm, 1 h) using 0.9 g of treated CPP adsorbent

Although the deprotonation of the adsorption sites would increase the attraction of metal cations to the sites, the rising concentration of hydroxyl ions (from the formation of anionic hydroxides) at higher pH changes the ionization degree of the metal ions, and thus hinders their ability to adhere to the adsorption sites on the adsorbents, which explains the decline in percentage removal after the peak pH values [6]. This is characterised in Eq. (5) as the hydrolysis of Cu^{2+} ions.

$$Cu(aq)^{2+} + 2H_2O \rightleftharpoons CuOH^+ + H^+ + H_2O \rightleftharpoons Cu(OH)_2 + 2H^+ \qquad (5)$$

Cu^{2+} is the dominant species below pH 6.0, which is involved in adsorption [27]. It was reported that $Cu(OH)^+$ begins to be formed around pH 4 to 5 and $Cu(OH)_2$ is precipitated at pH higher than 6 and therefore not completely removed *via* adsorption [12]. These hydroxyl ions interact with the metal ions to form hydroxide precipitates, which results in the reduction of free metal ions aside from the hydrolysis of metallic ions [6, 7, 18]. The increase in copper precipitation at higher pH causes the percentage removal to appear to flatten between pH 7.0 and 9.0 instead of drastically declining to the level similar to when the pH was 1.0. Cu^{2+} ions, which are detectable by AAS, are only dominant up to pH 7.5 [28]. At pH 6 to 8, Cu^{2+} ions will be hydrolysed, which will result in the formation of

$CuOH^+$ and $Cu(OH)_2$ hydrolysed forms at higher pH [29]. At pH near to 10 and above, the dominant species existing in the solution are $Cu(OH)_2$, $Cu(OH)_3^-$, and $Cu(OH)_4^{2-}$ [30].

Effect of contact time

Figure 3 shows the percentage removal of Cu at various contact times. There was a rapid increase in the percentage removal of Cu during the first 15 minutes of the experiment. The significant increase during the initial duration is because all of the adsorbent surfaces have not taken up any metal adsorbates, and therefore, a large surface area of the adsorbents is readily available and exposed for the adsorption of metal adsorbates to take place [7]. As adsorption of metal adsorbates on the surface of the adsorbents becomes saturated with time, fewer and limited spaces on the adsorbent surface are accessible for new adsorption to take place. The adsorption gradually flattens up to equilibrium at 45 minutes onwards, after which no significant additional removal was observed. At equilibrium, the adsorption rate is equal to the desorption rate. The highest percentage removal for Cu removal achieved at equilibrium (at minute 45) is 79%. A similar trend was also recorded in previous literature [6], where the adsorption flattens at an equilibrium.

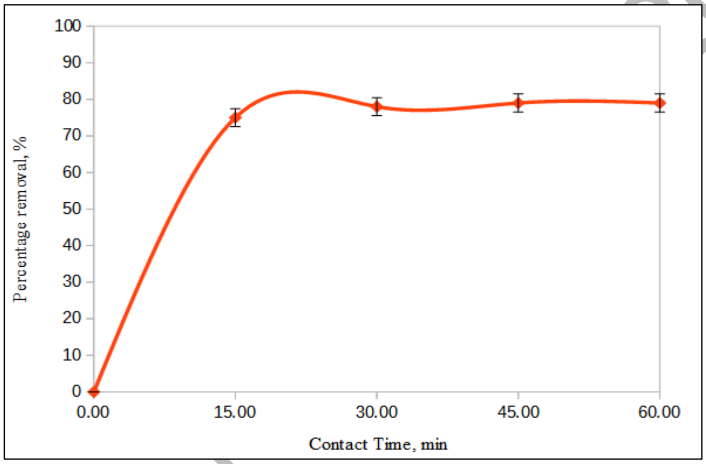

Figure 3. Percentage removal of Cu in aqueous solution (100 mL, 10 mg/mL) at various contact time intervals (0-60 minutes) using 0.9 g of treated CPP, adsorbents (pH 3, 200 rpm)

SEM analysis of adsorbents

It was observed that porous cavities did not exist in the untreated adsorbents in Figure 4, but the surface structure of NaOH-treated adsorbents in Figure 5 appeared to have porous cavities. The porous structure was also observed in previous literature on NaOH-treated adsorbents [31–33]. NaOH acts as an activating agent for the adsorbent, enlarging the pore size on the surface resulting from reduction and oxidative modifications [34]. A theory proposed by Pezoti et al. is that the reactions between active intermediates in the NaOH solution and the carbon surface of the adsorbent will cause the evolution of H_2, CO_2 and CO, and subsequently lead to the development of porosity [34]. The reactions are given in Eq. (6), Eq. (7) and Eq. (8) [34].

$$6NaOH + 2C \rightarrow 2Na + 2Na_2CO_3 + 3H_2\uparrow \quad (6)$$

$$Na_2CO_3 \rightarrow Na_2O + CO_2\uparrow \quad (7)$$

$$2Na + CO_2 \rightarrow Na_2O + CO\uparrow \quad (8)$$

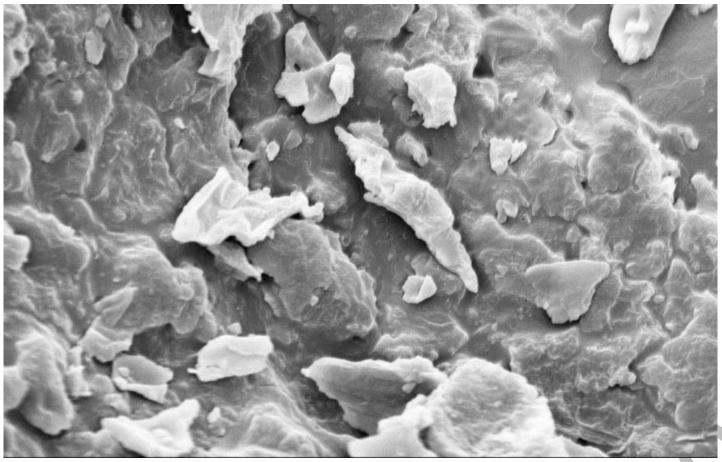

Figure 4. SEM micrograph of untreated CPP adsorbents at 2000x magnification (operating at 10 kV)

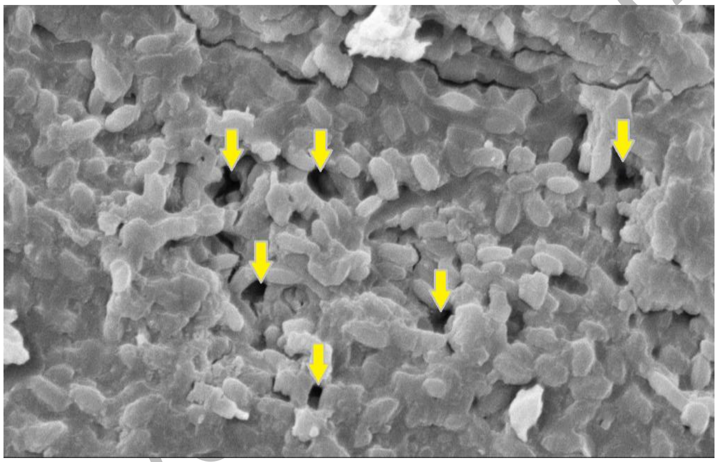

Figure 5. SEM micrograph of treated CPP adsorbents at 3500x magnification (operating at 10 kV). The arrows show the appearance of pores on the surface structure of treated adsorbents

These porous cavities provide an increased specific surface area available for penetration of metal adsorbates through the pores, allowing interactions with the surface functional groups and therefore increasing its adsorption capacity [35]. This porous structure provides more ligands for metal ion binding. Alkaline activation of adsorbents also allows the hydrolysis of surface functional groups to carboxylate ion (–COO$^-$) and alcohol (–OH) groups, which promotes cationic adsorption [35]. Figure 6 shows the adsorption of Cu ions on the surface structure of the treated adsorbents.

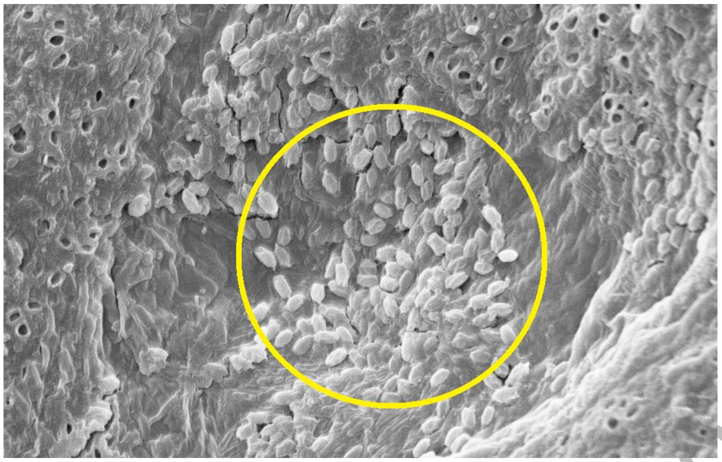

Figure 6. SEM micrograph of treated CPP adsorbents with adsorbed Cu ions at 2000x magnification (operating at 10 kV). The circle shows the presence of oviform Cu ions on the adsorbent surface

FT-IR analysis of adsorbents

Spectral characteristics of the adsorbents are recorded in Table 1. In general, for both treated and untreated adsorbents' spectra, the wavenumber range 3500–3200 cm^{-1} shows the broad absorption band of O–H stretching (can be assigned to alcohols, carboxylic acids and phenols). Two strong sharp absorptions of C–H stretching were present at wavenumbers in the range 2900–2850 cm^{-1} and 2850–2800 cm^{-1} that can be assigned to alkanes and carboxylic acids, which can be associated with the C–H stretching of the methyl sp^3 substituent. The wavenumber range 1750–1730 cm^{-1} displays a medium absorption of C=O stretching that can be assigned to the carbonyl functional group, from carboxylic acids or their esters. Another strong sharp absorption is visible in the wavenumber range 1680-1600 cm^{-1}, signifying the C=C stretching of alkenes. In the fingerprint region, two medium sharp absorptions were observed in the wavenumber range 1450–1375 cm^{-1} indicating the presence of –CH_3 symmetric bending. Various medium intensity peaks were observed in the wavenumber range 1300–1000 cm^{-1} and 950–690 cm^{-1} representing, respectively, C–O stretching and aromatic C–H group, out-of-plane bending. Major shifts were observed between the untreated and NaOH-treated adsorbents. The 3377 cm^{-1} peak in untreated adsorbents shifted to 3395 cm^{-1} in treated adsorbents, the 1413 cm^{-1} peak shifted to 1425 cm^{-1} and the 1105 cm^{-1} peak shifted to 1152 cm^{-1}. Other shifts apart from those mentioned are small. These visible shifts to a higher wavenumber are associated with a stronger bond that resulted in the formation of gases as demonstrated in Eqs. (6 – 8) as the result of NaOH solution interactions with the functional groups on the adsorbent [34].

Comparing before and after the metal adsorptions, the wavenumber shifts indicated the location at which the metal ions formed bonds. Cu ions interact with the –OH group region on the adsorbent as illustrated by the wavenumber shifts from 3395 cm^{-1} (before adsorption) to 3421 cm^{-1}. Another major shift is in the C=O stretching region where the wavenumber shifted from 1732 cm^{-1} before the adsorption to 1726 cm^{-1} after metal adsorptions for Cu ions, suggesting the formation of hydrogen bonding with hydroxyl oxygen (HO–C=O) [34]. Previous literature also showed that the shift in –OH, C–H bending, –C=O stretching vibration and –C=O functional groups spectra were caused by metal adsorption [35,37,38]. Figure 7 further characterises the spectral features of the adsorbents.

Table 1. FT-IR spectral characteristic of CPP adsorbents

Region	**Wavelength Range (cm^{-1})**	**Before Adsorption**		**After Adsorption Cu**	**Assignment**
		Untreated	**Treated**		
A	3500-3200	3377	3395	3421	H-bonded O–H group
B					C–H sp^3 stretching
	3000-2850	2925	2923	2922	(Alkanes)
	2900-2800	2859	2856	2859	(Aldehyde)
C	1750-1730	1732	1732	1726	C=O stretching (Ester)
D	1680-1600	1640	1639	1639	C=C alkenes
E	1450-1375	1413	1425	1426	$-CH_3$ symmetric bending
		1378	1378	1378	
F	1300-1000	1329 1248 1105 1060	1329 1248 1152 1060	1329 1248 1154 1060	C–O stretching
G	950-690	900	900	900	C–H aromatics, out-of-plane bending

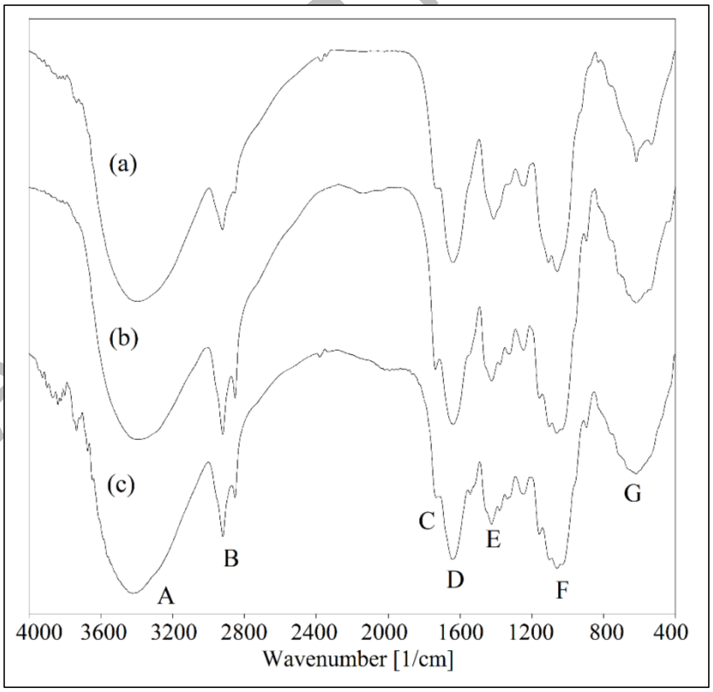

Figure 7. FT-IR spectra of (a) untreated adsorbents, (b) NaOH-treated adsorbents and (c) Cu-loaded adsorbents. Labels A to G are the peak regions, denoted in Table 1.

In *Carica papaya*, lignin and cellulose are the major constituents of its peel, which is embedded with polar functional groups including alcohols, aldehydes, ketones, carboxylic acids, ethers, and prominent phenolics (such as ferulic acid, caffeic acid and rutin) in the peel and carotenoids (such as lycopene) in the seeds, which are capable of binding to toxic metal ions via electron pair donation to form complexes [6, 11, 12].

Conclusion

A biosorbent was successfully produced from *Carica papaya* peels (CPP), by NaOH-treated modification, and was tested of its adsorption potential on the removal of Cu ions from an aqueous solution. The effects of adsorbent mass, pH and contact time were studied in batch experiments and the optimum value of adsorbent mass, pH of the aqueous solution, and contact time for Cu removal are 0.9 g, pH = 3, and 45 minutes, respectively. The optimum percentage removal of Cu ions obtained was 79%. The results from SEM and FT-IR further validate the efficiency of the CPP adsorbent in removing Cu from aqueous solution. FT-IR analysis showed that carboxyl and hydroxyl functional groups were involved in the adsorption of copper ions. It is suggested for future investigations to study on the combinations of different adsorbent sources into a singular composite material to test the synergistic effects they have on the adsorption of hazardous heavy metals. It is hoped that studies as these could be taken up by the industries to further investigates, manufacture and commercialize a practical biosorbent materials that can be utilized in the industrial and household sectors.

Acknowledgement

The project was funded by the International Islamic University Malaysia (Grant No. IRF 19-014-0014).

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