



Coconut Shell Biochar for Removal of Cu(II) from Aqueous Solution

Nur Hanani Hasana¹, Rafeah Wahi^{*1}, Yusralina Yusof¹, Wan Roslina Wan Yusof²
and Zeti Akhtar Abdul Manan¹

¹Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia.

²Centre for Pre-University Studies, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia.

*Corresponding Author Email: wrafeah@unimas.my

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Abstract

The ability of coconut shell biochar (CSB) and acid-base modified coconut shell biochar (MCSB) for the removal of copper (Cu(II)) from aqueous solution is examined. The basic characteristics of CSB as well as MCSB such as proximate analysis, pH value, surface area, surface morphology and surface functional groups are investigated. The individual effect of initial concentration and contact time on the removal efficiency of Cu(II) by CSB and MCSB was determined using one variable at a time (OVAT) approach. In addition, the response surface methodology (RSM) approach is applied to determine the combined effects of variables (pH, contact time and particle size) on the removal efficiency of Cu(II) ion. The RSM results for the MCSB showed that Cu(II) maximum removal efficiency is 99.50% at pH 7, contact time of 60 min, and particle size of 0.60 mm, respectively. It can be concluded that MCSB has greater potential than CSB to be utilized as an adsorbent for Cu(II) removal in water bodies.

Keywords: Coconut shell, Biochar, Adsorption, Cu(II), Response surface methodology

Introduction

Rapid population growth has triggered the development of industrial activities such as paint, coating, alloy preparation, plating and tanning [1]. The lack of attention given to the disposal of industrial wastes has resulted in the deterioration of the environment especially to natural bodies of water. The accumulations of dangerous pollutants like heavy metals in natural water bodies have raised concerns all around the world. Heavy metal pollution is one of the alarming environmental issues.

Heavy metals pollution in water bodies is a serious problem that may threaten human health, aquatic life and its environment [2]. The content of heavy metals that are beyond a

certain limit can lead to hazardous effects on living organisms such as nephropathy, blood and brain disorders, abdominal pains and miscarriage [2]. However, due to their scientific importance, heavy metals are still being applied in numerous industries and productions. Industries such as a battery, paint, electroplating and steel have been generated along with them, heavy metals like cadmium, copper, chromium, lead and nickel [2].

The use of Cu(II) in numerous industrial activities such as alloy industries, Cu polishing, plating, electronics plating and paint manufacturing are common [3]. Copper

polluted the water bodies via wastewater which came from Cu wire mill, insecticides, fungicides and coal-burning activities [3]. Excessive intake of Cu can cause kidney defects, liver disease, neurotoxicity, ulcer in the nasal septum, eye irritation and dermatitis in certain individuals [4]. Hence, Cu removal from wastewater before exuding it to natural water bodies is very crucial in protecting human health.

The maximum allowable limit of Cu in drinking water is 0.2 mg/L [5]. For public water supply, the maximum permissible limit of Cu is 1.0 mg/L whereas the maximum allowable limit of copper for industrial effluent discharge is 3.0 mg/L. The concentration of Cu in any water source differs in different countries. This could be due to the variations in the characteristics of water like pH and Cu availability in the system [6].

Today, various technologies such as adsorption, precipitation, reverse osmosis, ion exchange and solvent extraction have been developed and introduced for the removal of contaminants such as heavy metals and dyes from wastewaters [7, 8]. However, most of the methods mentioned, have a few drawbacks such as incomplete metal removal, require high energy and cost, and toxic which need careful disposal [7]. Among these methods, adsorption is the most preferred process for heavy metal as it has been proven to be effective, low cost and gives high removal capacity [7].

Coconut palm (*Cocos nucifera*) is mostly planted in the humid tropics and is grown in over 90 countries [9]. Coconut trees have a variety of functions since every part of the tree including fruits, leaves and stems can be used as food, shelter, medicine and clothing [10]. CSB has been applied in various industries mainly as an industrial fuel and

activated carbon. A few studies on heavy metals removal have been reported using carbon-based material from coconut shell (CS) which indicates its potential in removing Zinc (Zn), Cadmium (Cd), Lead (Pb) and Copper (Cu) from industrial wastewater [11]. At the same time, coconut shell biochar has also been successfully removing Cu^{2+} , Fe^{2+} , Zn^{2+} and Pb^{2+} ions from electroplating industrial wastewater [12] as well as Hg (II), Pb (II) and Cu (II) from dye effluent [13]. In another study, it has been proved that CS is an effective adsorbent with good adsorption capacity which has efficiently removes Bi (III) from aqueous solutions [14].

Biochar is a product rich in carbon which can be attained by heating organic material (also known as biomass) with limited or no access of oxygen and at relatively low temperature [14, 15]. Based on a research, biochar is biochar that has been modified and created under some conditions so that it can be applied in agriculture [16]. Biochar is produced through pyrolysis of biomass such as CS, sugarcane bagasse, empty fruit bunches of oil palms, rubber-wood sawdust waste, rice straw and palm kernel shells. Biochar can absorb hydrocarbons, organic and inorganic pollutants that make it possible water and soils remediation [17]. Biochar also has a higher sorption capability; thus, it can act as a sorbent in soil and water. This suggests that biochar could adsorb a variety of metal ions, such as Pb, Ni, Cu and Cr [17]. Concentrations of Pb in acidic aqueous solution exhibited a substantial decrease following the addition of biochar and modified biochar derived from conocarpus wastes, demonstrates that biochar can adsorb heavy metal [18]. Another research verified the effectiveness of the application of biochar and modified biochar made from giant Miscanthus to remove Cd from aqueous solutions [19]. Pine sawdust biochar was found to be effective for the adsorption of Cu and Cd. Based on the stated studies, in

comparison to the original biochars, the modified biochars showed a better adsorption ability to remove the heavy metals.

Current researchers are aiming to modify and alter biochar properties such as the surface area, surface functional groups, porosity and surface active sites in order to increase the removal efficiency of biochar for organic contaminants [17]. Chemical modification of biochar can improve the sorption ability of contaminants by generating additional adsorption sites on the surface areas, which allows better sorption capability through sturdier interactions with particular surface functional groups [17]. Some of the common chemical modification process include acid/base modification, amination, steam activation and magnetic modification [17]. Numerous researches demonstrated that modification using acid and base assists in improving the surface area and porosity of the biochar, hence enhancing the heavy metal adsorption process onto that biochar [20].

The objectives of this study are two-fold, namely (a) to investigate the potential of using CSB as adsorbents in heavy metals removal and (b) to compare the effectiveness of CSB and MCSB for the removal of Cu(II) from aqueous solutions.

Materials and Methods

Raw CS was dried beforehand to inhibit the growth of fungus [20]. Rotary kiln was used in the conversion of raw coconut shell to biochar. The rotary kiln was fed with raw coconut shells through conveyor. The shells were carbonized at temperature of 800 °C for 10 min in the absence of oxygen. The biochar was soaked in 20% sodium hydroxide (NaOH) for 2 h followed by 5 M hydrochloric acid (HCl) to get rid of impregnating salt followed by washing with distilled water until the modified biochar

achieved the pH of 4.5 and then dried overnight at 105°C. Both modified and unmodified biochars were crushed, grounded and sieved into three different sizes; 0.3 mm, 0.6 mm and 0.9 mm. The precision of the biochars size was maintained by using the exact mesh size of the sieves. The analytical determination of Cu(II) in this experiment was based on a previous research [21].

Characterization of Adsorbent

Proximate analysis was carried out based on its applicable standard which are ASTM D3173, ASTM D3174 and ASTM D3175. A scanning electron microscope (SEM) (JEOL JSM-6390LA) was used for surface morphology analysis. The pH value of CSB and MCSB was determined by pH meter. Surface area and pore volume of raw CS, CSB and MCSB were determined using the Brunauer–Emmett–Teller (BET) (Quantachrome® ASiQwin TM) method. The surface functional groups of biochars were investigated by Fourier transform infrared spectroscopy (FTIR) (Thermo Nicolet iS 10 FTIR Spectrometer) in the range of 400–4000 cm^{-1} .

Adsorption Studies

Effects of initial concentration on Cu(II) removal

Cu(II) solutions with seven different initial concentrations of 5, 10, 15, 20, 30, 50 and 100 ppm, with 25 mL of volume each, were prepared. 0.5 g of CSB and MCSB was added to these solutions at pH 7, respectively. The mixtures were shaken at 200 rpm for one hour and filtered. The 5 mL of the filtered solutions were then diluted with distilled water until it reached 50 mL in the polyethylene (PE) bottle. The final concentration was determined and obtained by using an Atomic absorption spectrometer (AAS) (Thermo Scientific iCE3500).

Effects of contact time on Cu(II) removal

The contact time used varied from 30 to 240 min (30, 60, 120, 150, 180, 210 and 240 min). The concentration of Cu(II) solution used was 30 ppm with 25 mL of volume each. 0.5 g of CSB and MCSB was added to these solutions at pH 7, respectively. The mixtures were shaken at 200 rpm for different time intervals. The mixtures were then filtered followed by diluting 5 mL of the solutions to 50 mL with distilled water before AAS analysis.

Adsorption isotherm

Langmuir isotherm operates based on three assumptions. The first assumption is adsorption is restricted to monolayer coverage. The second assumption is that all surfaces of adsorbents are identical and only can fit one adsorbed atom. The third assumption is the molecule to be adsorbed on a given site is independent of the adjacent molecules [22]. A straight line with slope ($1/q_{\max}$) and intercept ($1/K_L q_{\max}$) could be obtained by plotting C_e/q_e versus C_e [22]. Langmuir equation can be written in the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} C_e} + \frac{1}{K_L q_{\max}} \quad (1)$$

C_e : metal equilibrium concentration in liquid phase (mg/L)

q_e : metal equilibrium concentration in adsorbed phase (mg/g)

$q_{\max}$: Langmuir constants representing the adsorption capacity (mg/g)

K_L : Langmuir constant (L/mg)

Freundlich isotherm is an empirical equation that is dependent on a heterogeneous surface [22]. This isotherm can describe the adsorption of organic and inorganic

compounds on various adsorbents [22]. Freundlich isotherm can be expressed in the linear form [22]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

q_e : the amount of metal adsorbed at equilibrium time (mg/g)

K_F, n : Freundlich constants

C_e : Equilibrium concentration (mg/L)

K_F : indicates the adsorption capacity and n indicates the adsorption intensity. Freundlich constants can be obtained from the slope and intercept of the linear plot by plotting $\log q_e$ vs $\log C_e$ [22].

Experimental design and optimization of adsorption efficiency

Response surface methodology (RSM) is an arithmetical method that practices quantitative data from suitable experimentations to ascertain regression model equations and operating conditions [23]. RSM was used in this study to determine and evaluate the optimum variables for the removal of Cu(II) ion. The operating variables chosen were pH, contact time and particle size. The sizes given were 0.30 mm, 0.60 mm and 0.90 mm whereas, the pH ranged from 4 to 10. The contact times used were 30 min, 60 min and 90 min. Design Expert 7.1.6 was used to analyze the experimental results.

Results and Discussion**Characteristics of Adsorbents**

Table 1 shows the raw CS has the highest moisture content followed by MCSB and CSB. The moisture content for CSB decreased due to the loss of water molecules during the carbonization process where around 95% of the water molecules were removed

[24]. However, the moisture content increased in MCSB. The reason might be caused by the washing process during the modification of the CSB. The moisture content for all three samples is considered low which ranged from 5 to 13% whereas high moisture content is more than 40% [25]. High moisture content has a tendency to reduce the efficiency of the biochar as fuel [25].

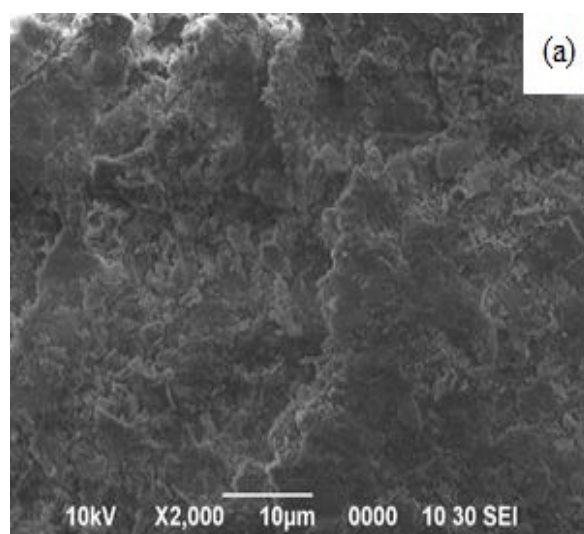
Table 1. Proximate analysis of raw CS, CSB and MCSB.

	Raw CS (%)	CSB (%)	MCSB (%)
Moisture content	12.75±3.18	5.00±1.41	8.75±4.60
Volatile matter	53.72±8.58	45.31±5.88	36.79±7.84
Ash content	2.02±0.47	1.58±0.03	1.38±0.45
Fixed carbon	31.52±4.92	48.11±7.33	53.08±2.79

Raw CS has the highest volatile matter (53.72%) followed by CSB (45.31%) and MCSB (36.79%). The volatile matter was removed during carbonization [24], thus explained the reduced value from raw CS to MCSB. The high temperature used during the carbonization process was responsible for the volatile matter to discharge from weaker bonds in the organic matrix and hence being released to the atmosphere [24]. The content of volatile matter for both CSB and MCSB are considered as high which might be due to the non-uniform carbonization of the CSB. Studies showed that at high temperature (between 450-600 °C) volatile matter content reported at 17.60-12.71%. On the other hand, CSB which were carbonized at the temperature range 350-400 °C attained the volatile matter between 50.17-24.82% [25]. Another study showed that the CSB has obtained volatile matter of 36.47% at 350 °C as well [26]. NaOH used during the biochar acid-base modification process also contributed to the discharge of volatile matter due to the organic matter decomposition in the biochar [24].

As for the ash content, MCSB has the lowest ash content with 1.38% as compared to raw CS and CSB. The fixed carbon of MCSB is 53.08% which indicates the sample has the highest carbon content. The escalation of the fixed carbon content was because of the removal of volatile matter [25]. High fixed carbon is associated with the efficiency of the said biochar [27]. The pH value of CSB is 10.94 and MCSB gives a pH value of 11.75. The pH value of MCSB could be high due to the NaOH washing during the modification process [28].

SEM images of raw CS, CSB and MCSB are shown in Fig. 1. It can be observed that the surface of raw CS is remarkably smooth and has no pore compared to the CSB and MCSB. The SEM images revealed that the surface morphology has been altered after the carbonization process and acid-base modification process. The presence of pores can be seen clearly in CSB and MCSB (Fig. 1(b) and (c)). However, it is observed that the MCSB has larger pores than CSB. The average pore diameters for MCSB is 50.6 µm which are far larger than CSB (16.7 µm) and raw CS (2.3 µm). The results indicated that the modification of the coconut shell is indeed successful.



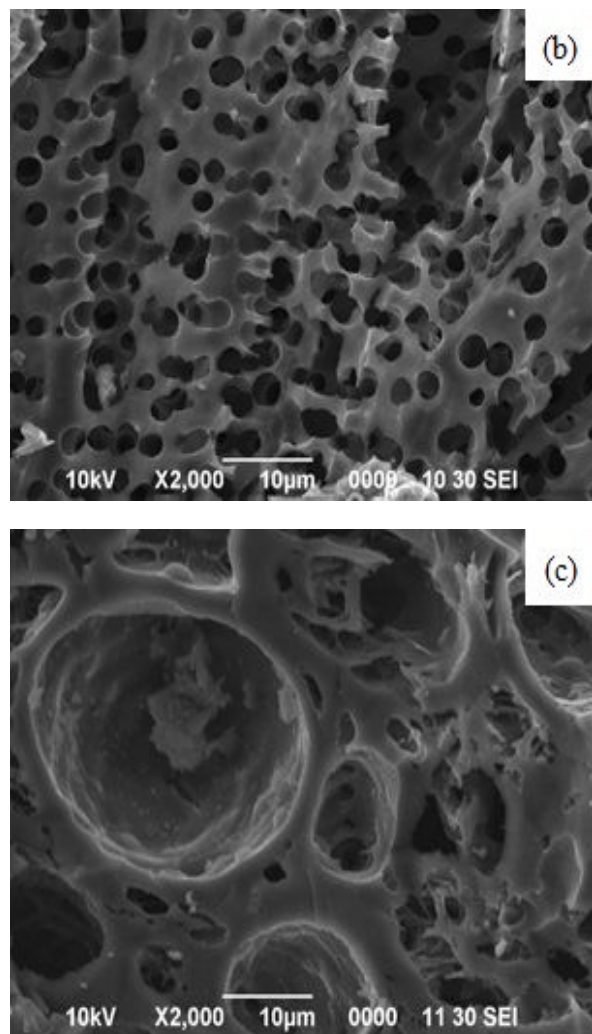


Figure 1. SEM images of (a) raw CS, (b) CSB 2000x and (c) MCSB at 2000x magnification

NaOH and HCl could increase the porosity of the modified biochar. This statement is supported by a study where the porosity of the adsorbent is high due to the presence of low volatile matter in the pores [27]. The addition of NaOH instigated an increment in the development of pores through an intercalation effect caused by the interaction of Na atom with the carbons in the biochar [29]. Base modification using NaOH and KOH can enhance the surface basicity and the amount of O-containing functional groups [26]. Whereas, the addition of HCl assists in removing the excess impregnating NaOH on the biochar surface and increasing surface

acidity which generates more acidic functional groups to enable strong interactions between the modified biochars and heavy metal later [22, 26]. Strong acids such as H_3PO_4 , H_2SO_4 , HNO_3 and HCl have been utilized to increase the acidities of the surface of the biochar as well as altering their porous structure [27]. Treatment with strong acids as a whole, can modify the surface functional groups of biochar via surface complexation and cation exchange thus enhancing the adsorption capability of the biochar [28]. MCSB has the lowest volatile matter thus indicating the high porosity of the said adsorbent. The large pores could efficiently enhance many liquid-solid adsorption processes [30]. Highly porous biochars have the advantage of more adsorption of pollutants such as heavy metals [30].

The surface area is one of the fundamental characteristics for carbon adsorbents such as biochar, activated carbon and biochar in order to identify its adsorption capacity [27]. The larger the surface area, the greater its adsorptive capacity [31]. In the present study, all samples were ground to the size of 0.30 mm. The surface areas obtained for both CSB and MCSB were quite small as compared to other studies, which might be due to the small size of the samples analyzed. Nevertheless, MCSB shows the highest surface area which is $246.896 \text{ m}^2/\text{g}$ followed by CSB ($185.712 \text{ m}^2/\text{g}$) and raw CS ($0.598 \text{ m}^2/\text{g}$).

The FTIR spectra of the raw CS, CSB, and MCSB are shown in Fig. 2. The pattern of the peaks is quite similar suggesting that all the samples should have a few functional groups that are comparable. The main characteristic that indicates the presence of lignocellulosic elements in the CS is when the functional groups such as C—O, C=O, C—H and O—H present in the spectra [32].

The presence of a strong and broadband between 3200 and 3500 cm^{-1} could be ascribable to the O—H stretching vibrations indicative of alcohol [33]. At the same time, this range of peak is ascribed to the presence of crystalline cellulose [18]. The peak at 2933.16 cm^{-1} (Fig. 2) corresponded to the stretching vibrations of aliphatic (C—H) which only presents in raw CS and absent in both CSB and MCSB [34]. Hence, indicating that the aliphatic stretching vibrations are lost after carbonization of CS due to the breaking of hydrogen bonding [34].

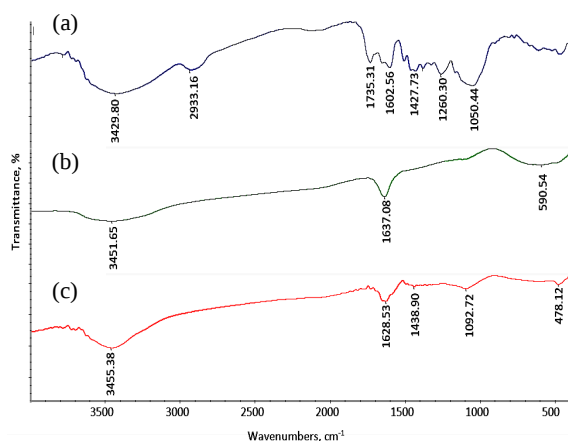


Figure 2. FTIR Spectrum of (a) raw CS, (b) CSB and (c) MCSB

Meanwhile, the peak at 1602.56 cm^{-1} in raw CS is also said to be C=C stretching vibration in the aromatic ring [33] though slightly weaker than peaks in CSB and MCSB. This implies that biochar has a higher metamorphic grade and the arrangement of its carbon structure is arranged more orderly as compared to its raw source [35]. Notably, C—O—C stretching vibrations at 1050.44 cm^{-1} and 1092.72 cm^{-1} in raw CS and MCSB, respectively, possibly indicate the presence of carbonyl components such as ethers, esters, carboxylic acid and alcohol groups [33]. These C—O—C stretching vibrations, however, do not appear in CSB. The peaks between 1400 and 1600 cm^{-1} could be ascribable to the C=O stretching which is responsible for adsorption characteristics [34, 36].

Adsorption Studies

Effect of initial concentration on Cu(II) removal

Adsorption studies were operated at different initial concentrations of 5, 10, 15, 20, 30, 50 and 100 ppm in mixed metal ions solution. The removal efficiency increased as the initial concentration of metal increases [37]. Based on Fig. 3, the percentage removal of Cu(II) ions by CSB appeared to be slightly increasing starting from the initial concentration of 5 ppm up to the initial concentration of 20 ppm. The increase in the adsorption of Cu(II) ions from the beginning until the end could be initiated by the interactions between Cu(II) ions and the active sites of MCSB [38]. The higher the Cu(II) ions concentration, the higher the amount of Cu(II) ions present in the solution, thus, the greater the adsorption of Cu(II) ions takes place on the adsorbent's adsorption site [38]. Despite that, a study of removal of Cu(II) from aqueous solution by activated carbon of palm oil empty fruit bunch showed a noticeably different result from the present study, as the percentage removal of Cu(II) ions decreased as the initial concentration increased [27]. The percentage removal of Cu(II) by both adsorbents at 30 ppm are also quite similar as the percentage removal for CSB was 98.46%, while the percentage removal for MCSB was 98.93%.

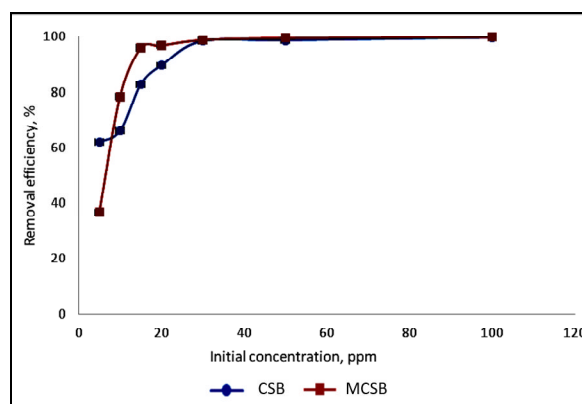


Figure 3. Effects of initial concentration on Cu(II) removal by CSB and MCSB

Effects of contact time on Cu(II) removal

The effect of contact time on the percentage removal of CSB and MCSB was studied for a contact time of 30, 60, 120, 150, 180, 210 and 240 min with constant concentration (30 ppm) and shaking speed (200 rpm). At 240 min, the amount of Cu(II) ions removed was (96.11%) which was the lowest percentage of removal by CSB (Fig. 4). The curve appeared to be declining after a slight increase in the initial stage. This might be ascribed to the great exposure of the adsorption sites on the adsorbents during the first 30 min [39]. Additionally, the decline curve might be caused by the repulsive forces between free Cu(II) ions in the solution which has limited access to the adsorptive sites of CSB [39]. The lowest percentage removal of Cu(II) by MCSB occurred at 60 min (96.74%) meanwhile the highest percentage removal of Cu(II) was at 150 min. The steep decrease which occurred at 60 min could be caused by the electrostatic forces between the ions in the solution or the solution could be simply contaminated [39].

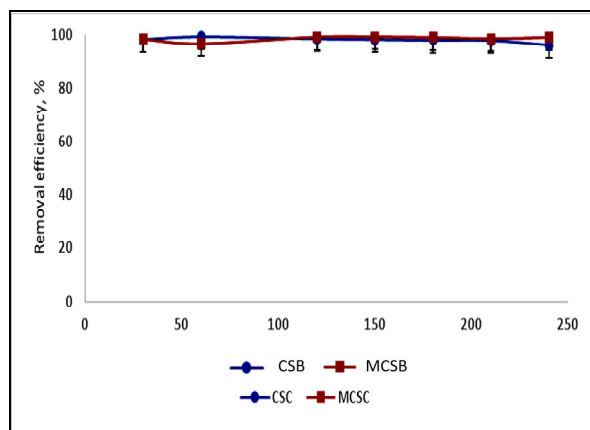


Figure 4. Effects of contact time on Cu(II) removal by CSB and MCSB

Adsorption isotherm

The Langmuir isotherm was tested for Cu(II) removal by CSB and MCSB. The linear plot of C_e/q_e against C_e was plotted to evaluate

the adsorption equilibrium of Cu(II) with CSB and MCSB, respectively (Fig. 5). Langmuir constants, $q_{\max}$ (maximum adsorption capacity) and K_L , can be obtained and calculated from the graphs shown. The value of $q_{\max}$ and K_L for Cu(II) ions adsorption by CSB were 0.3245 mg/g and -4.248 L/mg. The negative value of K_L indicates that Langmuir isotherm does not fit the data. Meanwhile, the value of $q_{\max}$ for MCSB was 4.027 mg/g and the value of K_L was 0.6989 L/mg. $Q_{\max}$ here implied that the CSB and MCSB have adsorption capacity of 0.3245 mg/g and 4.027 mg/g, respectively.

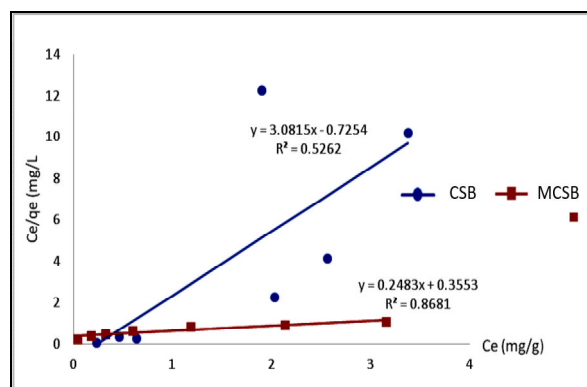


Figure 5. Langmuir isotherm for Cu(II) removal by CSB and MCSB

The value of the correlation coefficient, (R^2) for Cu(II) adsorption by CSB was 0.5262, whereas the value of R^2 for MCSB was 0.8681 indicating that the adsorption data for Cu(II) ion removal by both adsorbents do not fit well with the Langmuir model. A study of Cu(II) removal, displayed that adsorption data of Cu(II) fitted Langmuir isotherm [37]. As the Langmuir isotherm graph showed a linear plot, the adsorption of Cu(II) was said to be limited to only monolayer adsorption [32].

The Freundlich isotherm was tested based on the adsorption experiment for Cu(II). Linear plot of $\log q_e$ against $\log C_e$ was plotted to analyze the adsorption equilibrium of Cu(II) with CSB and MCSB, respectively

(Fig. 6). K_F and n are Freundlich constants which indicate adsorption capacity and adsorption intensity, respectively. Both constants can be calculated based on the equation from the graph.

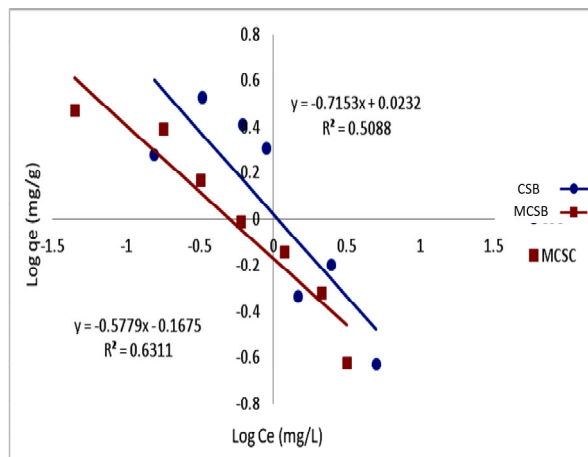


Figure 6. Freundlich isotherm for Cu(II) removal by CSB and MCSB

The value of K_F for CSB was 0.6790 and the value of n was -1.3980. On the other hand, the value of K_F and n for Cu(II) ions adsorption by MCSB were 1.0549 and -1.7304. The value of the R^2 for Cu(II) adsorption by CSB was 0.5088 meanwhile the value of R^2 for MCSB is 0.6311. Both Langmuir and Freundlich isotherms models could not be applied to explain and differentiate chemisorption and physisorption. However, isotherm models with heat of adsorption or mean adsorption energy gives information about chemisorption and physisorption [36]. Thus, it is strongly recommended to apply other isotherm models such as Dubinin-Radushkevich, in order to identify and describe the type of adsorption occurred during the adsorption of Cu.

From these results, it can be observed that the data fit with neither of the isotherms. Hence, other isotherms are strongly advised to be applied instead of Langmuir and Freundlich.

Experimental design and optimization of adsorption efficiency

A central composite design (CCD) with 17 experimental runs was used to develop the correlation between the operating variables of CSB and MCSB to the removal of Cu(II) from aqueous solution. Based on Table 2, the highest percentage removal for CSB was 99.53%, whereas 99.50% was the highest percentage removal for MCSB. This further concluded that the optimum condition for adsorption of Cu (II) by both adsorbents were pH 7, contact time of 60 min and particle size of 0.6 mm. In this study, both adsorbents worked best at pH 7. This result was in accordance with the result by a research [36], which also showed that pH 7.00 is the ideal pH for adsorption of Cu (II).

The response can be associated with the operating variables by linear or quadratic models [8]. In the present study, it was found that quadratic models fit the data as was suggested by the software. The equations of the quadratic model are as follows:

$$\text{Removal efficiency MCSB (\%)} = + 81.27 + 3.42A - 0.31B - 12.62C - 0.65AB + 7.04AC + 2.17BC - 27.8A^2 + 16.75B^2 + C^2 \quad (3)$$

$$\text{Removal efficiency CSB (\%)} = + 88.57 - 9.2A + 0.68B - 2.28C + 2.89AB + 2.91AC + 7.94BC - 27.67A^2 + 9.01B^2 + 10.75C^2 \quad (4)$$

which represents A: pH, B: Time and C: Particle size.

A, B and C represent pH of the solution, contact time and particle size, respectively. The coefficient with one factor demonstrates the effects of the variable itself, whereas the coefficient with two factors shows the effect of the interaction between

two factors [33]. Furthermore, the coefficient with the power of two represents the effect of quadratic factors. The negative signs indicate the antagonistic effect and the positive signs display synergistic effects [33]. The optimum conditions for time vs pH, time vs particle size and pH vs particle sizes for both CSB and MCSB can be seen in the three-dimensional response surfaces plotted in Fig. 7 and Fig. 8, respectively.

Table 2. Experimental factors and response with predicted and actual removal efficiency.

Standard	Parameters			Coconut shell biochar	Modified coconut shell biochar
	pH	Time (min)	Particle sizes (mm)	Actual removal efficiency (%)	Actual removal efficiency (%)
1	4.0	30.0	0.30	97.84 (105.18)	87.54 (89.91)
2	10.0	30.0	0.30	83.57 (75.20)	88.20 (83.95)
3	4.0	90.0	0.30	89.85 (84.89)	91.03 (86.24)
4	10.0	90.0	0.30	65.31 (66.45)	79.83 (77.70)
5	4.0	30.0	0.90	80.78 (78.93)	46.17 (46.25)
6	10.0	30.0	0.90	56.33 (60.58)	65.72 (68.45)
7	4.0	90.0	0.90	82.73 (90.40)	49.07 (51.26)
8	10.0	90.0	0.90	91.64 (83.60)	75.31 (70.89)
9	4.0	60.0	0.60	78.31 (70.10)	50.53 (50.67)
10	10.0	60.0	0.60	40.69 (51.71)	49.44 (57.50)
11	7.0	30.0	0.60	98.27 (96.89)	99.27 (98.33)
12	7.0	90.0	0.60	94.08 (98.26)	88.57 (97.71)
13	7.0	60.0	0.30	96.75 (101.59)	86.10 (94.89)
14	7.0	60.0	0.90	99.08 (97.04)	70.23 (69.65)
15	7.0	60.0	0.60	95.36 (88.57)	99.50 (81.27)
16	7.00	60.00	0.60	76.43 (88.57)	94.88 (81.27)
17	7.00	60.00	0.60	99.53 (88.57)	65.85 (81.27)

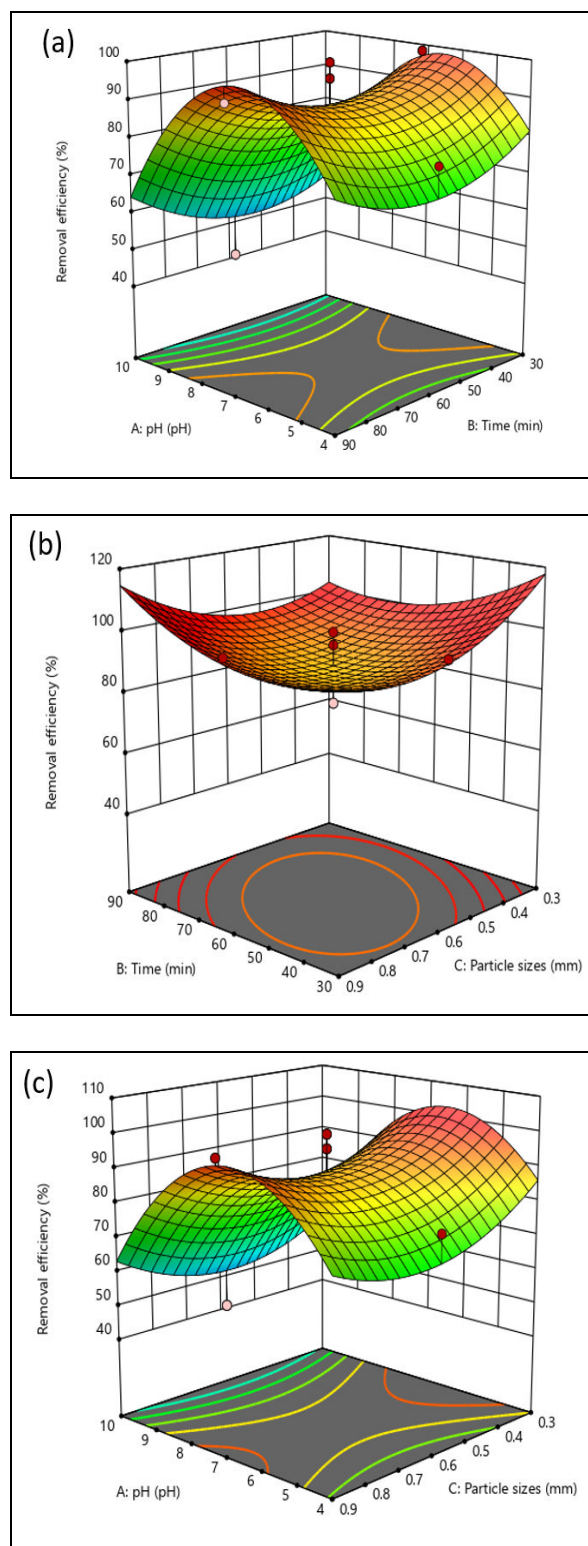


Figure 7. 3D response surface graphs showing the effect of (a) pH and time, (b) time and particle size, and (c) pH and particle size, on Cu (II) removal efficiency by CSB

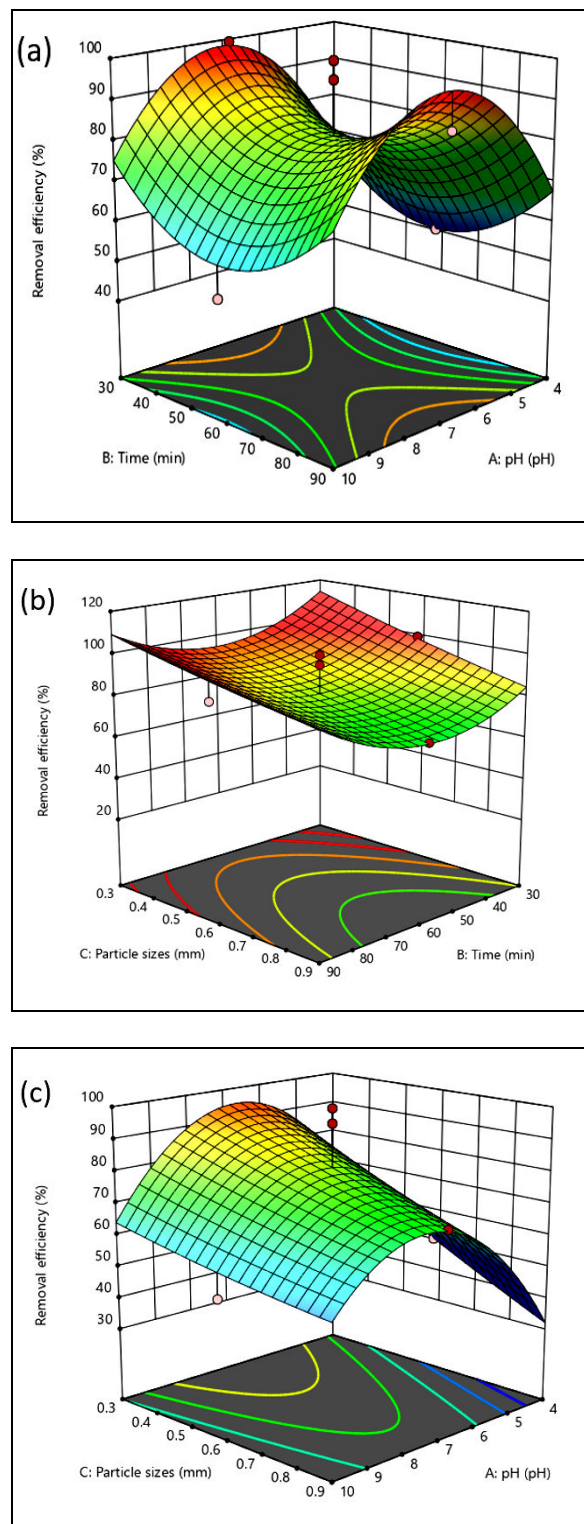


Figure 8. 3D response surface graphs showing the effect of (a) pH and time, (b) time and particle size, and (c) pH and particle size, on Cu (II) removal efficiency by MCSB

Conclusion

The current study concluded that MCSB can be applied as a low-cost adsorbent to remove Cu(II) from aqueous solution. MCSB is more effective than CSB in removing Cu(II) from aqueous solution. This is supported by the results where the average pore diameters for MCSB (50.6 μm) are far larger than CSB (16.7 μm), proving that the bigger the pore size of an adsorbent, the greater the adsorption capacity of that adsorbent. NaOH and HCl, which are used in modifying CSB, plays a significant role in increasing the adsorption capacity as it can enhance the expansion of microporous structure and create more porous sites in the carbon structure. Based on these results, MCSB can be potentially applied as an adsorbent in heavy metal removal.

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