Microcrystalline cellulose (MCC) as an adsorbent in copper removal from aqueous solution

N A Khalil¹, N S Abdullah¹, A S A Rahman¹, H A Hamid², A N S Fizal¹, M Zulkifli³, M S Hossain¹ and A N A Yahaya¹

¹Universiti Kuala Lumpur, Malaysian Institute of Chemical and BioEngineering Technology, 78000 Alor Gajah, Melaka, Malaysia
²Institute of Plantation Studies, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
³Green Chemistry & Sustainable Engineering Technology Cluster, Universiti Kuala Lumpur, Malaysian Institute of Chemical and BioEngineering Technology, 78000 Alor Gajah, Melaka, Malaysia
⁴School of Technology Industry, Universiti Sains Malaysia, 11800 USM Penang, Malaysia

Email: nafifah.khalil@s.unikl.edu.my

Abstract. Many studies have been done on the natural adsorbent, natural/raw cellulose, modified cellulose and modified MCC as media for removing copper. However, the usage of unmodified microcrystalline cellulose (MCC) as an adsorbent to remove heavy metals contaminants such as copper from an aqueous solution is scarcely being explored. Thus, the current study was done to assess the performance of the MCC, without any modification, based on the adsorption capacity and the Cu removal efficiency under varied process parameters. The MCC was successfully used for Cu²⁺ or Cu (II) removal at pH < pH6. The adsorption parameters such as pH (1 to 6), contact time (0.5 to 24 hours), temperature (25 to 70 °C), initial Cu concentrations (1 to 5 mg/L) and MCC dosage (0.05 to 0.5 g) were significantly influenced the adsorption performance of the MCC. This study indicated the adsorption process occurred at pH ranging from pH 2.8 to 6 with 3 to 24 hours of duration were required to achieve the equilibrium condition. Lower temperature ranges (25 to 30 °C) were more favourable for adsorption than higher temperature ranges (40 to 70 °C). The increase in initial Cu concentration enhanced the adsorption capacity of MCC but decreased Cu removal. On the other hand, the increase in the MCC dosage resulted in the decreased adsorption capacity, however, increased Cu removal. MCC dosage of 0.225 g managed to remove Cu (II) with 95% efficiency at the initial Cu concentration of 1 mg/L, pH 5 and temperature 25 °C within 24 hours of contact time with 0.18 mg/g of adsorption capacity. Overall, high Cu removal efficiency (up to 95%) was achieved by the MCC which render its usage as adsorbent.

1. Introduction

Heavy metals such as copper occur naturally as one of the constituents of the earth and are often described as reddish metal [1]. Copper (Cu) is the most precious and widely used metal in diverse industrial applications, for example, electroplating, metal polishing, building, automobiles, manufacturing of electrical machinery, cabling for power and telecommunications and making brass
and other similar alloys. Its major application such as in the electrical industries owing to its excellent electrical conductivity and heat conductor properties [2,3]. These industries generate a large volume of wastewaters containing copper as pollutants which can lead to several disorders and diseases if left untreated or inadequately treated [4]. This is because, heavy metals as pollutant such as Cu, has high resistance to biological and chemical degradation, high mobility and the potential to bioaccumulate in the food chain [5]. It has been mentioned that ingesting a certain level of Cu causes temporary gastrointestinal and intestinal problems, kidney or liver injury, and even cancer [4]. This warrants the treatment of Cu contaminated wastewater before discharging to the environment [6]. Cu can be removed either by utilizing adsorption, cementation, membrane filtration, electrodialysis or photocatalysis [3]. Adsorption has become an alternative treatment for those methods due to cleaner process, sustainable, cheap and eco-friendly process [7]. Adsorption is a process where a contaminant, which is Cu, is transferred onto the surface of an adsorbent from the liquid phase, bounded by physical and/ or chemical interactions [6].

Developments of polysaccharides-based adsorbents or biosorbent such as cellulose-based adsorbents have received extensive attention in recent years, due to their advantages such as low cost, renewability and non-toxicity [8]. In order to compete with other adsorbents, the new biosorbent materials must be an effective metal binder and perform well under various process conditions [9]. Sesame husk (SH) was studied as a natural adsorbent for Cu (II) with 2.5 mg/g adsorption capacity and 95.15% of removal at pH 6, 298 K, 1g of SH dosage, 30 mg/L of Cu (II) initial concentration and 300 rpm of agitation speed [10]. The study also indicated that cellulose participated in the adsorption and binding of Cu (II) ions beside other components. The disadvantages of cellulose including low adsorption or ion-exchange capacity and poor physical stability [11]. Therefore, modification of cellulose, for instance, chemical modification, crosslinking or copolymerization can be carried out to increase the adsorption capacity and efficient ion exchange capacity [8,9]. Raw cellulose from refined cotton was modified to cellulose nanofibrils managed to increase the adsorption capacity from 1.24 to 45.66 mg/g (condition: pH 5, temperature 30 °C, 100 mg/L initial Cu (II) concentration and 1 g/L adsorbent dosage) [12]. Cellulose nanofiber isolated from oil palm empty fruit bunch and synthesized into magnetic biosorbent composite with enhancing adsorption capacity of ~0.71 mg/g at 28 °C. 93.25% removal efficiency of Cu (II) by the composite (0.5 g/L dosage) was achieved after 30 mins under experiment conditions of pH 5 and 60 °C [13]. The composite may also easily be removed from an aqueous solution using a magnetic field and it has the potential to be reused. These are among chemical modifications that can give the cellulose new properties such as hydrophilic or hydrophobic character and improved water sorbency, ion-exchange capability elasticity and thermal resistance. The application of magnetic cellulose-based materials as adsorbents is also being explored for an easier separation adsorption process which facilitates regeneration [4].

Many studies have been done on the natural adsorbent, natural/raw cellulose, modified cellulose and modified microcrystalline cellulose as media for removing copper [10,12,13]. However, limited information is available on the adsorption performance of the unmodified microcrystalline cellulose, which is commercially available. The microcrystalline cellulose (MCC) is produced from natural polymeric cellulose of softwood, hardwood and other agricultural waste. The amorphous region of the cellulose was removed by partial depolymerization by enzymes or acids leaving the MCC in the crystalline form [14]. The process making it more suitable for heavy metal adsorption by increasing the surface area considerably [14]. Microcrystalline cellulose consists of separated crystalline aggregates of 1 to 100 μm in sizes with 3.5 to 4.5 m²/g of the specific surface area [15]. Microcrystalline cellulose is a readily available commercial source and could be used directly without any modification or pre-treatment [8]. Therefore, the objective of this work was to investigate the performance of the unmodified microcrystalline cellulose as an adsorbent for Cu removal. The focus was on the analysis of the parameter’s effects such as pH, contact time, temperature, initial Cu concentration and MCC dosage on the adsorption capacity and Cu removal efficiency.
2. Material and method

Microcrystalline cellulose, C_{14}H_{26}O_{11} (C.P., R&M Chemicals), copper (II) sulphate pentahydrate, CuSO_{4}.5H_{2}O (C.P., Bendosen) were used as an adsorbent and adsorbate in the batch experiment. 37% hydrochloric acid, HCl (Fisher Scientific) and sodium hydroxide pellets, NaOH (HmbG Chemicals) were used for pH modification. Figure 1 shows the overall flow of the experiment and analysis.

![Figure 1. The flow of the experiment and analysis.](image)

2.1. Preparation of solutions

2.1.1. 100 ppm Copper (II) Sulphate solution. 1000 ppm of copper (II) sulphate stock solution by adding 3.93 g of copper (II) sulphate pentahydrate in the 1L volumetric flask. Deionized water was filled until the calibration mark was reached, and the flask was well shaken.

2.1.2. 0.1 M Sodium hydroxide. 0.4 g of sodium hydroxide pellets were weighed, dissolved in deionized water, and stirred using a magnetic stirrer. The solution was poured into a volumetric flask of 100 mL. Deionized water was filled until the calibration mark was reached, and the flask was well shaken.

2.1.3. 0.1 M hydrochloric acid. 0.8 mL of 37% hydrochloric acid was transferred into a 100 mL volumetric flask using a pipette. Deionized water was filled until the calibration mark was reached, and the flask was well shaken.

2.2. Batch adsorption experiments

Microcrystalline cellulose powder was utilized without any modification in the batch adsorption study to assess the adsorption ability of the MCC on Cu. MCC will be used to indicate the unmodified MCC henceforth.

The adsorption studies were performed in a series of batch experiments. The effects of various adsorption parameters were studied, including pH (1 to 7), contact time (0 to 24 hours), temperature...
(25 to 70°C), initial concentration of Cu solution (1 to 5 mg/L) and dosage of adsorbent (0.02 to 0.5 g).

Generally, the experiment was conducted by the addition of MCC into Cu solution. The Cu solution of the intended concentration was prepared by diluting the necessary amount of 100 ppm copper (II) sulphate solution in deionized water. Followed by dosing the intended amount of the MCC with the intended dosage was added to the conical flask containing 50 ml of the Cu solution, which was then agitated. Sampling was done by pipetting the mixture using a 5 ml pipette at fixed intervals of 30 mins for the first hour and every 1 hour for the next hours. Each of the samples obtained was filtered before pipetting into the test tube for Cu analysis.

The effect of the pH experiment was conducted by the addition of HCl and NaOH to vary the pH value of the Cu solution. Concurrently, the effect of the contact time experiment was also being conducted by extracting samples at various time intervals. The conical flasks containing Cu solution was immersed in a water bath to obtain the desired temperature to study the effect of temperature. The MCC was added after the intended dosage (0.70°C), initial concentration of Cu solution (1 to 5 mg/L) and dosage of adsorbent (0.02 to 0.5 g).

The concentration of Cu was obtained by analyzing the sample extracted during the experiment. Atomic Absorption Spectroscopy (AAS) of PerkinElmer was used to analyze the Cu concentration in the sample. The adsorption capacity (q) was obtained based on the following equation [4]:

$$q = \frac{(C_0 - C_t) V}{M}$$  \hspace{1cm} (1)

where q is the quantity of Cu adsorbed onto the unmodified MCC [mg/g], C_0 is the initial Cu concentration [mg/L], C_t is the concentrations of Cu after the adsorption at a time [mg/L], V is the Cu solution volume [L] and M is the MCC mass [g].

The removal efficiency of Cu was be obtained based on the equation as follows [13]:

$$\text{Removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$  \hspace{1cm} (2)

where C_0 is the initial Cu concentration [mg/L] and C_t is the Cu concentrations the adsorption at a time [mg/L].

3. Results and Discussion

3.1. Effect of pH

Experiments were conducted by varying the pH of Cu solution from pH 1 to 7 at 25 °C, 24 hours of contact time, 5 mg/L of Cu initial concentration and 0.225 g of MCC dosage.

Figure 2 shows the adsorption capacity of the unmodified MCC in the Cu solution. The Cu adsorption was found constant at pH 1 to 2 (0.01 mg/g) and started to increase exponentially with an increase in pH from pH 2 to 5 (0.4 mg/g and 0.15 mg/g). The adsorption reached the highest value of 0.39 mg/g at pH 5, which was within an acidic region. The adsorption slightly declined at pH 6 (0.37 mg/g) and further declining to the lowest value (0.04 mg/g) at pH 7. This adsorption trend can be discussed by considering the MCC’s surface properties and the Cu species at various pH conditions [16]. The surface properties of the MCC can be explained by associating its isoelectric point (IEP) and zeta potential values. The IEP of the MCC particles occurred at a low pH value of pH 2.8 with a negative zeta potential value at pH above this IEP, which indicated the particles was negatively charged [8,15]. On the other hand, the species of Cu varied with pH where the predominant species is Cu^{2+} ions in pH < pH 6. Cu species such as CuOH^+, Cu(OH)_2^{2+}, Cu(OH)_2^+ and Cu(OH)_2^0 emerged when the pH of the solution was raised above pH 6 [10,17]. Therefore, the adsorption of Cu onto the MCC at pH < pH 6 was due to the interaction of Cu^{2+} ions (Cu (II)) with the binding site on the surface of
the MCC particle, which was negatively charged. As a result, the optimal pH for the adsorption process was determined at pH 5, as demonstrated by the highest adsorption at this pH.

The increasing trend at pH 1 to 6 range also can be explained by looking at the available ions in the solution due to pH adjustment. At pH 1 to 4, a lower value of Cu adsorption was observed as the H⁺ ions and Cu (II) competing to occupy the possible limited binding site on MCC [18]. The addition of HCl into the solution during pH adjustment resulted in high H⁺ ions concentration. The presence of H⁺ ions also resulted in repulsive force or electrostatic repulsion, restricting Cu (II) access to the functional groups of MCC [18,19]. As pH solution is being increased to pH 6, less HCl was added, implying that there were fewer H⁺ ions in the solution to compete with the Cu (II). As a result, the probability of Cu (II) binding to the MCC’s free binding sites was enhanced [20].

Figure 3 shows the removal efficiency of Cu at various pH. The removal efficiency of Cu shows the same trend as adsorption in between pH 1 to 6 and started to decline beyond pH 6. The removal of Cu at pH < pH 6 was via adsorption of Cu (II) by MCC, however, precipitation occurred above pH 6 [17,21]. Maximum removal of 39.3% was achieved and the optimum pH for removal was found at pH 6, by a possible combination of adsorption and precipitation processes.

![Graph](image_url)

**Figure 2.** Effect of pH on adsorption capacity (Contact time, 24 hours; Temperature, 25 °C; Initial Cu concentration, 5 mg/L; MCC dosage, 0.225 g).
3.2. Effect of contact time

Figure 4 shows the adsorption of Cu onto MCC for different contact time at pH 5 and 25 °C. Rapid adsorption was observed from 0 to 2 hours as the Cu (II) was easily attached to the unoccupied adsorption site of the MCC surface. The adsorption increased slightly in between 2 to 4 hours (0.35 to 0.36 mg/g). The adsorption rate was nearly consistent starting from 3 to 24 hours, indicated that most of the MCC adsorption sites were practically saturated with the Cu (II) [22]. The highest adsorption capacity was obtained at 24 hours, which was 0.39 mg/g. Figure 5 show a similar trend for Cu removal percentage, with the maximum Cu removal of 34.17% at 24 hours of contact time. Based on these analyses, the adsorption has reach equilibrium at 3 hours, with a maximum contact period of 24 hours.
Figure 4. Effect of contact time on adsorption capacity of Cu (pH, pH 5; Temperature, 25 °C; Initial Cu concentration, 5 ppm; MCC dosage, 0.225 g).

Figure 5. Effect of contact time on Cu removal (pH, pH 5; Temperature, 25°C; Initial Cu concentration, 5 ppm; MCC dosage, 0.225 g).
3.3. Effect of temperature

Adsorption capacity was analyzed at various temperatures of 25, 30, 40, 50, 60 and 70 °C for 3 hours of contact time and pH 5 to assess the temperature’s effect on adsorption, as shown in figure 6. The adsorption capacity was drastically increased with the increase of temperature from 25 to 30 °C (0.33 to 0.42 mg/g). The increased temperature subsequently increased the mobility of Cu (II) and ensure sufficient energy for the interaction of Cu (II) and the MCC’s active sites [23]. The adsorption started to decrease to the lowest value of 0.26 mg/g with the increase in temperature to 50 °C. However, an increasing adsorption trend was observed again from 50, 60 and 70 °C. The further increase in temperature reduced the viscosity of the solution and increase the rate of diffusion of the Cu (II) through the external boundary layer and in the MCC’s internal pores, hence, increased adsorption capacity [23]. Higher temperature applied in the adsorption process also caused the internal structure of the MCC to swell which allows more Cu (II) to infiltrate the pores of MCC [23].

The Cu removal efficiency is as shown in figure 7. The trend shows similarity to the adsorption capacity with the highest removal at 30 °C (38%), followed by 70 °C (34%) and the lowest removal happened at 50 °C (24%).

Figure 6. Effect of temperature on adsorption capacity of Cu (pH, pH5; Contact time, 3 hours; Initial Cu concentration, 5 ppm; MCC dosage, 0.225 g).
3.4. Effect of initial copper concentration

Figure 8 shows the adsorption capacity of MCC at varying initial Cu concentrations from 1 ppm to 5 ppm at two different temperatures (25°C and 70°C) and pH 5, respectively. The MCC as adsorbent at 25 °C shows the increasing trend when the Cu initial concentration was increased (1 to 4 mg/L) with the highest adsorption of 0.48 mg/g at 4 mg/L of Cu initial concentration. The increase of adsorption capacity with the increase of Cu initial concentration was due to more number of adsorption sites were available at low metal ion concentration, hence the process was highly effective within this range [24]. The increase in the initial concentration also can cause the mass transfer rate to increase due to the increase of driving force, hence, adsorption capacity increased [25]. A similar trend is shown with adsorption conducted at a higher temperature of 70 °C with a maximum of 0.45 mg/g of adsorption achieved at lower Cu initial concentration (3 mg/L). This trend suggested lesser surface interaction between MCC and Cu at a higher temperature. The high temperature might either tempered the texture of the adsorbent or possibly changed the surface chemistry by altering the amount of MCC’s active functional groups for adsorption. This lead to the reduction of sorption ability of the MCC due to degradation or damaging the surface active sites [10,26,27]. Besides, the active adsorption site may be destroyed due to bonds ruptured at higher temperatures leading to heavy metal’s desorption [28]. The thickness of the boundary layer of the biomass surface also decreases at higher temperatures causing the metal ions to flee into the solution phase and decreased the adsorption capacity [10]. Further increase of the initial concentration to 5 mg/L for both temperatures (25°C and 70°C) decreased the adsorption capacity to 0.33 mg/L. These declining values can be explained by beyond the said concentration, the adsorbent becomes saturated.

Figure 9 observed the declining trend of Cu removal efficiency for both temperatures (25 °C and 70 °C) with the increase of the initial concentration from 1 to 5 mg/L. When the initial Cu concentration was increased, more metal ions was available in the solution and trying to occupy the same amount of vacant site of MCC. This means lesser available adsorption sites compared to adsorbate, hence, lead to lower removal percentage of Cu (II) [24].
Figure 8. Effect of initial concentration on adsorption capacity (pH, pH5; MCC dosage, 0.225 g).

Figure 9. Effect of initial concentration on Cu removal (pH, pH5; MCC dosage, 0.225 g).
3.5. Effect of MCC dosage

The effect of MCC dosage on adsorption was analysed at two different temperature; 25 °C with 24 hours of contact time and 70 °C with 4 hours of contact time (pH 5 and 3 mg/L of initial Cu concentration) as shown in figure 10. At 25 °C, the adsorption capacity achieved the highest value of 0.35 mg/g when 0.1 g of MCC was added and slightly decreased when the dosage was increased to 0.3 g. At the lower dosage of MCC, the available adsorption sites were very low compared to the fixed metal ion concentration, hence, adsorption was easier to happen and achieved its capacity [29]. The adsorption value dropped significantly from 0.33 to 0.22 mg/g with further dosage addition to 0.4 g and remained constant at 0.5 g. In contrast, at higher MCC dosage, adsorbent particles had to compete each other to bind with the same metal ions which resulted in low unit adsorption of metal ions per unit mass of adsorbent [29]. Furthermore, the decreased in adsorption capacity was also due to the aggregation of adsorbent particles that lead to the reduction in total surface area and increased diffusion path length [10]. When the adsorption process was subjected to higher temperature of 70 °C, the adsorption capacity declined rapidly from 0.30 to 0.19 mg/g with the increased of MCC dosage (0.1, 0.225, 0.3, 0.4 and 0.5 mg/L). The higher temperature of 70 °C altered the surface of the MCC due degradation or damaging the active sites, hence the declining trend.

The removal percentage, contrastingly, shows the addition of MCC dosage increased the removal of Cu for both temperature (figure 11). The highest percentage removal was obtained at MCC dosage of 0.5 g/L for both temperatures within the experimental dosage range. The overall surface area and its availability of exchangeable binding sites on the surface for metal ion uptake were increased with the addition of MCC dosage, hence, rising the removal percentage of Cu [10].

![Figure 10. Effect of MCC dosage on adsorption capacity (pH, pH5; Initial Cu concentration, 3 mg/L).](image-url)
3.6. Comparison of MMC adsorption with another cellulose-based adsorbent

The adsorption of the MMC (0.44 mg/g) in this study is higher compared to sugarbeet pulp (0.15 mg/g) [10] as specified in table 1. However, the adsorption capacity is lower compared to other plant based adsorbent such as grape stalk wastes (0.78 mg/g), sawdust (1.7 mg/g), bagasse (2.89 mg/g), corn starch (8.57 mg/g) and sesame husk (11.37 mg/g) [10].

In addition, these cellulose-based adsorbents were normally went through modification in order to increase their adsorption capacity, i.e., cellulose nanofibril modified from cellulose of refined cotton managed to increase the adsorption from 1.24 to 45.66 mg/g [8,10]. Some researchers considered the application of magnetic cellulose-based materials as adsorbents due to its simple magnetic separation after the adsorption process which facilitate the regeneration [13,30].

Table 1. Adsorption capacity of various adsorbents.

| Type of adsorbent                             | Adsorption capacity (mg/g) | Reference |
|---------------------------------------------|----------------------------|-----------|
| Sugar beet pulp                             | 0.15                       | [10]      |
| Grape stalk wastes                          | 0.78                       | [10]      |
| Sawdust                                     | 1.70                       | [10]      |
| Bagasse                                     | 2.89                       | [10]      |
| Corn starch                                 | 8.57                       | [10]      |
| Sesame husk (D-R model)                     | 11.37                      | [10]      |
| Microcrystalline cellulose (unmodified)     | 0.44                       | This study|
| Raw cellulose (from refined cotton)         | 1.24                       | [12]      |
| Cellulose nanofibrils (from refined cotton) | 45.66                      | [12]      |
| Magnetic cellulose nanofiber composite      | 0.71                       | [13]      |

D-R = Dubinin-Radushkevich
4. Conclusion
The microcrystalline cellulose (MCC), without any modification, was successfully used as adsorbent for Copper (Cu) removal at pH < pH6 in the form of Cu$^{2+}$ or Cu (II). The adsorption parameters (pH, contact time, temperature, initial Cu concentration and MCC dosage) were significantly influenced the adsorption performance of the MCC. This study indicated that the adsorption process consists of MCC as adsorbent and Cu as adsorbate, occurred at pH ranging from pH 2.8 to 6, with 3 to 24 hours required to achieve the equilibrium condition. Lower temperature ranges (25 to 30 °C) were more favourable for adsorption than higher temperature ranges (40 to 70 °C). MCC dosage of 0.225 g managed to remove Cu (II) with 95% efficiency at 1 mg/L of initial Cu concentration, pH 5 and temperature 25 °C within 24 hours of contact time with 0.18 mg/g of adsorption capacity. The adsorption capacity was increased to 0.48 mg/g when the initial Cu concentration was increased to 4 mg/L, however, the removal efficiency reduced to 44%. The increased of initial Cu concentration increased the adsorption capacity of MCC but decreased the Cu removal. On the other hand, the addition in the MCC dosage resulted in declined adsorption capacity and increased the Cu removal. Overall, high Cu removal efficiency (up to 95%) was achieved by the MCC which render its usage as adsorbent.

Limitation of the unmodified MCC as adsorbent was due to the lower adsorption capacity, which translated into a lower active binding site compared to other adsorbents. Modification of the MCC by chemical modification, copolymerization, crosslinking or grafting can enhance the adsorption capability of the unmodified MCC. The MCC is favourable as a modified adsorbent framework due to its salient features of chemical and mechanical properties as well as the advantages due to its crystalline nature [31].

Acknowledgement
This work was supported by the Ministry of Higher Education (MoHE), Malaysia under Fundamental Research Grant Scheme (FRGS/1/2018/STG07/UNIKL/03/1). The authors would also like to acknowledge Universiti Kuala Lumpur for providing support under UniKL Excellent Research Grant Scheme (UniKL/CoRI/UER20016).

References
[1] Lenntech 2021 Copper - Cu Lenntech
[2] Market Research Reports 2021 Copper industry market research reports, analysis & trends Market Research Reports
[3] Al-Saydeh S A, El-Naas M H and Zaidi S J 2017 Copper removal from industrial wastewater: A comprehensive review J. Ind. Eng. Chem. 56 35–44
[4] Peng S, Meng H, Ouyang Y and Chang J 2014 Nanoporous magnetic cellulose-chitosan composite microspheres: Preparation, characterization, and application for Cu(II) adsorption Ind. Eng. Chem. Res. 53 2106–13
[5] Hokkanen S, Bhatnagar A and Sillanpää M 2016 A review on modification methods to cellulose-based adsorbents to improve adsorption capacity Water Res. 91 156–73
[6] Barakat M A 2011 New trends in removing heavy metals from industrial wastewater Arab. J. Chem. 4 361–77
[7] Lichtfouse E 2021 Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water vol 49 (Cham, Switzerland)
[8] Tan K B, Abdullah A Z, Horri B A and Salamatinia B 2016 Adsorption mechanism of microcrystalline cellulose as green adsorbent for the removal of Cationic methylene blue dye J. Chem. Soc. Pakistan 38 651–64
[9] Holan Z R, Volesky B and Prasetyo I 1993 Biosorption of cadmium by biomass of marine algae Biotechnol. Bioeng. 42 548–548
[10] El-Araby H A, Ibrahim A M M A, Mangood A H and Abdel-Rahman A A 2017 Sesame husk as adsorbent for copper(II) ions removal from aqueous solution J. Geosci. Environ. Prot. 05
[11] Kamel S, Hassan E M and El-Sakhawy M 2006 Preparation and application of acrylonitrile-grafted cyanoethyl cellulose for the removal of copper (II) ions J. Appl. Polym. Sci. 100 329–34

[12] Zhang N, Zang G L, Shi C, Yu H Q and Sheng G P 2016 A novel adsorbent TEMPO-mediated oxidized cellulose nanofibrils modified with PEI: Preparation, characterization, and application for Cu(II) removal J. Hazard. Mater. 316 11–8

[13] Khalid A M, Hossain M S, Ismail N, Khalil N A, Balakrishnan V, Zulkifli M and Yahaya A N 2021 Isolation and characterization of magnetic oil palm empty fruits bunch cellulose nanofiber composite as a bio-sorbent for Cu(II) and Cr(VI) removal Polymers (Basel). 13 1–22

[14] Nag S and Biswas S 2021 Cellulose-based adsorbents for heavy metal removal Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water ed Inamuddin et al. (Cham: Springer International Publishing) pp 113–42

[15] Mosur P M, Chernobezhzskii Y M and Lorentsson A V 2008 Electrosurface properties of microcrystalline cellulose dispersions in aqueous solutions of aluminum chloride, nitrate, and sulfate Colloid J. 70 462–5

[16] Hossain M A, Ngo H H, Guo W S and Nguyen T V 2012 Removal of copper from water by adsorption onto banana peel as biosorbent Int. J. GEOMATE 2 227–34

[17] Wang X S and Qin Y 2005 Equilibrium sorption isotherms for of Cu²⁺ on rice bran Process Biochem. 40 677–80

[18] Tan K L and Hameed B H 2017 Insight into the adsorption kinetics models for the removal of contaminants from aqueous solutions J. Taiwan Inst. Chem. Eng. 74 25–48

[19] Cao J, Fei D, Tian X, Zhu Y, Wang S, Zhang Y, Mao Q and Sun M 2017 Novel modified microcrystalline cellulose-based porous material for fast and effective heavy-metal removal from aqueous solution Cellulose 24 5565–77

[20] Reddy D H K and Lee S M 2013 Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions Adv. Colloid Interface Sci. 201–202 68–93

[21] Aydin H, Bulut Y and Yerlikaya Ç 2008 Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents J. Environ. Manage. 87 37–45

[22] Zango Z U and Shehu Imam S 2018 Evaluation of microcrystalline cellulose from groundnut shell for the removal of Crystal Violet and Methylene Blue Nanosci. Nanotechnol. 8 1–6

[23] Hameed B H and Ahmad A A 2009 Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass J. Hazard. Mater. 164 870–5

[24] Vijayalakshmi K, Gomathi T, Latha S, Hajeeth T and Sudha P N 2016 Removal of copper(II) from aqueous solution using nanochitosan/sodium alginate/microcrystalline cellulose beads Int. J. Biol. Macromol. 82 440–52

[25] Lin C, Qiao S, Luo W, Liu Y, Liu D, Li X and Liu M 2014 Thermodynamics, kinetics, and regeneration studies for adsorption of Cr(VI) from aqueous solutions using modified cellulose as adsorbent BioResources 9 6998–7017

[26] Shafqat F, Bhatt H N, Hamif M A and Zubair A 2008 Kinetic and equilibrium studies of Cr(III) and Cr(VI) sorption from aqueous solution using Rosa Gruss An Teplitz (Red Rose) waste biomass J. Chil. Chem. Soc. 53 1667–1672

[27] Areco M M and dos Santos Afonso M 2010 Copper, zinc, cadmium and lead biosorption by Gymnogongrus torulosus. Thermodynamics and kinetics studies Colloids Surfaces B Biointerfaces 81 620–8

[28] Ang X W, Sethu V S, Andresen J M and Sivakumar M 2013 Copper(II) ion removal from aqueous solutions using biosorption technology: Thermodynamic and SEM–EDX studies Clean Technol. Environ. Policy 15 401–7

[29] Argun M E, Güclü D and Karatas M 2014 Adsorption of reactive Blue 114 dye by using a new adsorbent: Pomelo peel J. Ind. Eng. Chem. 20 1079–84
[30] Peng S, Meng H, Ouyang Y and Chang J 2014 Nanoporous magnetic cellulose-chitosan composite microspheres: Preparation, characterization, and application for Cu(II) adsorption Ind. Eng. Chem. Res. 53 2106–13

[31] El-Naggar M E, Radwan E K, El-Wakeel S T, Kafafy H, Gad-Allah T A, El-Kalliny A S and Shaheen T I 2018 Synthesis, characterization and adsorption properties of microcrystalline cellulose based nanogel for dyes and heavy metals removal Int. J. Biol. Macromol. 113 248–58