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Synthesis of Copper Supported on Natural Rubber-derived Mesoporous Carbon/Silica Composite for Efficient Adsorption of Caffeine

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Abstract

Caffeine (CAF) removal from water resources is important because it is widely distributed and can be toxic to aquatic life. The copper supported on mesoporous carbon/silica composite (Cu/MCS) in this research was developed as a novel adsorbent to remove caffeine from aqueous solutions. The Cu/MCS material was prepared in two steps. The first step was the preparation of a precursor consisting of copper and natural rubber distributed inside a hexagonal mesoporous silica matrix (Cu/NR/HMS). Then, the composite was carbonized at high temperature under inert gas conditions to obtain Cu/MCS material. The amount of Cu loading in the MCS structure was studied. The Cu/MCS composites revealed a high level of copper distribution incorporated into the mesoporous carbon/silica framework as confirmed by Powder X-ray diffraction (XRD) and Scanning Electron Microscope and Energy Dispersive X-ray Spectrometer (SEM-EDS). The Cu/MCS materials possessed a high specific surface area (523–748 $m^2\ g^{-1}$), large pore volume (0.80–0.86 $cm^3\ g^{-1}$) and mesoporous diameter (3.07-3.30 nm). Fourier Transform Infrared Spectroscopy (FT-IR) and CHN analysis revealed a high amount of carbonaceous species dispersed in the Cu/MCS material. The Cu (0.010)/MCS, with copper loading of 1 mmol/g, revealed good properties for CAF removal when compared to other series of Cu/MCS adsorbents. Moreover, the Cu (0.010)/MCS composite exhibited the maximum adsorption capacity for CAF as 55.8 mg/g.

Keywords: *mesoporous carbon; carbon/silica composite; Adsorption of Caffeine; Natural Rubber; adsorbents*

1. Introduction

Caffeine (CAF) is one of the most consumed stimulant substances in the world, around 70 mg/day to 177.69 mg/day. It is a purine alkaloid and can be found as an ingredient in many different foods, beverages, and medications (Bachmann et al., 2021; Li et al., 2020). In addition, CAF is one of the personal care products most frequently found in, highly consumed, and constantly discharged into the global aquatic environment (Ondarza et al., 2019; Santos-Silva et al., 2018). Therefore, CAF poses problems for both environmental and public health. Many researchers aim to develop novel approaches to eliminate the polluted substances from environmental matrices. According to the literature, advanced technologies including ozonation (Ternes et al., 2003), membrane filtration, oxidation processes (Afonso-Olivares et al., 2016), and adsorption (Ptaszkowska-Koniarz et al., 2018) can be used to remove CAF from aqueous.

The adsorption approach is a promising method for eliminating CAF from water due to its many benefits, including an uncomplicated and adaptable design, ease of use, low initial costs, resistance to harmful contaminants, and reusability. In addition, the intermediate by-products are not generated during adsorption process (Li et al., 2020). The many literature reports of the adsorbents that can be used to treat environmental matrices polluted with CAF such as metal-organic frameworks (MOFs), activated carbon, zeolite, and mesoporous silica (Li et al., 2020; Santos-Silva et al., 2018). Recently, reports have emerged on synthesizing amine groups and copper modified carbon xerogels to enhance the adsorption efficiency of CAF. They exhibited high sorption capacities in the range 91–118 mg/g (Ptaszkowska-Koniarz et al., 2018). In addition, Cabrera-Lafaurie et al. (2012) reported the addition of copper (II) ions on the adsorbent surface also increased the affinity to caffeine molecules containing the heterocyclic-N group.

Mesoporous carbon/silica composites (MCS) have garnered significant attention in various fields such as drug delivery, energy storage, catalysis, and adsorption (Xu et al., 2011). The interest of this composite is in the combination of inorganic mesoporous silica and organic carbon species, which contributes to their unique mesostructure. Mesoporous silica framework has a high mesoporosity and specific surface area, as well as excellent thermal and mechanical stability. Its surface can be easily modified by post-synthesis grafting or direct co-condensation to introduce various active functionalities, broadening the application of use. Typically, the preparation of MCS composite is two steps. Initially, an organic substance (e.g., glucose, furfuryl alcohol and formaldehyde) is introduced as a carbon species into mesostructured silica. Subsequently, the organic material is carbonized or hydrothermally treated to turn it into carbon inside the silica matrix. This approach enables the development of adaptable materials with applications in a variety of fields. (Castillo, & Vallet-Regí, 2019). Yousatit et al. (2020) reported the synthesis of mesoporous carbon/silica composites using natural rubber (NR) as a cheap carbon source and applied them as the potential adsorbent for diclofenac adsorption. For this reason, the development of copper-containing mesoporous carbon/silica composite is interesting and can be applied to remove caffeine from wastewater.

The goal of this research was to synthesize and characterize copper supported on natural rubber-derived mesoporous carbon/silica composite (Cu/MCS) in various Cu loadings, and their application as adsorbents of CAF from aqueous. The structural and textural characteristics including morphology of Cu/MCS with respect to adsorption were examined by advanced analyses. The effects of different types of Cu/MCS adsorbents on the adsorption performance for CAF removal were investigated.

2. Objectives

The objective of this research is to find a method to synthesis and develop a highly efficient copper supported on mesoporous carbon/silica composite as adsorbent for removal caffeine in wastewater. This research also aims to study the interaction of Cu loading in MCS structure to enhance the adsorption capacity of caffeine and to compare them with that of pristine MCS.

3. Materials and methods

3.1 Materials and chemical reagents

Standard Thai Rubber (STR 5L) was provided from Thai Hua Chumphon Natural Rubber Co., Ltd., Thailand. Copper acetate monohydrate, Ethanol and Tetrahydrofuran (THF) were purchased from QREC Chemicals Co., Ltd., Tetraethyl orthosilicate (TEOS) and the dodecylamine (DDA) used in this research were purchased from Sigma-Aldrich.

3.2 Preparation of adsorbents

3.2.1 Preparation of MCS

As previously reported by Yousatit et al. (2020) the MCS composite preparation was carried out. A nanocomposite based on NR and hexagonal mesoporous silica (HMS) was a precursor to prepare MCS material. The NR/HMS composite was synthesized via an *in-situ* sol–gel technique. Typically, 10 grams of TEOS was applied to swell

0.5 g of the NR sheet with a thickness of 1 mm for 16 hours at room temperature.

The resulting swollen NR was weighed to determine the amount of TEOS uptake (~1.8 g), and then dissolved in THF (≈13.34 g) under vigorous stirring overnight to produce a colloidal solution. DDA (3.2 g) was then combined with a colloidal solution, and TEOS (≈ 8.7 g) was added dropwise while being stirred. Deionized water (52.3 g) was gradually filled to the mixture after 30 minutes, and it was stirred for an hour at 40°C. The gel that was formed completed a 3-day aging process at a temperature of 40°C, after which it was precipitated using 100 mL of ethanol. The solid product was obtained by the process of filtering and subsequent drying at a temperature of 100°C overnight. Finally, the DDA template was extracted from the 3.0 grams of as-synthesized NR/HMS nanocomposite by treatment in 150 mL of 0.05 M H_2SO_4/ethanol solution at 70 ºC for 4 h. Subsequently, the material was washed with ethanol and dried at 100°C for a duration of 2 hours.

The MCS composite was produced by subjecting the 10 grams of NR/HMS material to carbonization in a tube furnace. This process included employing under an argon atmosphere at temperatures of 350°C, 450°C, or 700°C. Each temperature was maintained for 1 hour, with a heating rate of 2°C per minute. The black solid obtained was subjected to a washing process using deionized water. Subsequently, it was filtered and dried at a temperature of 100°C for a duration of 2 hours to obtain the MCS material.

3.2.2 Preparation of Cu/MCS

The Cu/MCS composite materials with different amounts of Cu loading were prepared by adapting from previous report of Yousatit et al. (2020) and Ptaszkowska-Koniarz et al. (2018) First, the NR colloidal solutions were prepared using the same procedure as section 3.2.1 for 3 batches. Subsequently, DDA (3.2 g) was combined with each batch of rubber solution, and then TEOS (≈ 8.7 g) was added dropwise while agitating. After 30 min, 2 grams of copper acetate solutions with different concentrations of 0.003, 0.005 and 0.010 M were slowly added to the mixture while stirring at 40°C for a duration of 1 h. The blue gels obtained were subjected to a temperature of 40°C for a duration of 3 days, after which they were precipitated using ethanol. Finally, the retrieval of the solid product and the process of removing the template followed the exact steps outlined in section 3.2.1. The template-free composites were designated as Cu/NR/HMS materials.

The Cu/MCS composites were produced using the carbonization process of Cu/NR/HMS materials. The carbonization condition and procedure were the same as the preparation of MCS material in section 3.2.1. The resultant Cu/MCS samples are designated as Cu(*n*)/MCS, where *n* represents the concentration of copper acetate solution.

3.3 Characterization of MCS and Cu/MCS materials

The structural property of the synthesized materials was examined by powder XRD using an Empyrean 3 Panalytical diffractometer equipped with a Cu Kα radiation (λ = 1.5406 Å). The diffractometer was operated at 40 kV and 40 mA. The XRD patterns were obtained at ambient temperature, covering the 2θ range of 10 to 80°.

The measurement of N_2 physisorption isotherms was conducted at -196°C using Micrometrics ASAP 2020 equipment. A sample (≈50 mg) was subjected to heating in a vacuum at 150°C for 2 hours to remove any trapped gases. The determination of the specific surface area (S_{BET}) was conducted based on the Brunauer–Emmett–Teller theory, using adsorption information obtained at relative pressures (P/P_0) ranging from 0.05 to 0.3. The total pore volume (V_t) was determined using a relative pressure of around 0.99. The pore diameter was determined using the Barrett–Joyner–Halenda technique on the desorption branches.

The morphology of the adsorbent was investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). SEM images were acquired using a JEOL JSM IT800 instrument (JEOL Ltd., Tokyo, Japan) operating at an accelerating voltage of 15 kV. The sample powder was dispersed on copper tape and subsequently coated with gold to enhance image quality. The SEM micrographs were captured with a magnification of 50,000×. The EDS was used to examine the distribution of Cu crystallites. Transmission electron microscopy (TEM) was employed to examine the dispersion of copper tape within the material. TEM images were collected at a magnification of 500,000× using a JEOL JEM-

2100 Plus (JEOL Ltd., Tokyo, Japan), which operated at an accelerating voltage of 200 kV.

The carbon content in the mesoporous silica structure was determined using an Elementar Vario Micro Cube CHN elemental analyzer. The functional groups in composite adsorbents were characterized using a Perkin-Elmer Fourier-transform infrared spectrometer (FTIR). The sample wafer was made using the KBr technique. The FTIR spectra were obtained using transmittance mode within the frequency range of 400 to 4000 cm^{-1}.

3.4 Adsorption procedure

The effectiveness of MCS and Cu/MCS composites in adsorbing CAF was evaluated using static adsorption at room temperature. In general, a volume of 10 mL of CAF solution (150 mg/L) was combined with 0.01 g of a dried absorbent. The flask was carefully sealed and agitated on a shaker at a speed of 120 revolutions per minute for 12 hours to achieve the adsorption equilibrium. After that, the solution was passed through a filter to eliminate the adsorbent, then performed HPLC analysis. Equation (1) was used to determine the adsorption capacity (q_e).

Adsorption capacity:

$$q_e = \frac{(C_0 - C_e)V_i}{W} \tag{1}$$

where q_e represents adsorption capacity at equilibrium (mg/g$_{\text{dried adsorbent}}$); C_0 and C_e represent the initial and equilibrium concentrations, respectively, of CAF in the solution (mg/L); V_i represents the volume of the initial solution (L); and W represents the gram of the dried adsorbent (g).

4. Results and Discussion

4.1 Physicochemical properties of MCS and Cu/MCS composites

Figure 1 displays the XRD patterns and N_2 physisorption isotherms of the MCS and Cu/MCS, with various amounts of Cu loading. As shown in Figure 1A, the reflection peak at 2θ in the range of 15–30° was observed in all composite materials, indicating the presence of amorphous silica (Jermjun et al., 2023; Khumho et al., 2021). The distinctive peaks corresponding to Cu and/or CuO were not detected in the Cu(0.003)/MCS sample, indicating the MCS surface exhibited well-dispersed small crystallites of Cu and/or CuO. The characteristic peaks of CuO were strengthened by increasing the quantity of Cu placed on the MCS surface to 0.005 and 0.010 M at 2θ = 38° and 64.5° related to (111) and (022) reflection plane of CuO phase, respectively (Tounsi et al., 2015). In addition, the characteristic peak of Cu was observed at 2θ = 44° related to (111) reflection of Cu (Tounsi et al., 2015). These results indicated partly enlarged Cu and/or CuO particles in MCS structure (Yin et al., 2015).

The N_2 adsorption-desorption isotherms exhibited the mesoporous characteristics of all materials (Figure 1B), as per the IUPAC classification. The S_{BET} and V_t of Cu/MCS decreased significantly compared to the pristine MCS because of the dispersion of Cu content within the mesostructure framework (Table 1). However, the N_2 physisorption isotherms of Cu/MCS materials demonstrated that the mesoporous characteristics of MCS were preserved even after the addition of Cu (Figure 1B). The pore size distribution of the synthesized materials is shown in Figure 1B: inset. On the contrary, the Cu/MCS series displayed a broader pore size distribution than MCS, probably due to the incorporation of Cu inside the mesopores. The textural characteristics of all adsorbents are summarized in Table 1. The incorporation of Cu onto the MCS material resulted in a reduction in S_{BET} and V_t. Furthermore, as the quantity of Cu loading increased, the Cu/MCS series demonstrated an enhancement in textural characteristics. In addition, the Cu/MCS sample exhibited an elevated carbon content (12.1–15.6 wt%) as the Cu loading increased, as shown in Table 1. These results were consistent with Thiensuwan et al. (2023) who reported an insignificant change in the carbon species of Ru-based catalyst supported on an exfoliated LDO/carbon composite prepared in different Ru Loading and calcined at 500°C. These results suggested that the high content of carbon in Cu(0.010)/MCS, originated from CH_3COO^- remaining in the Cu/NR/HMS structure during the synthesis procedure. Therefore, the carbonization of Cu/NR/HMS to Cu/MCS material resulted in a high carbon content in Cu(0.010)/MCS attributable to high amount of copper acetate loaded in synthesis mixture.

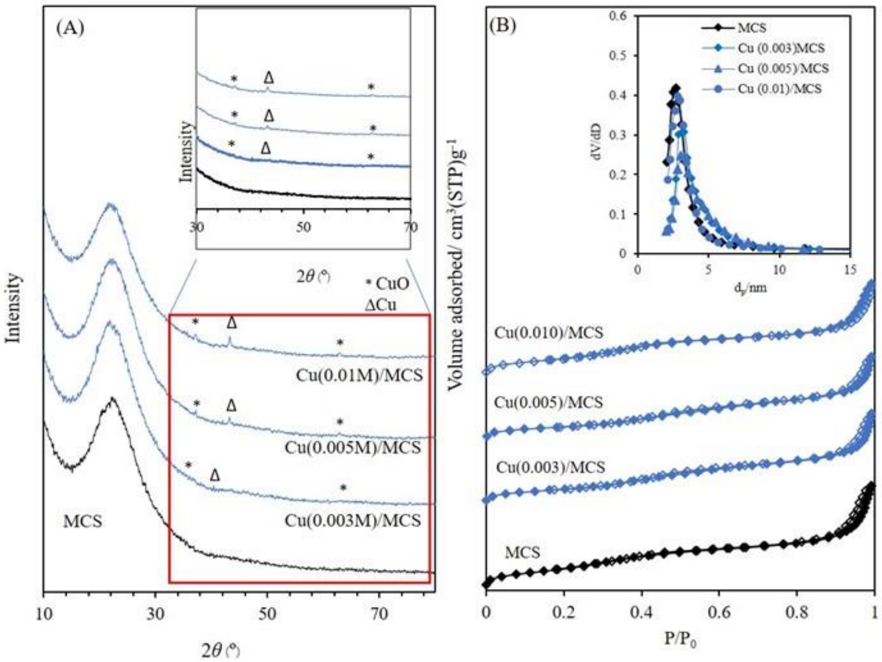

Figure 1 (A) XRD patterns, and (B) N_2 adsorption-desorption isotherms of MCS and Cu/MCS composites in various Cu loading amounts

Table 1 Cu, Carbon contents and textural characteristics of MCS and Cu/MCS materials.

Sample	Cu Content[a] (wt.%)	Carbon Content[b] (wt.%)	S_{BET}[c] (m^2 g^{-1})	D_p[d] (nm)	V_t[e] (cm^3 g^{-1})
MCS	*n.d.*	10.2	834.42	2.70	0.97
Cu(0.003)/MCS	4.2	12.1	523.66	3.07	0.80
Cu(0.005)/MCS	10.3	14.3	570.07	3.16	0.84
Cu(0.010)/MCS	18.6	15.6	747.70	3.30	0.85

[a] Determined by XRF.
[b] Determined by CHN analyzer.
[c] BET surface area
[d] Pore diameter, evaluated by the BJH method
[e] Total pore volume, evaluated by the volume adsorbed at P/P_0 = 0.99

Figure 2A and 2B show TEM images of MCS and Cu(0.010)/MCS, respectively. All samples showed the conventional uniform wormhole-like mesopores, corresponding to the previous report by Yousatit et al. (2020) However, the TEM images of both materials showed unclear morphology differences. The TEM image of Cu(0.010)/MCS (Figure 2B) exhibited more distribution of little black spots than that of MCS, which might be a result of the Cu and/or CuO crystallites being more evenly distributed on the surface of the absorbent. Furthermore, with higher levels of Cu loading, these crystallites might form agglomerates.

To observe the morphology and distribution of copper content on these materials, SEM-EDS were carried out (Figure 2C–2F). The pristine MCS exhibited tiny spherical particles and were found to be carbon moieties well dispersed in the silicate framework (Figure 2C and 2E), corresponding to previous report of Yousatit et al. (2020). However, the Cu loading resulted in significant agglomeration of Cu(0.010)/MCS composite (Figure 2D and 2F). However, the Cu/MCS material still revealed the good dispersion of carbon and Cu content on the mesoporous silica surface. From this result, it could be confirmed that Cu can be incorporated into the MCS structure, and it was evenly distributed on the surface of the adsorbent.

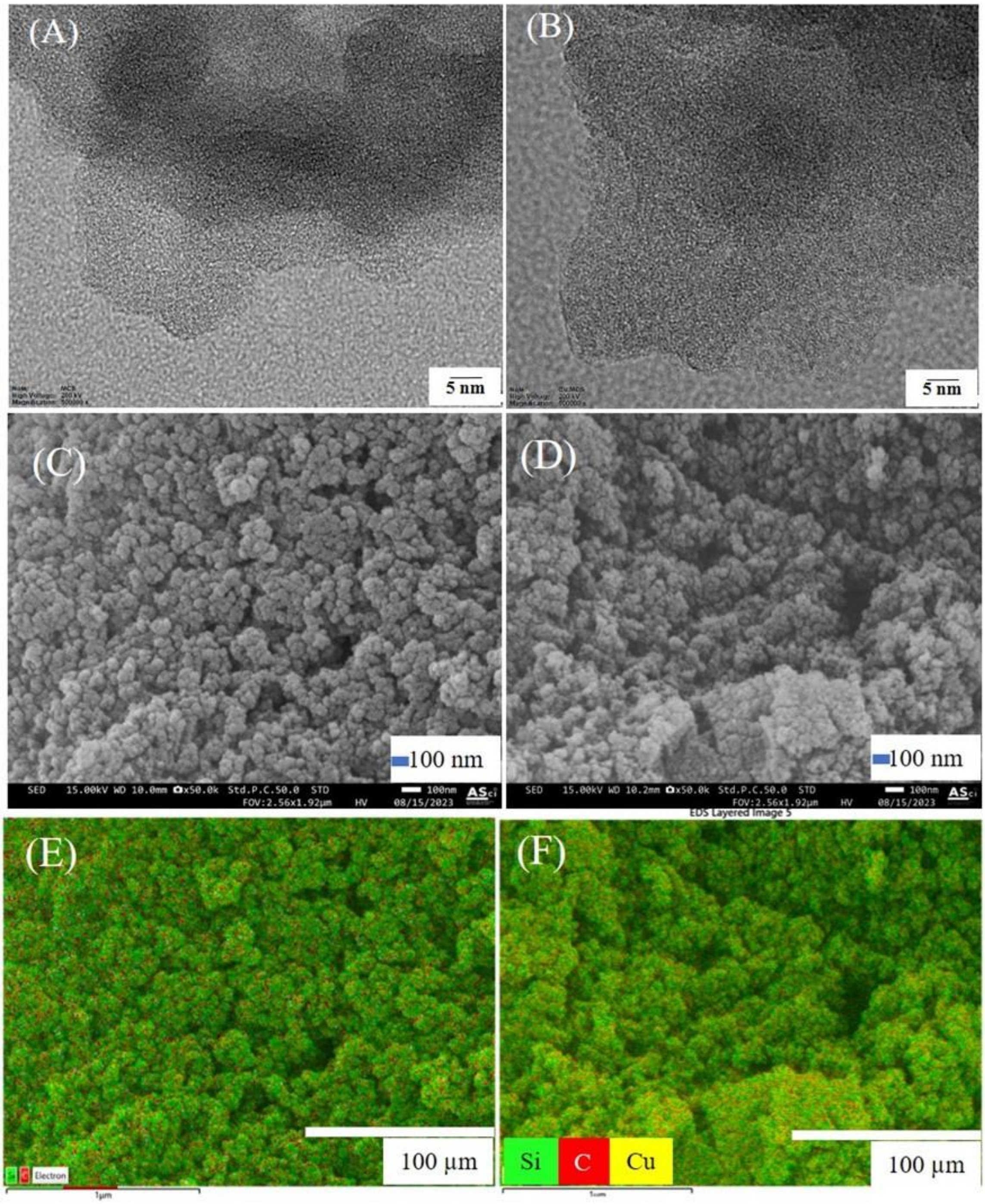

Figure 2 TEM images of representative (A) MCS and (B) Cu(0.010)/MCS composite at magnification of 500,000×; SEM-EDS images of (C, E) MCS and (D, F) Cu(0.010)/MCS composite at magnification of 50,000×.

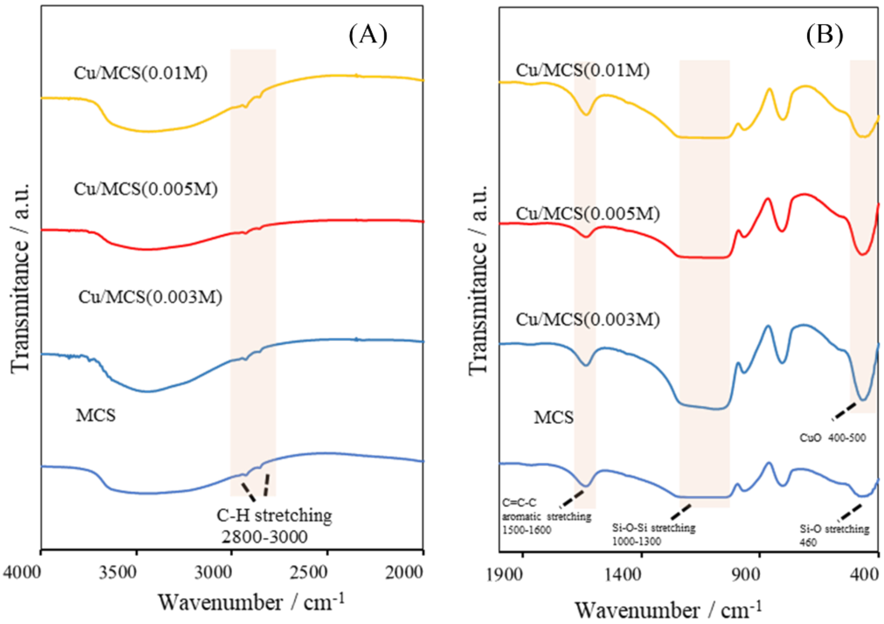

Figure 3 FTIR spectra of MCS and Cu/MCS composites at (A) high and (B) low energy ranges.

The presence of aromatic carbon and/or CuO in the silica structure of the MCS and Cu/MCS composites was evaluated using FTIR analysis. Figure 3 shows the presence of MCS and Cu/MCS composites in the range of 1000 to 1300 cm^{-1}, which corresponded to the stretching of the silica framework's Si–O–Si bonds. Additionally, a board peak at 3450 cm^{-1} indicated the presence of free silanol groups (Si–OH) (Jermjun et al., 2023). In addition, they observed the bands which corresponded to characteristics of the aromatic carbon at 1,550–1600 cm^{-1}, which related to C=C–C stretching (Yousatit et al., 2020). These results suggested that the NR phase was converted to aromatic carbon residue after the carbonization process. The presence of CuO in the MCS structure (Figure 3) was deduced from the bands observed between 400 and 500 cm^{-1}, which corresponded to the CuO (Tounsi et al., 2015). The Cu/MCS materials showed an intense peak at around 480 cm^{-1}, compared to the initial MCS material. This is consistent with the XRF results in Table 1, which exhibited an increase in the amount of Cu in the adsorbents. This result implied that CuO was incorporated into silica framework.

From the results of this study, we have developed a mechanistic model to explain the creation of Cu/NR/HMS composites by the sol-gel method. In addition, we have seen the transformation of the Cu/NR/HMS precursor into Cu/MCS composites via carbonization, as shown in Figure 4. Initially, the TEOS and DDA were uniformly dissolved in the NR solution, using THF as the solvent for the synthesis process. By introducing a solution of copper acetate, the TEOS underwent hydrolysis with H_2O to form silicate species. At the same time, the DDA molecules completed a rearrangement, forming micelles with a hexagonal rod-like structure. This rearrangement was facilitated by the hydrogen bonding between the hydroxyl groups of the silicate species and the amine groups of DDA. Furthermore, the silicate species and Cu^{2+} performed co-condensation, leading to the formation of copper-silicate aggregates that encapsulated the micellar rods. These aggregates subsequently arranged themselves into a hexagonal assembly in a random manner. During that time, the NR molecules emerged from the outer surface where the copper-silicate rods were irregularly arranged. Following the precipitation of the slurry in ethanol, the THF solvent was subsequently eliminated. The NR molecules were condensed and arranged inside the hexagonal copper-silica arrays, forming a composite framework of Cu/NR/silica.

The aim of this study was to use the Cu/NR/HMS composite as a precursor to convert it into Cu/MCS composite via carbonization. The thermal degradation of NR is a radical reaction. At temperatures over 450°C, the isoprene monomers of NR facilitated the breakdown and conversion of the substances into aromatic compounds, as reported by Yousatit et al. (2020).

4.2 Adsorption study of CAF on MCS and Cu/MCS composites

All composite materials obtained were evaluated as adsorbents of caffeine in water. Figure 5 shows the CAF adsorption capacity and percent removal of CAF by MCS and Cu/MCS composites in the simulated solutions. The amount of CAF adsorbed on the surface of the Cu/MCS adsorbents increased with increasing amount of Cu loading. Despite the Cu/MCS adsorbents having lower S_{BET}, and V_{t} compared to the pristine MCS, the composites exhibited greater adsorption capacities for CAF than the MCS material. These results corresponded with the research conducted by Ptaszkowska-Koniarz et al., (2018) which reported that the CAF molecule has a heterocyclic-N group that displays a high attraction to copper (II) ions found on the carbon xerogel adsorbent, which had been treated with copper to modify its surface (Ptaszkowska-Koniarz et al., 2018). In the case of CAF, the main driving force for adsorption was the interaction with the Cu content and the availability of a relatively large surface area, as evident by the Cu content and S_{BET} in Table 1. In terms of the adsorption driving force, these results suggested that it was a result of a mechanism involving hydrophobic partitioning, electrostatic interaction, and complexation with the Cu, which was reported by Cabrera-Lafaurie et al. (2012) The sorption capacities of Cu/MCS adsorbents varied in the range of 45–56 mg/g, which corresponded to a caffeine removal percentage of 70 – 78 %. In addition, the Cu(0.010)/MCS with high amount of Cu and carbon contents exhibited the maximum sorption capacity and % CAF removal as 56 mg/g and 78%, respectively. Since the aromatic carbon and Cu content could increase the adsorption affinity between CAF molecules and adsorbent surface due to chemical interaction, which was reported in previous studies (Ptaszkowska-Koniarz et al., 2018; Yousatit et al., 2020). Therefore, this sample was the most effective adsorbent of CAF.

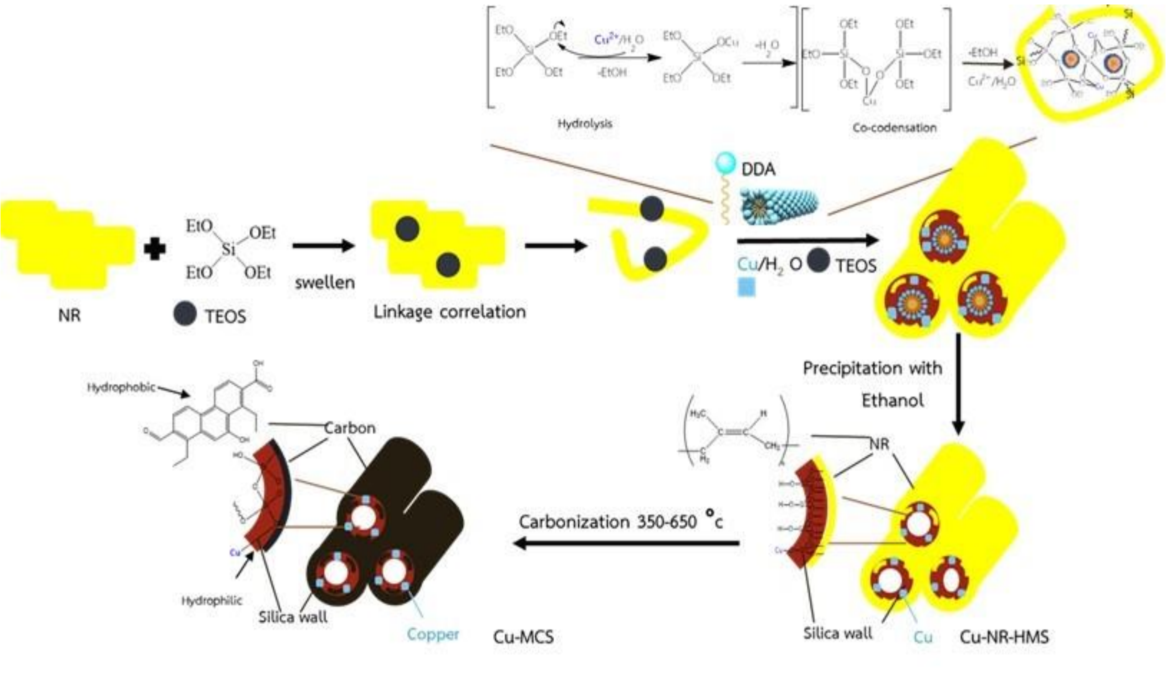

Figure 4 Schematic diagram of mechanistic model illustrating the creation of Cu/NR/HMS composite and its subsequent transformation into Cu/MCS.

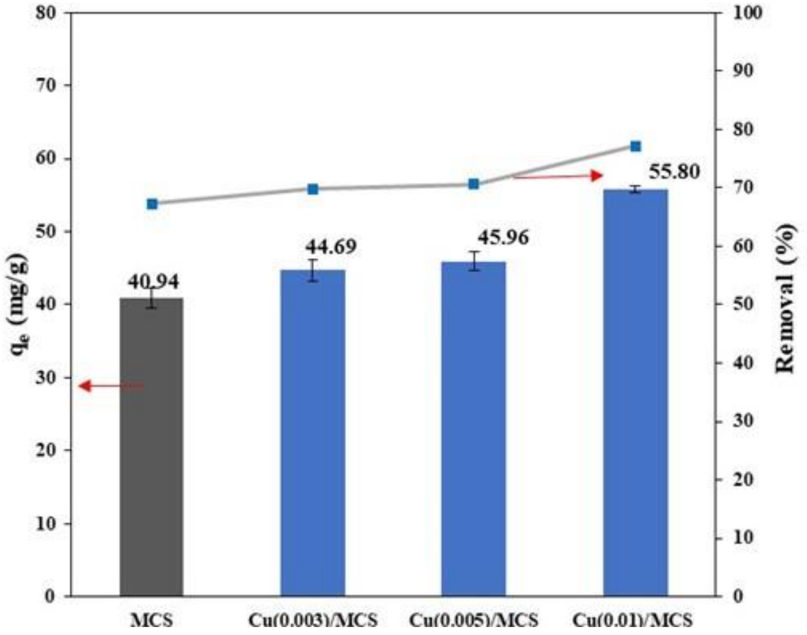

Figure 5 Adsorption capacity and % Removal of CAF on MCS and Cu/MCS composites.

5. Conclusion

The Cu/MCS composites with diverse mesoporosity and varying amount of Cu loading were successfully prepared via carbonization using the synthesized mixture of copper acetate and NR distributed in mesoporous silica as a precursor. They were applied as a potential hybrid/composite adsorbent for CAF removal from water. It was found that using the Cu/MCS adsorbents for the adsorption of CAF from water was more effective compared to the original MCS material. The characterization study indicated that the Cu/MCS composites exhibited an amorphous silica structure with aromatic carbon residue and CuO integrated into their surface. The Cu/MCS exhibited a good dispersion of carbon and Cu content on the mesoporous silica surface. Furthermore, they exhibited extensive surface area and pore volume, making them very effective adsorbents. Following the adsorption results, the Cu(0.01)/MCS adsorbent, which had a significant amount of Cu loading, demonstrated efficacy in removing CAF. The Cu(0.01)/MCS material exhibited a maximum adsorption capacity of 55.8 mg/g for CAF.

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