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Reversible adsorption of metalworking fluids (MWFs) on Cu-BTC metal organic framework



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ABSTRACT

Metalworking fluids (MWFs) are classified as hazardous substances. Due to the characteristics of the stable oil–water emulsions, it requires more costly and complicate treatment techniques to remove oil from spent MWFs. Metal organic frameworks (MOFs) are a porous network material used to remove contaminants from environment. One of the most prominent of MOFs is HKUST-1 or Cu-BTC. In this study, the Cu-BTCs were prepared by solvothermal method in various conditions and used as adsorbent for removing oil micelles in MWF emulsion. The particle size of all synthesized Cu-BTCs ranged from ≈ 80 to 400 nm. The ability of all synthesized Cu-BTCs to remove oil micelle was greater than 95% in 60 min, while the capacity of GAC was obtained the result for only 6.8%. The maximum adsorption capacity ($q_{\max}$) of oil micelles on Cu-BTCs was $1666.7 \text{ mg} \cdot \text{g}^{-1}$. The highest removal capacity of oil micelles in MWF emulsion is greater than 99% in 24 h by using Cu-BTCs washed with either butanol or ethanol.

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1. Introduction

Metalworking fluids (MWFs) or cutting fluids, a group of industrial lubricating oil, are used for cooling, lubricating and carrying away any chip and fine produced during cutting, turning, grinding and drilling processes. Therefore, the spent MWFs are considered as one of the hazardous wastes. The main environmental risk associated with the discharge of spent MWFs is the mineral oil portion of the MWF emulsion, which is usually recalcitrant to biological degradation and threatens the biological activity in natural water bodies [1]. On the surface water, they could form a thin film which inhibits the exchange of gases between the water and the atmosphere; consequently it causes the ecosystem perturbations. The pretreatment of spent MWFs before further disposal requires multifarious methods due to their stable oil–water emulsions. Presently, coagulation, advanced oxidation processes, ultrafiltration, and biological treatment are used to reduce hazardous wastes in spent MWF. However, the destabilization to remove oil in spent MWF emulsions cannot be achieved in one step because they contain emulsifying agents such as fatty acid soap, fatty acid ethoxylates, and petroleum sulfonates [2].

Metal organic frameworks (MOFs) are a porous network material synthesized by combining metal ions and multidentate organic anions.

MOFs have been applied in many applications such as gas storage and separations of gases, catalyst, drug delivery and adsorbent for metal ions, dyes, and other organic compounds [3–8]. A very few studies have been conducted in the oil-droplet separations.

One of the most prominent MOFs is HKUST-1. It is composed of copper (Cu) as a metal part and benzene-1,3,5-tricarboxylate (BTC) as an organic part or linker. It was first explored and reported the crystal structure in 1999 by Chui *et al.* [9]. The synthesis was carried out by using a solvothermal method under solvent ratio (water to ethanol) of 1:1, aging at 180 °C for 12 h. Wang *et al.* (2002) established the synthesis of Cu-BTC for a large-scale production at lower temperature (110–150 °C). The material was further applied for the gas separation such as CO_2 –CO, CO_2 – CH_4 and C_2H_4 – C_2H_6 with high sorption selectivity [10]. It was reported that the lower amounts of Cu_2O would lower aging temperature condition required in the synthesis [11]. To synthesize Cu-BTC at room temperature, amide solvent such as dimethylformamide (DMF) has been recommended by Khan *et al.* (2009) to be added in the reaction [12]. Rowsell and Yaghi (2006) prepared Cu-BTC at 85 °C for 20 h under a solvent mixture of DMF/ H_2O /ethanol and studied the effect of H_2 adsorption properties [13]. They found that the H_2 adsorption of Cu-BTC was approximately two times greater than that of IRMOF-1 (Zn-Benzene-1,4-dicarboxylate, Zn-BDC) at 1 atm. Although, the Cu-BTCs observed at low temperature conditions were well-formed crystallites with high purity, they have to be activated by immersion in dichloromethane for 3 days and evacuation

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at 170 °C overnight. Liu *et al.* (2007) developed the activation process by extracting solvated DMF from Cu-BTC crystals with methanol in a Soxhlet extractor overnight. They found that the measured pore volumes and the total amount of H₂ adsorbed were larger for the material activated with this procedure than any other Cu-BTC material in the previous report [14]. Even though, DMF is necessary for the formation of MOFs in low temperature conditions in order to facilitate deprotonation of carboxylic acid group [12,15], however, it is classified as toxic to reproduction and have to use complicated procedures and take more time for activation to remove these solvents from obtained Cu-BTCs. Therefore, the normal condition for the preparation of Cu-BTC has been a remarkable issue for further study. A selection of copper precursor is very important, because the copper acetate could form Cu-BTC more easily at low temperature and shorter of the aging time, which further produce acetic acid as a by-product. Copper acetate was also highly recommended because of its paddle wheel dimers in properties and less toxic in by-product [16].

In this work, the Cu-BTCs were prepared by solvothermal method in various conditions and used as absorbent for removing oil micelles in MWF emulsion. A reusability of the prepared Cu-BTC by washing with ethanol and butanol was also studied. The surface properties for both pristine and spent adsorbents have been characterized and also reported in this study.

2. Experimental

2.1. Chemicals and materials

Copper acetate monohydrate (SDFCL, ≥98%), benzene-1,3,5-tricarboxylic acid (Acros organics, ≥98%) and ethanol (CARLO ERBA Reagents, ≥99.9%) were used for Cu-BTC preparation by solvothermal method. Butanol (Fluka, ≥98%) and ethanol (CARLO ERBA Reagents, ≥99.9%) were used for the regeneration of the used Cu-BTC. Metalworking fluid (Solar Ultra-coolant 105 soluble cutting oil) was obtained from Solaris Petrochemical Ltd., Part., Thailand. Activated carbon used for a comparative adsorbent was in granular form, GAC, supplied by Carbokarn Co., Ltd., Thailand.

2.2. Synthesis of Cu-BTC

Copper acetate monohydrate (18 mmol) was dissolved in deionized water. Then, benzene-1,3,5-tricarboxylic acid or H₃BTC (12 mmol) dissolved into ethanol was added into the copper acetate solution. The ratios of water to ethanol in 150 ml of solutions were 3:1, 2:1 and 1:1 (v/v). The solution was stirred for 30 min and transferred into 200 ml teflon-lined stainless steel autoclave. The autoclave was kept at 80, 100 or 120 °C for the timing periods of 8, 16 or 24 h in the oven. Then the autoclave was allowed to cool down to the room temperature naturally and the Cu-BTC (blue powder) was isolated by using a centrifuge. Finally, the blue powder was washed with the ethanol for 3 times and dried in a vacuum oven at 100 °C for 24 h.

2.3. Characterizations

The crystalline structure of the synthesized Cu-BTC was identified by an X-ray diffractometer (Bruker AXS Model D8 Discover, Germany). The thermal stability was studied by Thermogravimetric analyzer (Shimadzu TGA-50, Japan). The sample was heated in a nitrogen atmosphere from room temperature to 450 °C with a rate increase of 5 °C·min⁻¹. Fourier transform infrared (FT-IR) spectra were taken with a FT-IR spectrophotometer (Bruker vertex70, Germany) at room temperature. Scanning electron microscope (SEM; JEOL JSM-6610LV, Japan) was used to observe the morphologies of the synthesized Cu-BTC. The surface areas were determined using N₂ adsorption-desorption technique at 77 K. The sample was degassed at 150 °C for 12 h under vacuum prior to the measurement.

2.4. Oil micelles removal and adsorption study

Oil-in-water emulsion was prepared by mixing soluble oil MWF in D.I. water. Oil micelles removal was conducted by adding the synthesized Cu-BTC into MWF emulsion and stirred for 1 h. Each of the experiment was performed with an initial MWF emulsion concentration of 0.5 g·L⁻¹ and 50 mg of the synthesized Cu-BTC was added in 50 ml of MWF emulsion.

To investigate the characteristics and the oil removal capacities of Cu-BTCs, the equilibrium adsorption was studied. The experiments were conducted by adding 0.05 g of synthesized Cu-BTC into 50 ml of various initial concentrations (C₀) of MWF emulsion ranging from 250 to 2200 mg·L⁻¹. They were stirred for 24 h to ensure that the reaction reached the equilibrium.

The turbidity of the emulsion was also measured to investigate the efficiency of oil micelles removal by using a turbidimeter (WTW TURB 350IR, Germany).

2.5. Reusability of Cu-BTC

The oil-rich Cu-BTC was dissolved in butanol and the mixture will be stirred at 300 rpm for 2 h at ambient temperature to remove the oil adsorbed from Cu-BTC. The washed Cu-BTC was centrifuged, washed with ethanol, and dried in a vacuum oven at 100 °C for 24 h to remove the residual solvent from the Cu-BTC. Then, the regenerated Cu-BTC was characterized and used to remove oil micelles in the MWF emulsion.

3. Results and Discussion

3.1. Characterization of Cu-BTCs

The XRD patterns of 27 Cu-BTC samples synthesized with different solvent ratios of water to ethanol (3:1, 2:1 and 1:1 v/v), temperatures (80, 100 and 120 °C), and aging times (8, 16, 24 h) are not significantly different from each other. They show the major diffraction peaks at 2θ ≈ 6.7°, 9.6°, 11.7° and 13.4° representing the planar of {200}, {220}, {222} and {400}, respectively. Hence, they corresponded to the characteristic pattern in the literature, however, the moisture from the air could affect to the variations in intensities of peaks [10,11,17,18]. Moreover, the XRD patterns for all of the samples did not occur for the peaks of Cu₂O at 2θ ≈ 36.4°, 42.3° and 43.3°. Therefore, these results indicate that all of the Cu-BTC samples were successfully synthesized with high purity for all of the conditions in this study. Fig. 1 shows the

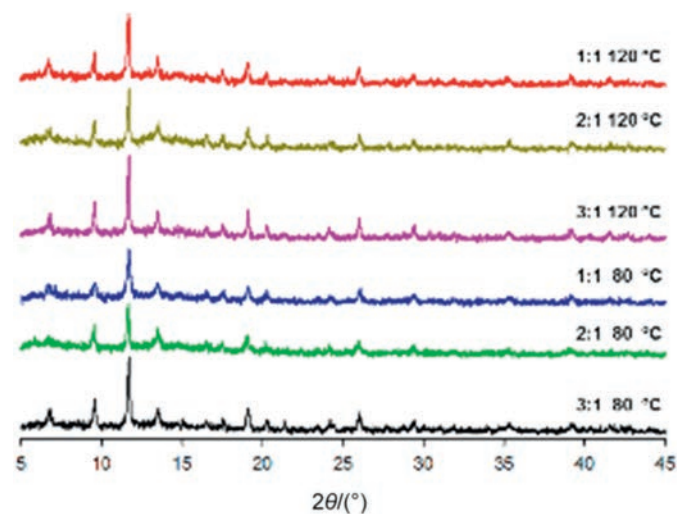


Fig. 1. XRD patterns of Cu-BTCs synthesized in solvent ratio 3:1, 2:1 and 1:1 of water to ethanol at 80 and 120 °C for 8 h.

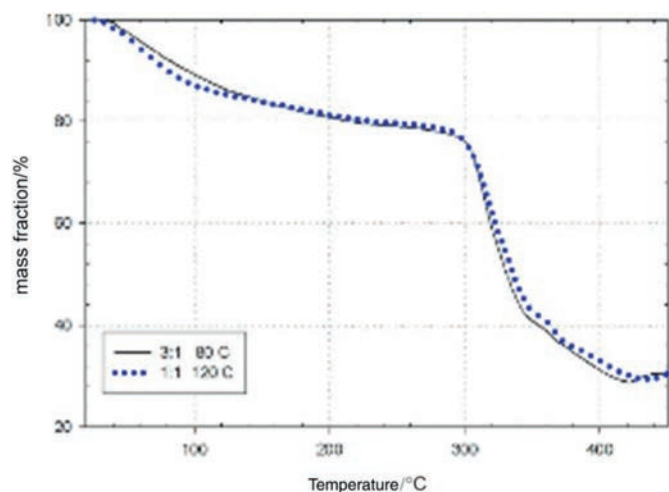


Fig. 2. Thermogravimetric analysis of Cu-BTCs synthesized in solvent ratio 3:1 and 1:1 of water to ethanol at 80 and 120 °C for 8 h.

selected XRD patterns of 6 Cu-BTC samples synthesized with different solvent ratios and temperatures for 8 h.

The syntheses for all of the samples using copper acetate as a precursor with the different conditions show the high yields from 87.3% to 94.7%. The maximum yield was obtained at 120 °C for 8 h in the solvent ratio of 2:1 water to ethanol. Shekhah *et al.* (2009) found that the dominant unit in the copper acetate solutions is the acetate-bridged

paddle wheel which is similar with BTC-bridged dimers of Cu-BTC framework [16]; therefore, using copper acetate as a metal source could actually activate the improvement of the productivity in a short period of reaction time.

The thermal stability of synthesized Cu-BTCs was studied from room temperature to 450 °C. The thermogravimetric curves of 2 Cu-BTC samples synthesized for 8 h in solvent ratios of 3:1 water to ethanol at 80 °C and 1:1 water to ethanol at 120 °C were shown in Fig. 2. During the first stage of ca. 30–200 °C, the weight loss of ca. 20% was observed. This was caused by the dehydration of water combined in the Cu-BTC framework. The decomposition of the framework was observed at the temperature greater than 280 °C [17]. Because the curves for the samples were not significantly different, therefore, the thermal stability was not affected by temperatures and solvent ratios using in the synthesis of Cu-BTC.

SEM images of Cu-BTCs synthesized for 8 h with the different temperatures and solvent ratios of water to ethanol were shown in Fig. 3. The particle size ranged from ≈ 80 to 400 nm which was quite smaller than the size of those particles which were synthesized by solvothermal method in previous reports ($> 10 \mu\text{m}$) [10,17–19]. The small particles are useful for regeneration of the used catalyst and it is also effective to prepare membranes or films [12].

The morphology of synthesized Cu-BTCs is octahedral losing sharp edges as shown in Fig. 4. Moreover, the syntheses of Cu-BTC in wholly aqueous solvent system at 80 °C for 8, 16 and 24 h are not successful because the obtained results of the blue solids do not show morphology patterns of crystals as shown in Fig. 5. This may be caused by the insolubility of H_3BTC in the water. The reaction between H_3BTC and Cu to form the Cu-BTC crystals cannot be occurred completely.

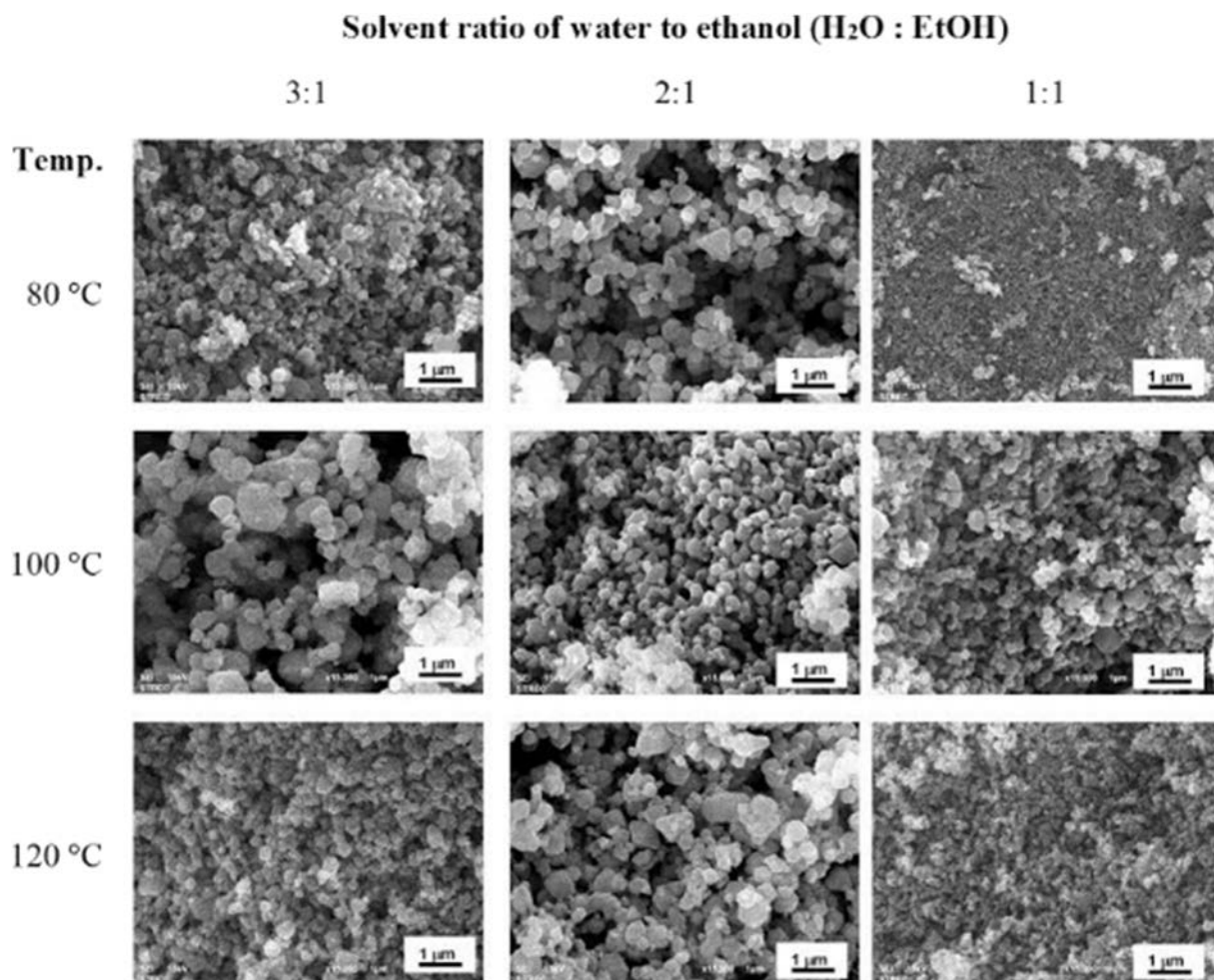


Fig. 3. SEM images of Cu-BTCs synthesized for 8 h with different temperatures and solvent ratios of water to ethanol.

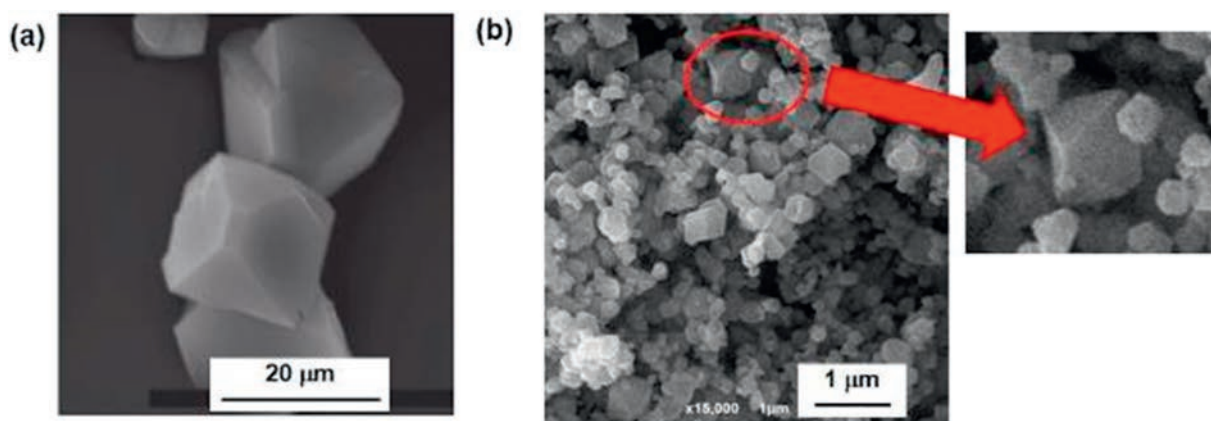


Fig. 4. SEM images of (a) Cu-BTC reported in previous research (Al-Janabi *et al.*, 2015) and (b) Cu-BTC synthesized in solvent ratio of 3:1 water to ethanol at 80 °C for 8 h.

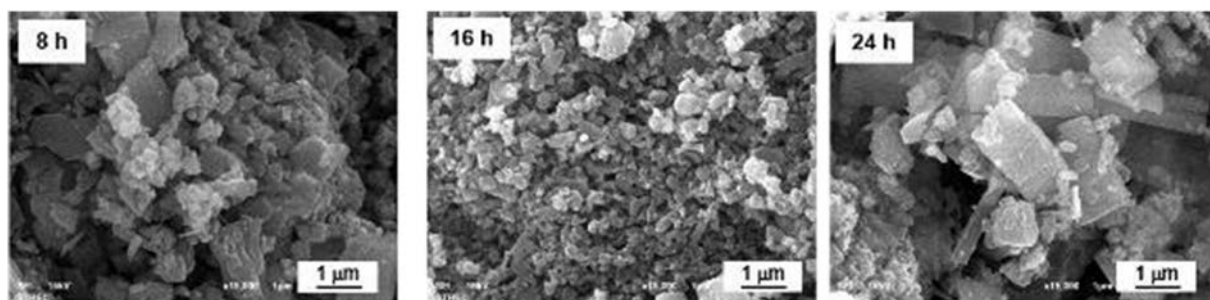


Fig. 5. SEM images of Cu-BTCs synthesized in wholly aqueous solvent system at 80 °C for 8, 16 and 24 h.

The surface areas of Cu-BTC synthesized in the solvent ratio of 3:1 water to ethanol for 8, 16 and 24 h at 80 and 120 °C are also measured and shown in Table 1. The surface areas of synthesized for Cu-BTC were from 443.7 to 917.1 $\text{m}^2 \cdot \text{g}^{-1}$. Al-Janabi *et al.* (2015) described that variations of the surface areas might result from the differences of washing and activation of the samples after the aging procedure [17].

Table 1

Surface areas of Cu-BTCs synthesized in solvent ratios of 3:1 water to ethanol with different temperatures and aging times

Synthesis conditions		Surface area/ $\text{m}^2 \cdot \text{g}^{-1}$
Temperature/°C	Aging time/h	
80	8	549.5
	16	554.3
	24	443.7
120	8	525.7
	16	549.5
	24	917.1

3.2. Oil micelles removal

Each of the experiment was conducted by adding 0.05 g of synthesized Cu-BTC into 50 ml of $0.5 \text{ g} \cdot \text{L}^{-1}$ MWF emulsion and stirred for 60 min. The ability of all synthesized Cu-BTCs adsorbed oil micelles was $477 \text{ mg} \cdot \text{g}^{-1}$ or remove oil micelles greater than 95% in 60 min. However, the results indicated that the highest removal capacity was 99.8% by using Cu-BTC synthesized in the solvent ratio 2:1 of water to ethanol at 80 °C for 24 h. Furthermore, the results of Cu-BTC synthesized in the solvent ratio 3:1 of water to ethanol at 80 °C for 8 h were given an interesting result along with an effective adsorbent (given 98.3% oil removal or $491.5 \text{ mg} \cdot \text{g}^{-1}$). This can be caused by the synthesized reaction that occurred at short period of time with the small amount of organic solvent.

The oil removal performance of Cu-BTC synthesized at 80 °C for 8 h in the solvent ratio of 3:1 water to ethanol and wholly aqueous solvent was compared to the granular activated carbon (GAC) as shown in Fig. 6. After the 60 min of stirring adsorbents in MWF emulsion, the oil removal capacity of GAC has obtained the result of only 6.8% (*ca.* $31.7 \text{ mg} \cdot \text{g}^{-1}$) while the capacity of Cu-BTCs synthesized in 3:1 water to ethanol and wholly aqueous solvent was 98.3% and 22.2%, respectively. However, the surface area of GAC ($955 \text{ m}^2 \cdot \text{g}^{-1}$) was higher than those of Cu-BTCs synthesized in wholly aqueous ($471.7 \text{ m}^2 \cdot \text{g}^{-1}$)

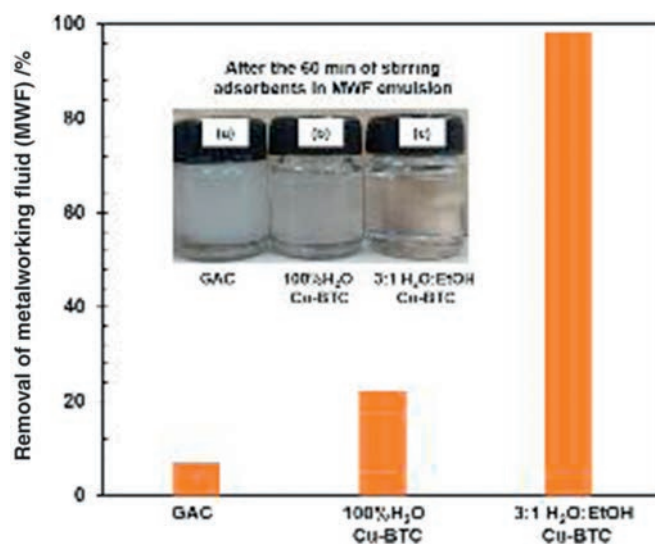


Fig. 6. Removal capacity of oil micelles in MWF emulsion by using (a) activated carbon and Cu-BTCs synthesized in (b) wholly aqueous solvent and (c) 3:1 water to ethanol at 80 °C for 8 h.

and 3:1 of water to ethanol solvent ($549.5 \text{ m}^2 \cdot \text{g}^{-1}$), the oil removal performance of GAC was lower. These results may be attributed to that the performance of oil adsorption does not only depend on the surface area or porosity of the materials but also on their functional groups. Vlasova *et al.* (2016) proposed the adsorption mechanisms of free fatty acids with the Al-BDC (BDC = benzene-1,4-dicarboxylic acid) [20]. The functional groups of Cu-BTC are similar with Al-BDC; therefore, it may be attributed that emulsifiers, such as fatty acid soap or fatty acid ethoxylate, in MWF can be adsorbed on Cu-BTCs by the interaction of coordinatively unsaturated Lewis centers (Cu atoms) in MOFs with the carboxylate groups (R-COO^-) in emulsifiers. In MWF emulsion solution, oil droplets combine with emulsifiers in micelle form; therefore, oil droplets can be removed from the solution when the emulsifiers are adsorbed on MOFs.

3.3. Adsorption study

Adsorption data were evaluated by using two general isotherm models, the Langmuir and Freundlich models. The Langmuir model assumes that the surface of the adsorbent is uniform and do not interact with the adsorbate molecules. The Langmuir isotherm and its linear form are expressed as follows:

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

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \quad (2)$$

where q_e is amount of adsorbate per unit mass of adsorbent at equilibrium ($\text{mg} \cdot \text{g}^{-1}$), C_e is the concentration of MWF emulsion at the equilibrium ($\text{mg} \cdot \text{L}^{-1}$), $q_{\max}$ is the maximum adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), and K_L is Langmuir constant related to bonding energy of adsorption ($\text{L} \cdot \text{mg}^{-1}$).

Dimensionless constant referred to as separation factor or equilibrium parameter (R_L) is used to understand further the adsorption process. The adsorption is considered as favorable when $0 < R_L < 1$ and unfavorable when $R_L > 1$. R_L is defined as follow:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where R_L is the separation factor, K_L is Langmuir constant ($\text{L} \cdot \text{mg}^{-1}$) and C_0 is initial concentration of adsorbate ($\text{mg} \cdot \text{L}^{-1}$).

The Freundlich isotherm expresses adsorption of multilayer on heterogeneous surface. The Freundlich isotherm and its linear form are expressed as follows:

$$q_e = K_f C_e^{1/n} \quad (4)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

where, K_f and n are the Freundlich constants which correspond to adsorption capacity and adsorption intensity of the adsorbent, respectively.

The adsorption isotherm and the regression fitting curves with Langmuir and Freundlich models are shown in Fig. 7. The isotherm parameters were calculated and listed in Table 2. The experiment data could not fit with Freundlich model, while they could fit well with the Langmuir model. As the results, it suggests that the adsorption of oil micelles in MWF emulsion on the surface of Cu-BTCs could be as a monolayer. Moreover, the separation factor (R_L) values were in range of 0.003–0.025 representing favorable adsorption of oil emulsified in water on Cu-BTCs. Maximum adsorption capacity ($q_{\max}$) and the Langmuir constant (K_L) were $1666.7 \text{ mg} \cdot \text{g}^{-1}$ and $0.1538 \text{ L} \cdot \text{mg}^{-1}$, respectively.

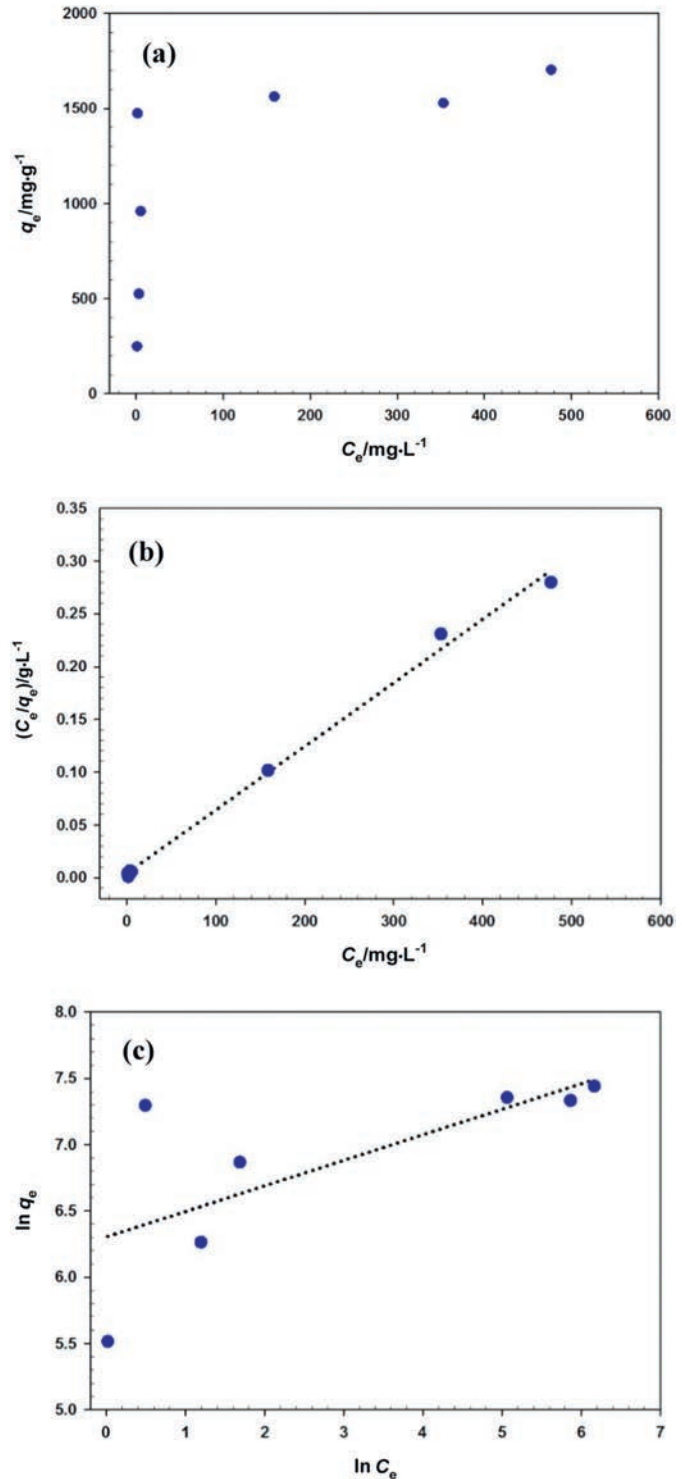


Fig. 7. (a) Equilibrium adsorption isotherm for oil micelles in MWF emulsion onto Cu-BTCs, (b) Langmuir model, (c) Freundlich model.

Table 2

Isotherm parameters for oil micelles in MWF emulsion fit on Langmuir and Freundlich models

	Langmuir	Freundlich	
$q_{\max}/\text{mg} \cdot \text{g}^{-1}$	1666.7	$K_f/(\text{mg} \cdot \text{g}^{-1}) \cdot (\text{L} \cdot \text{mg}^{-1})^{1/n}$	546.4
$K_L/\text{L} \cdot \text{mg}^{-1}$	0.1538	n	5.195
R^2	0.9959	R^2	0.4995

3.4. Reusability of Cu-BTC

The used Cu-BTCs were washed with ethanol and butanol for 2 h at ambient temperature and activated at the temperature of 100 °C in vacuum oven for 24 h to remove the oil adsorbed from Cu-BTCs. The results of FT-IR spectra of synthesized Cu-BTC, metalworking fluid (MWF), Cu-BTC adsorbing MWF and washed Cu-BTC are shown in Fig. 8. The bands at 2854 and 2925 cm^{-1} are characteristics of the C—H stretching mode of saturated C—C bonds in MWF. The appearance of these bands on the spectrum of Cu-BTC adsorbing MWF indicated that oil micelles in MWF emulsion were captured by Cu-BTC. Moreover, the bands at 2854 and 2925 cm^{-1} did not appear on the spectrum of regenerated Cu-BTC. It indicated that oil captured on Cu-BTC was removed by washing with ethanol and butanol.

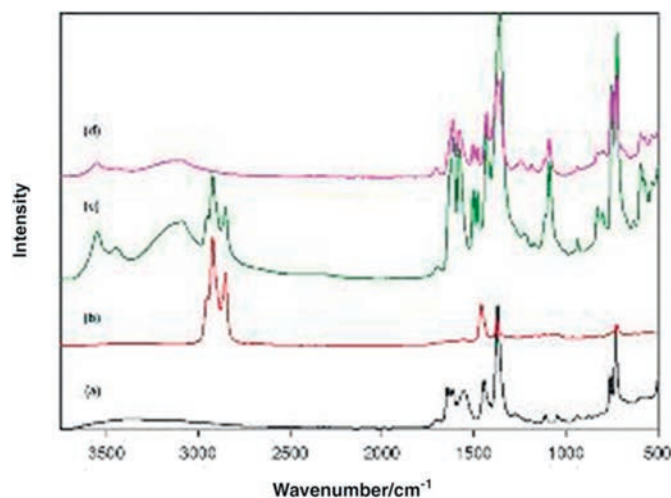


Fig. 8. FT-IR spectrum of (a) synthesized Cu-BTC, (b) metalworking fluid (MWF), (c) Cu-BTC adsorbing MWF and (d) regenerated Cu-BTC.

The oil removal capacity of Cu-BTCs washed with ethanol is compared to Cu-BTCs washed with butanol as shown in Fig. 9. After 3 h of stirring Cu-BTCs in 0.5 $\text{g} \cdot \text{L}^{-1}$ MWF emulsion, the oil removal capacity of Cu-BTCs washed with butanol and ethanol is only 73% and 82%,

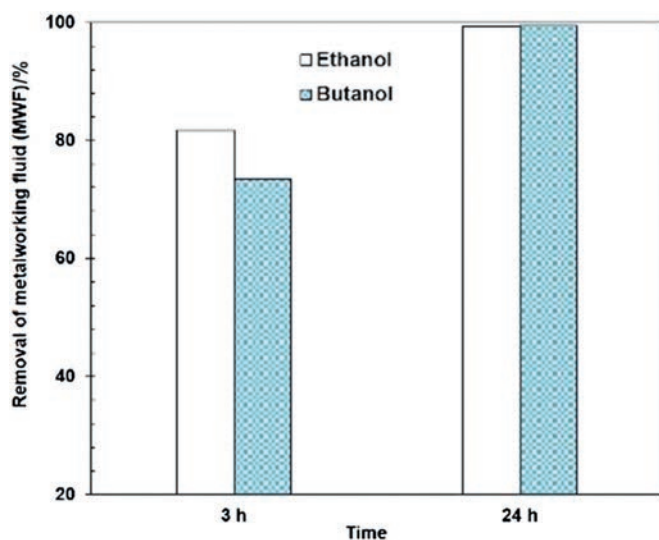


Fig. 9. Removal capacity of oil micelles in MWF emulsion at 3 and 24 h by using Cu-BTCs washed with butanol and ethanol.

respectively, while the capacity after 24 h of Cu-BTCs washed with butanol and ethanol is not significantly different in the percentage of oil removal (>99% oil removal)

4. Conclusions

The XRD patterns of 27 Cu-BTC samples synthesized with different solvent ratios of water to ethanol (3:1, 2:1 and 1:1 v/v), temperatures (80, 100 and 120 °C) and aging times (8, 16, 24 h) are not significantly different from each other and they do not occur as the peaks of Cu_2O . The maximum yield was obtained at 120 °C for 8 h in the solvent ratio of 2:1 water to ethanol. The thermal stability of Cu-BTC samples was not affected with temperatures and solvent ratios using in the synthesis.

The decomposition of the framework was observed for the temperature greater than 280 °C. The morphology of synthesized Cu-BTCs is octahedral losing sharp edges and the particle size was in the range from ≈ 80 nm to 400 nm which was quite smaller than the size of those from the previous reports. The surface areas in this study ranged from 443.7 to 917.1 $\text{m}^2 \cdot \text{g}^{-1}$. The highest removal capacity of oil micelles in MWF was 99.8% using Cu-BTC synthesized in solvent ratio 2:1 of water to ethanol at 80 °C for 24 h. The FT-IR spectra of synthesized for Cu-BTC, metalworking fluid (MWF), Cu-BTC adsorbing MWF and washed Cu-BTC indicated that oil captured on Cu-BTC was removed by washing with ethanol and butanol. The highest removal capacity of oil micelles in MWF emulsion was greater than 99% in 24 h using Cu-BTCs washed with either butanol or ethanol.

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