Recycling of surfactant template in mesoporous MCM-41 synthesis

J Y Lai¹, F Twaiq¹, L H Ngu¹
¹Faculty of Engineering, Computing and Science, Swinburne University of Technology Sarawak Campus, Jalan Simpang Tiga, Kuching 93350, Sarawak, Malaysia

Email: ftwaiq@swinburne.edu.my

Abstract. The recycling of surfactant template is investigated through the reuse of the surfactant template in the mesoporous MCM-41 synthesis process. In the synthesis of MCM-41, tetraethylorthosilicate (TEOS) solution in water was utilized as the silica source while hexadecyltrimethylammonium bromide (CTAB) solution in ethyl alcohol was used as a surfactant template. The synthesized gel is formed thoroughly by mixing the two solutions under acid conditions with a pH value of 0.5 for 1 hour and kept for crystallization for 48 hours. The as-synthesized MCM-41 powder is recovered by filtration while the filtrate (mother liquor) was then reused for the second synthesis cycle. The synthesis procedure was repeated till no further solid product was formed. The synthesized gel was not produced in the unifying solution in the fifth cycle of MCM-41 synthesis. The quality of the calcined MCM-41 powder produced in each synthesis cycle was evaluated by calculating the amount of MCM-41 produced and the surface area of the powder product. The result showed that 1.28, 0.37, 1.64, 1.90 and 0.037 g were obtained in the 1st, 2nd, 3rd, 4th and 5th synthesis cycle, respectively. The surface area of the powder produced was found to be 1170, 916, 728, and 508 m²/g for 1st, 2nd, 3rd and 4th respectively. The concentration of the surfactant template has reached value lower than the critical micelle concentration (CMC) and remained constant after the 4th cycle. There was no further formation of gel due to low availability in the interaction between silicate anions and surfactant cations when the amount of TEOS was fixed for every synthesis cycle.

1. Introduction
Mesoporous silica materials were synthesized and found with great potential as catalysts and adsorbents in many chemical industrial applications because of their thermal stability, high specific surface area and high pore volume [1]. MCM-41 is a hexagonal mesophase material that is synthesized using silica source and a surfactant template which is then removed to form the structured mesoporous materials.

Two methods were reported for the synthesis of MCM-41 that are hydrothermal synthesis and liquid templating methods. The first method used normal heating or microwave heating in an autoclave to synthesize the mesoporous material at high temperature under alkaline condition in the presence of surfactants for up to 72 hours. The synthesis consists of two methods of treatment that are direct hydrothermal synthesis or post-hydrothermal synthesis [2]. The second method synthesized the MCM-41 using cationic surfactants as template at different surfactant/silica molar ratios [1]. The synthesis is conducted under a basic or an acidic condition by initiating the aggregation of surfactant
micelles at below the critical micelle concentration (CMC) such as 0.0009 mol·L\(^{-1}\) in water system, 0.022 mol·L\(^{-1}\) in ethanol-water system (95 vol% ethanol) and 0.24 mol·L\(^{-1}\) in ethanol system (100 vol% ethanol) [3]. The silica source was condensed around the surfactant template to form silica walls while the surfactant template was then removed from the mesopores [4]. The use of silica source, includes sodium silicate (Na\(_2\)SiO\(_4\)) and fumed silica were commonly used in hydrothermal synthesis, whereas TEOS was used in the liquid templating method. Three types of surfactant such as the anionic, cationic and neutral surfactant are required in the synthesis of MCM-41. Anionic surfactants consist of high potent detergency and lower cost of carboxylate, sulfate, sulfonate and phosphate. The typical anionic surfactant used as the surfactant template for mesoporous silica material synthesis is sodium dodecylbenzenesulfonate (SDBS), sodium dodecylsulfate (SDS) and lauric acid sodium salt (LAS) [5]. The neutral surfactant is the surfactant contains neutral primary amine with structural formula of C\(_{2n+1}\)H\(_{4n+1}\)NH\(_2\) such as dodecylamine (C\(_{12}\)H\(_{25}\)N) is generally used as the surfactant template in the synthesis process [6]. Other than anionic and neutral surfactant, the cationic surfactant includes n-alkyltrimethyl ammonium bromides, or chloride with different lengths of alkyl chain (C\(_{12}\) to C\(_{20}\)). For instance, CTAB is typically used for mesoporous material synthesis as the surfactant template [7].

Conventionally, the removal of surfactant template was carried out by calcination at high temperature that causes the transformation of mesophase, though the surfactant template was effectively burnt off under high temperature [7]. Alternative surfactant template removal methods, including solvent extraction, supercritical fluid extraction (SFE) enhanced with sonication, oxidation by hydrogen peroxide (H\(_2\)O\(_2\)) or ammonium perchlorate (AP) and ultraviolet light (UV)-ozone treatments were investigated in order to achieve efficient removal of the surfactant template and have less negative effect on the structure of the material [4]. These methods have enhanced the removal process of the surfactant template from the as-synthesized mesoporous material by obtaining a more order structure of material and effectively recovered the surfactant template [8].

Some attempts have been reported in previous studies that solvent extraction is efficient in removing the surfactant template and causes less destructive effect on the mesostructure [8]. The resulting surfactant template extracted is being recovered by refluxing the as-synthesized MCM-41 powder in acidified ethanol solution at 70°C for 30 hours and the filtrate is then undergone distillation at 80 °C, neutralization and recrystallization using acetone/ethanol mixture in order to separate out the ethanol and acid as well as obtaining the surfactant powder for reuse in the next synthesis cycle [9]. Other than that, surfactant template recovered through sublimation under vacuum was investigated. The result showed that 67% of the surfactant template was recovered by sublimating the sample using 60wt% non-surfactant, menthol as a surfactant template in ethanol under vacuum at 50 °C [10]. The menthol solid was collected and reused for the next mesoporous material synthesis. Besides solvent extraction and sublimation, the application of ultrasound irradiation with methanol has greatly improved the efficiency of the removal by disrupting the aggregation of the surfactant micelles in the MCM-41 structure to break into monomers [11]. The monomers, that are the surfactant molecules, are released into the methanol and can be recovered to reuse in further MCM-41 synthesis. Furthermore, supercritical fluid extraction (SFE) was evaluated to be an effective surfactant template removal method with a very high extraction efficiency, enhanced by methanol and water [12]. High surfactant recovery (over 90%) was achieved from mesoporous material such as MCM-48 through the water-enhanced supercritical CO\(_2\) extraction over pressure ranging from 80 to 140 bar at temperature 85-105 °C for 3 h [12]. The extracted aqueous surfactant was recovered from water by stripping, distillation or adsorption [13] and could be reused as a surfactant template for further mesoporous material synthesis. Although these removal methods have increased the efficiency of removal and enhanced the recovery of the surfactant template, however the usage of mother liquor from filtration during the synthesis of MCM-41 that contained the surfactant molecules was not reported. Therefore, this issue urges us to investigate a way to recycle the surfactant in the mother liquor and the quality of the MCM-41 synthesized by utilizing the recycled surfactant template.

In the present paper, the recycling of surfactant template is performed by utilizing the surfactant template in the filtrate to synthesize MCM-41 mesoporous material for consecutive MCM-41
synthesis cycle. The ethanol produced by the TEOS hydrolysis will be utilized as an extraction solvent. The number of reuse will be examined by the amount of calcined MCM-41 produced. The quality of the produced product will be evaluated by surface area analysis and nitrogen adsorption and desorption isotherms.

2. Experimental procedure

2.1. Materials
TEOS (C₈H₂₀O₄Si, 98%, Sigma-Aldrich) and CTAB powder (C₁₉H₄₂BrN, R&M) were used as silica source and surfactant template respectively. The commercially available nitric acid (HNO₃, 65%, Fisher) was used as catalyst in hydrolysis process and pH adjustment. Ethanol (C₂H₅OH, 95%, DULAB) was used as solvent.

2.2. Synthesis of MCM-41
TEOS with total volume of 5 mL was initially dissolved in 15 mL of distilled water referred to as Solution 1 (S1). While, 3.17 g of CTAB was added to ethanol and the solution was named Solution 2 (S2). S1 and S2 were stirred vigorously for 30 min. After stirring, the mixture was tested to evaluate the concentration of surfactant template, ethanol and TEOS using PerkinElmer LAMBDA 35 UV/Vis spectrophotometer. The mixture was kept for homogenization for 1.5 h. 2 mL of nitric acid (HNO₃) was added and the mixing was continued for an hour. The pH was monitored and the mixture was kept for 48 h without mixing for gel formation. The resulting gel was then filtered to separate the resulting powder (as-synthesized MCM-41) and the mother liquor. The as-synthesized powder was further calcined at 550 °C for 8 h. The mother liquor was reused for the 2nd synthesis cycle by adding 5 mL TEOS. The procedure for successive MCM-41 synthesis batches was continued until no significant powder is produced. Figure 1 illustrates the complete synthesis and surfactant template reuse cycles.

2.3. Characterization
The synthesized MCM-41 powder from first (1st) MCM-41 synthesis cycle to fourth (4th) MCM-41 synthesis cycle were characterized using nitrogen (N₂) adsorption-desorption isotherms by performing ASTM D3663-03(2008) test method using Autosorb Quanta Chrome 6B gas sorption analyzer under vacuum at 77.35 K. The Brunauer-Emmett-Teller (BET) analysis was used to determine the specific surface area. The pore size and the pore volume of the MCM-41 powder produced in the respective synthesis cycles were determined using Barrett-Joyner-Halenda (BJH) method. Besides, scanning electron microscopy (SEM) was carried out using scanning electron microscope model FEI Quanta 200 FESEM with accelerating voltage ranging from 2 kV to 30 kV to characterize the morphology of the synthesized MCM-41 powder.
3. Result and discussion

3.1. Relative yield produced
In the previous studies as stated in section 1, the synthesis of MCM-41 was performed up to three subsequent batches through the recycling of the extracted CTAB powder [9]. In comparison to the present work, the surfactant template in the filtrate was found to be utilized up to four synthesis cycles of MCM-41 synthesis. The relative amount of the calcined white powder produced in each synthesis
cycle is shown in Table 1. As observed the relative yield of calcined white powder tabulated in Table 1, a large quantity of calcined white powder was being produced in 1st, 3rd and 4th MCM-41 synthesis cycles than in 2nd and 5th synthesis cycle. This can be explained that the effect of CTAB concentration influenced the formation of synthesis gel. In the MCM-41 synthesis experiment, more gel formation was observed in 1st, 3rd and 4th synthesis cycle when the concentration of CTAB/ethanol increases that becomes the molar ratio of CTAB/ethanol for the respective three cycles were 0.044, 0.027 and 0.026 as shown in Table 1. As compared to 2nd cycle, the resulting gel formation observed in the 2nd synthesis cycle was lesser than 1st, 3rd and 4th cycle when the molar ratio of CTAB/ethanol was 0.025. When the CTAB concentration steadily decreased until it reaches constant, neither gel or powder was formed in the 5th synthesis cycle. This is because an increase in CTAB concentration resulted more interaction between surfactant cations and silicate anions which increases the rate of silicate polymerization and causes more gel formation to occur when the amount of TEOS was fixed for every synthesis batch [14]. Therefore, a total mass of 0.37 g and 0.037 g calcined white powder were obtained in the respective MCM-41-S2 and MCM-41-S5 which was lesser than the resulting 1.28 g MCM-41-S1, 1.64 g MCM-41-S3 and 1.90 g MCM-41-S4.

Besides, the formation of MCM-41 was found to occur at low concentration of surfactant [14]. As shown in Table 1, low molar ratio of CTAB/ethanol was resulted for all samples. Therefore, the calcined white powder in all samples exhibited the characteristic type of MCM-41 mesoporous material with hexagonal shape in nature.

### Table 1. Experimental results of MCM-41 synthesis.

| Sample Name | Cycle No. | Mass of Calcined MCM-41 (g) | TEOS/Ethanol Ratio | CTAB/Ethanol Ratio |
|-------------|-----------|------------------------------|--------------------|--------------------|
| MCM-41-S1   | 1st       | 1.280                        | 1.2                | 0.044              |
| MCM-41-S2   | 2nd       | 0.370                        | 0.6                | 0.025              |
| MCM-41-S3   | 3rd       | 1.640                        | 0.6                | 0.027              |
| MCM-41-S4   | 4th       | 1.900                        | 0.6                | 0.026              |
| MCM-41-S5   | 5th       | 0.037                        | 0.6                | 0.026              |

#### 3.2. Structural and physical characteristics

The SEM micrograph of MCM-41-S1 is shown in Figure 2. The calcined white powder in MCM-41-S1 showed the smooth surface morphology composed of an array of uniformly regular spherical shaped particles. Thus, the sample of MCM-41-S1 was identified as the white hexagonal shape of mesoporous material. Since the synthesis procedure repeated the same throughout the five cycles except different amount of HNO₃ was added when the pH was adjusted to 0.5, hence the calcined white powder of MCM-41-S2 and MCM-41-S4 was assumed to have the same characteristics as MCM-41-S1 except MCM-41-S3, which exhibited irregular shape particles.

![Figure 2. SEM images of MCM-41-S1.](image)

*The specific surface area, pore volume and pore size calculated using the BET method for the respective MCM-41-S1, MCM-41-S2, MCM-41-S3 and MCM-41-S4 were tabulated in Table 2.*
concentration of CTAB also affected the surface morphology of calcined white powder for four samples. An increase in the CTAB concentration causes more spherical particles to form [14]. The highest molar ratio of CTAB/ethanol in sample MCM-41-S1 as observed in Table 1 has resulted the formation of spherical shape calcined powder with high surface area of 1170 m²/g. As compared to the other three samples such as MCM-41-S2, MCM-41-S3 and MCM-41-S4, less spherical calcined powder with their respective specific surface area of 916 m²/g, 728 m²/g and 508 m²/g were formed respectively when the molar ratio of CTAB/ethanol was found steadily decreased and remained nearly constant.

The isotherms of MCM-41-S1, MCM-41-S2, MCM-41-S3 and MCM-41-S4 are shown in Figure 3. MCM-41-S1 showed the type I (b) isotherms whereas MCM-41-S3 has the typical type II isotherms according to IUPAC classification. For MCM-41-S2 and MCM-41-S4, type IV isotherms based on the IUPAC classification [15] are illustrated in Figure 3. The isotherms of MCM-41-S1 stated that the calcined white powder produced in 1st MCM-41 synthesis cycle has a narrow mesopore size with 1.96 nm while the calcined white powder in the consecutive 2nd, 3rd and 4th synthesis cycles indicated mesoporous materials with larger pore size with value of 2.89 nm, 5.02 nm and 3.41 nm respectively. The calcined white powder produced in all four consecutive synthesis cycles has the pore diameter within the mesoporous size ranging from 2 to 50 nm [16]. Therefore, the calcined white powder in the sample MCM-41-S1, MCM-41-S2, MCM-41-S3 and MCM-41-S4 were identified as mesoporous material.

At a high relative pressure, a hysteresis loop with steep parallel adsorption and desorption isotherms was illustrated in the isotherms of MCM-41-S1 which was indicating the calcined white powder produced in the 1st synthesis cycle has a uniform pore structure. Whereas, the isotherms of MCM-41-S2 and MCM-41-S4 showed a smooth adsorption step with sharp desorption step in the hysteresis loop at higher relative pressure. This can be explained that the calcined white powder obtained from 2nd and 4th cycle of MCM-41 synthesis were mesoporous materials with non-uniform pore sizes. As compared to the first three isotherms, type H3 of hysteresis loop was shown in the isotherms of MCM-41-S3 at high P/P₀ according to IUPAC classification. The calcined white powder produced in the 3rd MCM-41 synthesis cycle consists of an agglomeration of plate-like particles with irregular slit-shaped mesopore structure [15]. Agglomeration that resulted due to the altering pH value in the mixture causes the enlargement of particle size and the shape alteration to occur in sample MCM-41-S3 without changing the surface area of particles [17]. Therefore, the resulting calcined white powder obtained in sample MCM-41-S3 has larger size of pores and larger pore volume with irregular shape particles than the other three samples as shown in Table 2.

![Figure 3. N₂ adsorption-desorption isotherms.](image-url)
4. Conclusions
In this current work, the recycling of surfactant was achieved up to five MCM-41 synthesis cycles. The effect of CTAB concentration on the gel formation and the calcined white powder surface morphology was studied. The resulting calcined white powder with a total mass of 1.28 g, 1.64 g and 1.90 g were obtained in the respective 1st, 3rd and the 4th synthesis cycle when the concentration of CTAB increases to reach the molar ratio of CTAB/ethanol with a value of 0.044, 0.027 and 0.026. Whereas, 0.37 g and 0.037 g of calcined white powder were formed in the 2nd and 5th cycle due to the decrease in molar ratio of CTAB/ethanol that was 0.025 in 2nd cycle as compared to 1st, 3rd and 4th cycle while remained constant after the 4th cycle that causes no further formation of gel to occur in the 5th cycle. The formation of spherical shape mesoporous material was resulted in 1st, 2nd and 4th synthesis cycle with their respective specific surface area value of 1170 m²/g, 916 m²/g and 508 m²/g except MCM-41-S3. Agglomeration occurred in the 3rd cycle causes MCM-41-S3 exhibited irregular slit-shaped mesopore structure with a surface area of 728 m²/g, a larger pore size and a larger pore volume. Both SEM result and the measured molar ratio of CTAB/ethanol confirmed that the calcined powder for all five samples possessed the MCM-41 characteristics and hexagonal shape in nature.

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References
[1] Barrera D, Villarroel-Rocha J, Marenco L, Oliva M I and Sapag K 2011 Non-hydrothermal synthesis of cylindrical mesoporous materials: influence of the surfactant/silica molar ratio Adsorption Science & Technology 29 ed Müller E A (UK: Multi-Science Publishing Co Ltd) pp 975-988
[2] Xu R, Pang W, Yu J H, Huo Q S and Chen J S 2009 Synthesis and structure Chem. Zeolites and Relat. Porous Mater. (New Jersey: Wiley) pp 533-535
[3] Li W, Han Y C, Zhang J L and Wang B G 2005 Effect of ethanol on the aggregation properties of cetyltrimethylammonium bromide surfactant Colloid J. 67 159-63.
[4] Twaiq F, Nasser M S and Onaizi S 2014 Effect of the degree of template removal from mesoporous silicate materials on their adsorption of heavy oil from aqueous solution Front. Chem. Sci. Eng. 8 488-97.
[5] Steen E V, Callanan L H and Claeys C 2004 Recent advances in the science and technology of zeolites and related materials Proc. 14th Int. Zeolite Conf. Cape Town South Africa 25-30th April 2004 (Amsterdam: Elsevier).
[6] Twaiq F, Nasser M, Al-Ryami S and Al-Ryami H 2012 Performance of mesoporous organosilicates on the adsorption of heavy oil from produced water Int. Conf. on Fundamental and Applied Sciences 2012:(ICFAS2012) 1482 579-584.
[7] Du P D, Khieu D Q and Hoa T T 2013 Removal of organic template from mesoporous MCM-41 Tạp chí Khoa học Đại học Huế 69.
[8] Jabariyan S and Zanjanchi M A 2012 A simple and fast sonication procedure to remove surfactant templates from mesoporous MCM-41 Ultrason. Sonochem. 19 1087-93.
[9] Ng E P, Goh J Y, Ling T and Mukti R 2013 Eco-friendly synthesis for MCM-41 nanoporous
materials using the non-reacted reagents in mother liquor Nanoscale Res. Lett. 8 1-8.

[10] Mukherjee I, Chen J, Yin H and Wei Y 2011 Use of sublimation for template removal from menthol templated mesoporous organosilica prepared via sol–gel process Powder Technol. 206 214-17.

[11] Zanjanchi M A and Jabariyan S 2014 Application of ultrasound and methanol for the rapid removal of surfactant from MCM-41 molecular sieve J. Serb. Chem. Soc. 79 25-38.

[12] Huang Z, Luan D Y, Shen S C, Hidajat K and Kawi S 2005 Supercritical fluid extraction of the organic template from synthesized porous materials: effect of pore size J. Supercrit. Fluids 35 40-8.

[13] Scovazzo P, Chen W Y, Wang L and Shammas N 2006 Solvent extraction, leaching and supercritical extraction Advanced Physicochemical Treatment Processes ed Wang L, Hung Y T and Shammas N (New York: Humana Press).

[14] Ahmed S and Ramli A 2011 Effect of surfactant concentration on the physico-chemical characteristics of mesoporous molecular sieve J. Appl. Sci. 11 1178-84.

[15] Thommes M, Kaneko K, Neimark A V, Olivier J P, Rodriguez-Reinoso F, Rouquerol J and Sing K 2015 Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report) Pure Appl. Chem. 1-19

[16] Othman A L and Zeid A 2012 A review: fundamental aspects of silicate mesoporous materials Mater. 5 2874-902.

[17] Forsch D 2013 Nanomaterials (Germany: Wiley-VCH).