

Article

## Exploring Qualitative and Quantitative Decoration on Amine-Modified Mesoporous Silica for Enhance Adsorption Performances

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**Abstract.** Using the triblock copolymer Pluronic F127 as a surfactant, tetraethyl orthosilicate (TEOS) as a silica source, and hydroxylamine hydrochloride as an amine source, a group of amines-modified mesoporous silica Santa Barbara Amorph-16 (SBA-16) materials with different template withdrawal methods and amine loading concentrations were prepared through sol-gel conditions. The investigation will provide qualitative and quantitative information on amine-modified SBA-16 decoration with a brief overview of the non-destructive analysis methods for advanced materials as adsorbent candidates. Highly ordered mesostructured amine-modified SBA-16 materials were prepared using high-temperature (or calcination) and solvent extraction de-templating methods. Mesostructured amine-modified SBA-16 has been successfully examined using a Synchrotron Radiation Low-Angle X-ray Diffraction (SR-LXRD) instrument for phase identification, Small-Angle Synchrotron X-rays Scattering (SAXS) for identifying structural changes in a porous material, Fourier Transform Infrared (FTIR) for identifying functional groups, Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) elemental analyzer for determining the number of silica, oxygen, and nitrogen elements, and a Specific Surface Area (SSA) analyzer for measuring the specific surface areas. The SR-LXRD and SAXS results demonstrated that the synthesized novel materials were defined unambiguously as a bi-continuous cubic body center Im3m mesostructured. FTIR and SEM-EDS analyses verified that the amine groups were uniformly deposited on the SBA-16 surface. The SSA analyzer results also clarified that the novel materials exhibited ordered and meso-framework amine-modified SBA-16 with a large surface area. Novel materials can be considered high-potential uranium adsorbent candidates. Preliminary adsorption investigations have shown that the amine-modified SBA-16 materials can adsorb uranium in natural seawater showing an uptake capacity of as much as 24.48 mg-U/g-adsorbent.

**Keywords:** Mesoporous silica, SBA-16, amine-modified, adsorption, uranium.

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## 1. Introduction

Mesoporous silica materials, whether occurring naturally or synthesized artificially, can be extremely useful in a wide range of human endeavors. Their pore structure is usually created during the crystallization process or subsequent treatment, and it comprises solitary or interconnected pores of varying shapes and sizes. Any of the three fundamental pore models, (a) cylindrical, (b) ink-bottled, and (c) slit-shaped pores, can roughly match the pore shape. The porous solid materials are categorized by IUPAC (International Union of Pure and Applied Chemistry) according to the principal pore size: (1) microporous materials with pore diameters less than 2.0 nm, (2) micro-porous materials with pore sizes between 2.0 and 50.0 nm, and (3) macro-porous materials with pore sizes greater than 50.0 nm [1]. Large pores, thick pore walls, and great stability characterize SBA-type mesoporous materials. Santa Barbara Amorph-16 (SBA-16) is an interesting meso-architecture because it contains a 3D cubic cage that is big (5-15 nm) and structured (body-centered cubic ordering of cages with 8 linking entrances, Im3m symmetry) with multidirectional and wide pore systems, giving superior functionalization accessibility. It, like SBA-15, is made in an acidic environment with a non-ionic Pluronic surfactant, and so provides intra-wall complement porosity. SBA-16 is usually synthesized in an acidic medium with Pluronic F127 (PEO<sub>106</sub>PPO<sub>70</sub>PEO<sub>106</sub>) as a surfactant [2-4].

The novel silicate materials have resulted in a family of materials whose structure, composition, and pore size can be customized during synthesis. To obtain mesoporous silica SBA-16, the synthesis system includes three main components namely: (1) template (surfactant) which has assembly properties and becomes a guide in the formation of mesophase, (2) inorganic species for the formation of mesoporous walls, and (3) reagent media (solvent) [1]. The interaction among these components plays a key role during the synthesis process to produce the mesostructured amine-modified SBA-16 material. Surfactant molecules will form self-assembled micelles in the form of a liquid crystal phase. Several factors such as concentration, temperature, the addition of additives, and inorganic precursors will affect the self-assembled process. The structure of the crystal micelles will determine the structure of the mesophase products related to the template effect.

Many researchers have been attracted to the development of mesoporous silica materials as an adsorbent alternative in the last decade for a variety of environmental remediation applications [5]. Heavy metals [6-8], dye colors [9], and other pollutants [10] have all been removed using mesoporous silica materials, which have been widely employed as effective adsorbent candidates. The morphological, structural, and textural features of mesoporous silica materials are excellent. Previous research has reported adjusting the decoration groups to optimize the performance for specific applications. Hydroxyl groups predominate in pure mesoporous silica

materials. To increase the adsorption performance of uranium or heavy metals in aquatic ecosystems and CO<sub>2</sub> capture, the hydroxyl groups were modified with another functional group such as an amine [4, 11, 12]. The simple modification procedure is a direct grafting method in which the candidate for the precursor is directly inserted during the preparation step using the sol-gel process [13, 14].

Synthesis of amine-modified SBA-16 involves a Pluronic F-127 template for the formation of the mesoporous structure. To obtain a more open and hollower pore channel to elevate its adsorption capacity, the Pluronic F-127 template should be removed. Thus far, several methods have been proposed including the calcination process [15], dialysis [16], and solvent extraction [17]. The calcination is carried out under an open atmosphere with a temperature of over 500°C. This method is simple and effective, resulting in an entire elimination of surfactants/template, as well as the thermal condensation of the silicate framework. The dialysis procedure takes time, and it frequently includes the use of a substantial amount of acetic acid-containing water, which is neither environmentally friendly nor cost-effective in large-scale manufacturing. One of the potential template removals is extraction with an organic solvent. This method is considered in the present investigation because it does not destroy the decoration properties of materials. As a result, it can maintain many functional groups in the decoration of materials.

The mesostructured characteristics and performances of modified mesoporous materials are highly correlated. High-energy electron radiation or synchrotron radiation low-angle x-ray diffraction (SR-LXRD) is an advanced and distinctive characterization procedure that investigates the mesostructured material by steeping the interaction between synchrotron radiation (SR) and matter [18]. Moreover, the decoration of amine-modified SBA-16 was also quantitatively explored using instruments such as small-angle X-rays scattering (SAXS), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), and specific surface area (SSA) analyzer. Although numerous materials have been evaluated using mentioned instruments in prior studies, there is no published information on employing them to determine the decoration information of amine-modified SBA-16 materials in the study of template withdrawal and amine loading concentrations. The present investigation proposes a novel technique for determining qualitative and quantitative decoration information of amine-modified SBA-16 using advanced and in-house instruments to fill the gap in mesostructured material synthesis and analysis. The findings provide insights into the advanced technique technology for analyzing mesostructured materials. Uranium extraction from seawater using the synthesized amine-modified SBA-16 materials were investigated to illustrate the functionality and performance of the adsorbents.

## 2. Chemicals and Methods

### 2.1. Chemicals

The chemicals used in this study were 99% tetraethyl orthosilicate (TEOS) obtained from Sigma Aldrich as a silica source, triblock copolymer Pluronic F127 (EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>) from Sigma Aldrich as a template, hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) from KEMAUS as an amine source, methanol (CH<sub>3</sub>OH) from Sigma Aldrich, n-butanol (BuOH) from Ajax Finechem, 37% hydrochloric acid (HCl) from QRec, ethanol (C<sub>2</sub>H<sub>5</sub>OH) from Sigma Aldrich, and deionized (DI) water produced locally in the laboratory.

### 2.2. Methods

The molar recipe [3] was 1.27 TEOS: 0.00035 F-127: 1.61 BuOH : 0.91 HCl: 117 H<sub>2</sub>O: x (1, 1.27, and 1.5M) NH<sub>2</sub>. The synthesis procedures were as follows: 3.36 g of F127 was dissolved in 7.22 g of 37% HCl and 161 g of DI water. After the template was completely dissolved, 9.1 g of BuOH was added to the mixture at room temperature for 1 h with stirring. Then, 19 g of TEOS was added dropwise. After 1 h, several amines were added to the solution and were mixed at 45-50°C for 24 h with stirring. Subsequently, the mixture was aged at 95-100°C for 24 h under stirring conditions. The obtained material was filtered without washing and dried at ambient temperature. To remove the template, the obtained material was treated by using an extraction template or a calcination process. For the extraction template, the obtained material was washed three times with 2 mL of 37% HCl and 100 mL of ethanol at 50-60°C for 5 h until the pH was 5-6. For the calcination process, the template of the material was removed at 550°C for 6 h. Table 1 summarizes the sample treatment variation given for each sample.

Table 1. Sample treatment variation.

Sample code	Treatment
S1C	SBA-16 pure; Calcination
S2C	SBA-16-1.27M amine; Calcination
S3C	SBA-16-1.00M amine; Calcination
S4C	SBA-16-1.50M amine; Calcination
S1E	SBA-16 pure; Solvent Extraction
S2E	SBA-16-1.27M amine; Solvent Extraction
S3E	SBA-16-1.00M amine; Solvent Extraction
S4E	SBA-16-1.50M amine; Solvent Extraction

### 2.3. Preliminary Adsorption Process

A sample of 100 mL filtered natural seawater was added with 143 ppm UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4+</sup> at a pH of 6.0. 0.1 gram of amine-modified SBA-16 was added with continuous

stirring at room temperature for 1 h. After that, the solution was filtered, and the supernatant was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine the remaining uranium concentration.

### 2.4. Characterization

#### 2.4.1. Synchrotron Radiation Low-angle X-ray Diffraction (SR-LXRD)

This characterization was employed to investigate the structural properties of mesoporous silica SBA-16. The analysis of SR-LXRD was conducted with the source of high-energy electron or synchrotron radiation in beamline 1.1 at Synchrotron Light Research Institute (SLRI), Thailand. SR-LXRD profiles of the samples were shined with an energy of 6 keV (CuK-alpha) (wavelength of 0.20664 nm) at 0.5-6° for 900 sec/sample. The collected data were plotted in graphic 2 thetas vs. diffraction intensity.

#### 2.4.2. Small-angle X-rays Scattering (SAXS)

The data were processed in the range of the scattering peak of about 0.3 <q<1.5 nm<sup>-1</sup>. The distance between the sample and the detector was 2.2 m. The samples were characterized using x-rays synchrotron radiation in beamline 1.3 at SLRI, and the scattering data were detected and collected using the Rayonix SX165 CCD detector. The first step performed after obtaining the scattering data using SAXS was the data reduction step. The raw data were obtained in the \*.mccd file and \*.txt file for each sample and background. The data reduction step was performed using SAXIT software to cut the background and calculate the scattering profile of the intensity versus momentum transfer (q). The collected data were plotted in graphic q versus scattering intensity.

#### 2.4.3. Fourier Transform Infrared (FTIR)

As supported data, Fourier Transform Infrared (FTIR) analysis has also been used for analyzing the presence of amine groups on SBA-16. The analysis technique was transmittance analysis at wave number 4000-400 cm<sup>-1</sup> using FTIR Thermo DSC-1 in Science Instrument Center for Standard and Industry, King Mongkut University of Technology Thonburi, Thailand.

#### 2.4.4. Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)

SEM-EDS analysis was performed to quantify the amount of silica, oxygen, and nitrogen elements present on the decoration of amine-modified SBA-16 materials. The samples were analyzed using SEM-EDS: FEI QUANTA 450-Oxford EDS XMax in Microscopy Laboratory at SLRI.

#### 2.4.5. Specific Surface Area (SSA) Analyzer

A specific surface area analyzer was employed to obtain the specific surface area of synthesized samples. Nitrogen gas adsorption or static volumetric gas adsorption Micro metrics ASAP2460 using BET (Brunauer, Emmett, and Teller) was used to obtain the SSA in the Office of Scientific Instrument and Testing (OSIT), Prince of Songkhla University, Thailand.

#### 2.4.6. Inductively coupled plasma-optical emission spectrometry (ICP-OES)

ICP-OES was utilized to determine the amount of uranium adsorbed by amine-modified SBA-16. The supernatant of the solution after the adsorption process was taken at 10-15 mL for the analysis process. The uranium concentration differences in the prepared uranium-spiked seawater sample and the supernatant were assumed to be the amount of uranium adsorbed in amine-modified SBA-16.

### 3. Results and Discussion

#### 3.1. Pore Structure Analysis (SR-LXRD)

Structural characterization of mesoporous silica SBA-16 with different de-templating treatments was determined by using SR-LXRD in the range of  $2\theta$  from  $0.5$  to  $6^\circ$ . The SR-LXRD spectra of pure SBA-16 with calcination (S1C) and solvent extraction (S1E) treatment are demonstrated in Fig. 1. As can be seen in the figure, the SR-LXRD spectra of samples display one sharp peak. The diffraction spectra obtained for both samples also exhibit one sharp peak at  $2\theta \sim 1.1^\circ$  indexed as [110] planes. Furthermore, the one weak peak at  $2\theta \sim 1.7^\circ$  [200] can be defined as a bi-continuous cubic-body center Im3m, which is typical of the 3D cubic structure of mesoporous silica SBA-16 materials [19]. The highly ordered structure of SBA-16 has been observed even after the different de-templating treatments.

The diffraction patterns for amine-modified SBA-16 utilizing the calcination de-templating process are illustrated in Fig. 1(a). The bi-continuous cubic body center of SBA-16 is represented by two SR-LXRD patterns, one of which has a high peak at  $2\theta \sim 1.2^\circ$  indexed as [110] plane and one weak peak indexed as [200] planes. However, there is a significant deviation concerning the intensity and location of the SR-LXRD peaks visible on the pattern. It was predicted because of the increasing amine groups loading on the SBA-16 surface.

Unlike the samples treated with the calcination method, for all treated samples using the solvent extraction de-templating method shown in Fig. 1(b), the SR-LXRD patterns showed no significant difference in the intensity and location of the main peaks. All samples treated using the solvent extraction clearly showed a sharp peak indexed as [110] plane and one weak peak indexed as [200] plane in S1E and S3E samples. The presence of

these weak peaks was identified because the surface of the materials was not uniformly occupied by amine groups. In conclusion, the greater loading of the amine precursors caused these weak peaks to vanish.

#### 3.2. Pore Structure Analysis (SAXS)

Since the synthesized mesoporous silica SBA-16 was not categorized as crystalline at the atomic level, no reflections at higher angles can be obtained. When the Bragg conditions are fulfilled, the ordered mesoporous silica SBA-16 can be observed to produce distinct momentum scattering of SAXS patterns in the range of about  $0.3 < q < 1.5 \text{ nm}^{-1}$  as illustrated in Fig. 2. If the SAXS spectra of calcination and solvent extraction treatments are compared, the results concluded that the produced samples exhibited the same pore structures. The scattering patterns of pure SBA-16 (S1C and S1E) reported high pore order, which is marked by the increasing number of peaks.

However, by increasing the amine concentration, the only major peak is observed, suggesting the minor scattering peaks also disappeared and were occupied by the amine groups. The major peak was identified as uniformly narrow, suggesting that the ordered degree of the material is high [20]. The major scattering peaks represent reflection peaks of the [110] plane recorded in all prepared samples, which is consistent with the SR-LXRD results. By analyzing the scattering peaks ratio from SAXS for lyotropic liquid crystals (LLCs), the synthesized samples were also confirmed as bi-continuous cubic mesoporous silica with space group Im3m, as has been studied by an earlier researcher [21].

#### 3.3. Amine Functional Groups Analysis

FTIR was employed to locate the silica network's characteristic functional groups and surface functionalization. The vibration bands that are typical of mesoporous silica were widely reported in the previous study and can be easily identified in the following spectra. Figure 3 shows the FTIR spectra of amine-modified SBA-16 and SBA-16. The appearance of a broad peak at  $3445 \text{ cm}^{-1}$  due to water molecule absorption confirmed -OH functional groups. The stretching and bending of water molecules adsorbed by SBA-16 also produced a strong peak at  $1643 \text{ cm}^{-1}$  [22]. The vibrational band of the silanol group (Si-OH) at  $961 \text{ cm}^{-1}$  is seen in the spectra of SBA-16 obtained using various template removal procedures. The existence of symmetrical and asymmetrical Si-O-Si or siloxane bands is confirmed by the presence of the two peaks at  $1080$  and  $800 \text{ cm}^{-1}$ , respectively.

Guo et al. (1998) and Chandra et al. (2016) reported that the main functional groups of templates Pluronic F127 are present at  $1324 \text{ cm}^{-1}$  due to C-H bending vibration of the -CH<sub>3</sub> group signaling the presence of the poly (propylene oxide) blocks (PPO), whereas the bands at  $1285$  and  $1243 \text{ cm}^{-1}$  are the properties of the CH<sub>2</sub> twisting region of the poly(ethylene oxide) blocks (PEO).

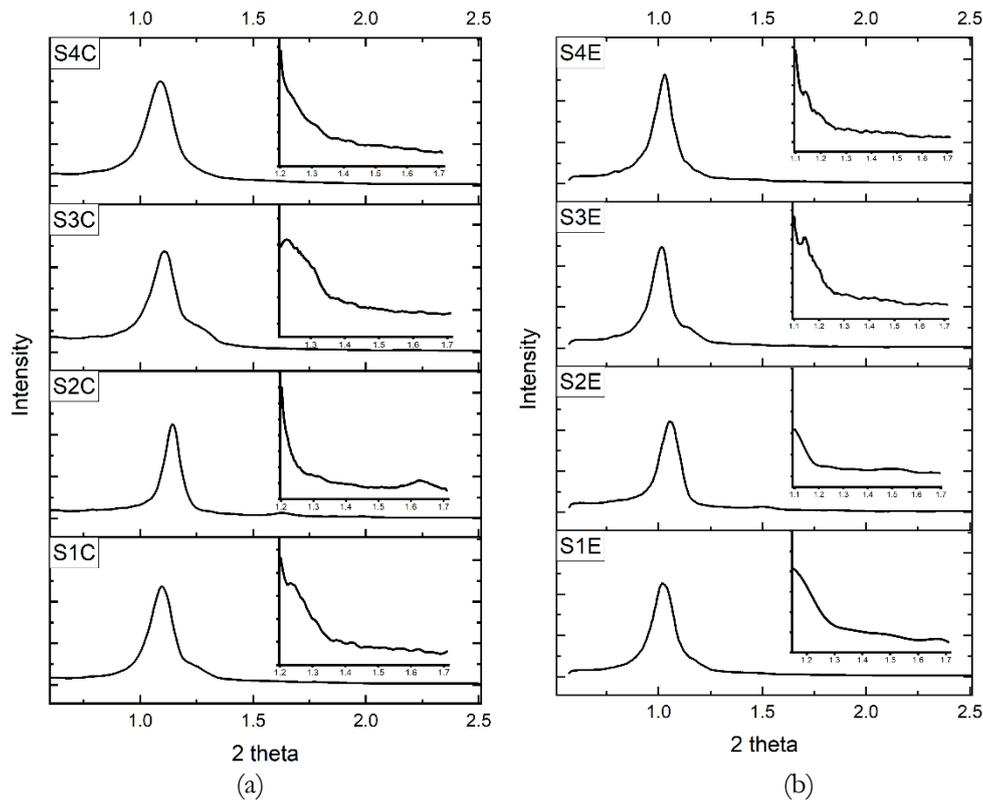


Fig. 1. Low-angle XRD spectra of amine-modified SBA-16 with (a) calcination (C-code) and (b) solvent extraction (E-code).

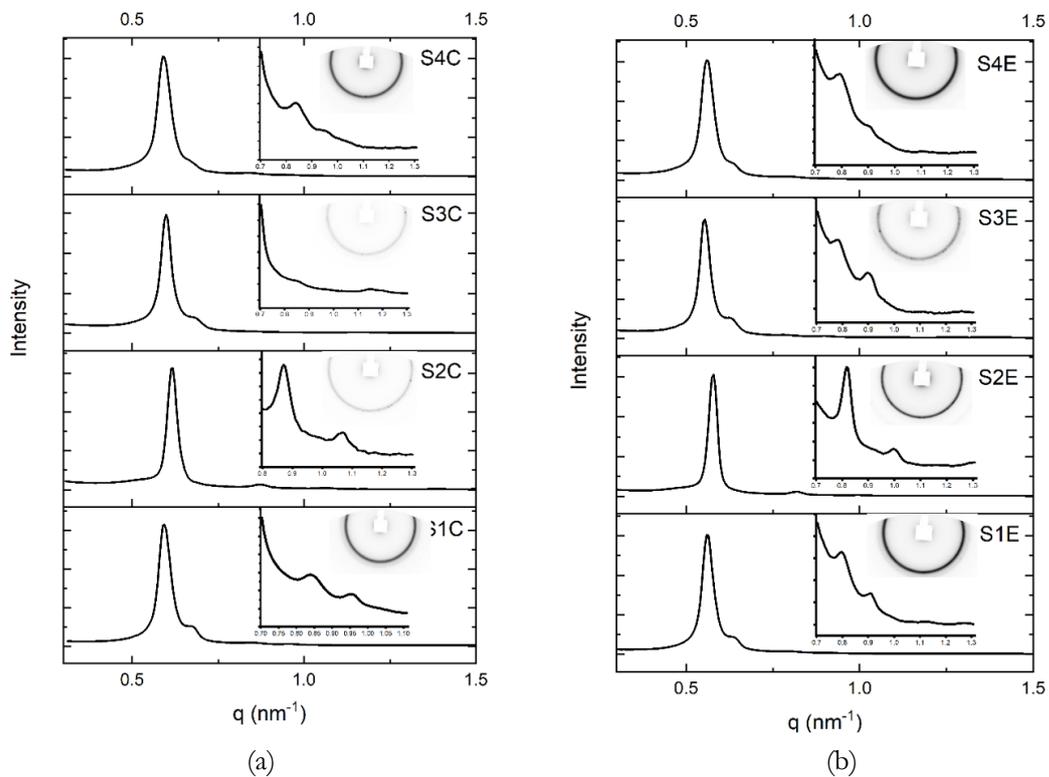


Fig. 2. SAXS spectra of amine-modified SBA-16 with amine concentration variation using (a) calcination and (b) solvent extraction de-templating techniques.

As a result, the absence of those peaks (1285 and 1243  $\text{cm}^{-1}$ ) in the S1C sample could confirm the successful de-templating of the SBA-16 template. Being in line with the previous investigation by Adeli (2016), it indicates that the S1C sample was classified as SBA-16 [23].

The reduced intensity of strong -OH bands at 3445  $\text{cm}^{-1}$  in the calcination sample (S1C) confirms the effective removal of the block copolymer. It was also confirmed by Li et al. (2017) in their study on the utilization of modified Pluronic F-127 as a drug vehicle [24]. However, a band at 2969  $\text{cm}^{-1}$  should be associated with CH<sub>2</sub> bonds, and the C-H vibrations cause a slight elevation at 1711  $\text{cm}^{-1}$  in the solvent extraction treatment sample (S1E). The presence of both vibration bands (2969 and 1711  $\text{cm}^{-1}$ ) predicted that the template would not completely vanish from SBA-16.

Figure 3(a) shows the FTIR spectra for the calcination treatment and amine concentration variation on SBA-16. The conversion of siloxane and silanol groups into the amine counterparts at 3445 and 1643  $\text{cm}^{-1}$  bands was confirmed. Branca et al. (2016) reported that the presence of amine groups occasionally overlapped with the -OH groups. The highly engrossed amine groups on SBA-16 were predicted in the S4C samples due to the presence of sharp vibrational peaks compared to S1C (pure SBA-16). The broadband plateau from 2700 to 1700  $\text{cm}^{-1}$  shows that the material is transparent in this region. With increasing amine concentration loading, no major peaks appeared. The main vibrational bands of silanol, symmetrical siloxane, and asymmetrical siloxane groups were confirmed at 1080, 961, and 800  $\text{cm}^{-1}$ , respectively. All the prepared samples were classified as SBA-16. These findings affirm that the amine groups were successfully engrossed by the SBA-16 matrix without making any chemical bonds [25].

For solvent extraction treatment and amine concentration variation in the amine-modified SBA-16, the FTIR spectra were shown in Fig. 3(b). After amine groups loading on the SBA-16 matrix, it was observed that there are small gaps between pure SBA-16 (S1E) and other amine-modified SBA-16 samples (S2E, S3E, and S4E) at 3445 and 1080  $\text{cm}^{-1}$  bands, indicating that the conversion from hydroxyl groups to amine groups did not take place. This is because of the presence of the block copolymer, and it is consistent with the preliminary uranium adsorption test (see Table 3) that the calcination process is well-used to withdraw the template from the SBA-16 framework due to its consistent presence of amine on SBA-16. Thus, it exhibited a higher adsorption capacity. All samples show similar FTIR patterns and were claimed as SBA-16 due to the presence of the main vibrational peaks at 1080, 961, and 800  $\text{cm}^{-1}$ .

### 3.4. SEM-EDS Analysis

Figure 4 depicts SEM micrographs and the elemental composition distribution of the materials SBA-16-NH<sub>2</sub> as determined by elemental superficial mapping EDS. According to the result, the materials SBA-16-NH<sub>2</sub> are

primarily formed by silica (Si), oxygen (O), and nitrogen (N). On the surface of the SBA-16, the nitrogen element appears uniformly embedded. The nitrogen element dispersion was not detected on S1C and S1E because these samples were pure SBA-16 with no amine groups or nitrogen. The gold element was present as a result of sample preparation before SEM analysis. The nitrogen deployment on the solvent extraction de-templating sample (S4E) increases more than the calcination de-templating sample (blue-colored area) (S4C). Higher temperatures were predicted to eliminate the presence of nitrogen elements in the prepared samples [26]. These findings are in good agreement with the previous study by Barczak (2018) that the calcination process reduced the silanol groups by almost 2 folds when compared to the as-synthesized sample [27].

Figure 5 demonstrates the emission spectra of SBA-16- NH<sub>2</sub> materials. It was revealed that silica (Si), oxygen (O), and nitrogen (N) were present in the materials. In all samples, the oxygen content dominates over other elements. According to the elemental mapping results, the solvent extraction de-templating process contained more nitrogen.

### 3.5. Physical Properties Analysis: Specific Surface Area (SSA) Analysis

Table 2 summarizes the physical parameters presented in the BET-specific surface area (SSA). The obtained pure SBA-16 sample using calcination for template removal treatment (S1C) showed an exceedingly high SSA of 883  $\text{m}^2/\text{g}$ , which is in the range of SBA-16 physical characteristics (700-900  $\text{m}^2/\text{g}$ ) [28]. After the modification, the higher the amine concentration, the lower the observed SSA. The reason behind the decreased surface area of the samples is the presence of the amine groups on the decoration of SBA-16 blocking the adsorption of nitrogen molecules. For the S3C sample, the reported SSA was lower than that of other samples. This was predicted because of the aggregation or agglomeration of nanoparticles [29].

Table 2. Specific surface area (SSA) of synthesized samples.

Sample code	SSA ( $\text{m}^2/\text{g}$ )	Loss of SSA (%)
S1C	833	-
S2C	698	16.20
S3C	342	58.94
S4C	581	30.25
S1E	721	-
S2E	657	8.87
S3E	553	23.30
S4E	552	23.44

Based on the adsorption test of prepared materials, S1C, S4C, and S3E showed high uranium intake (shown

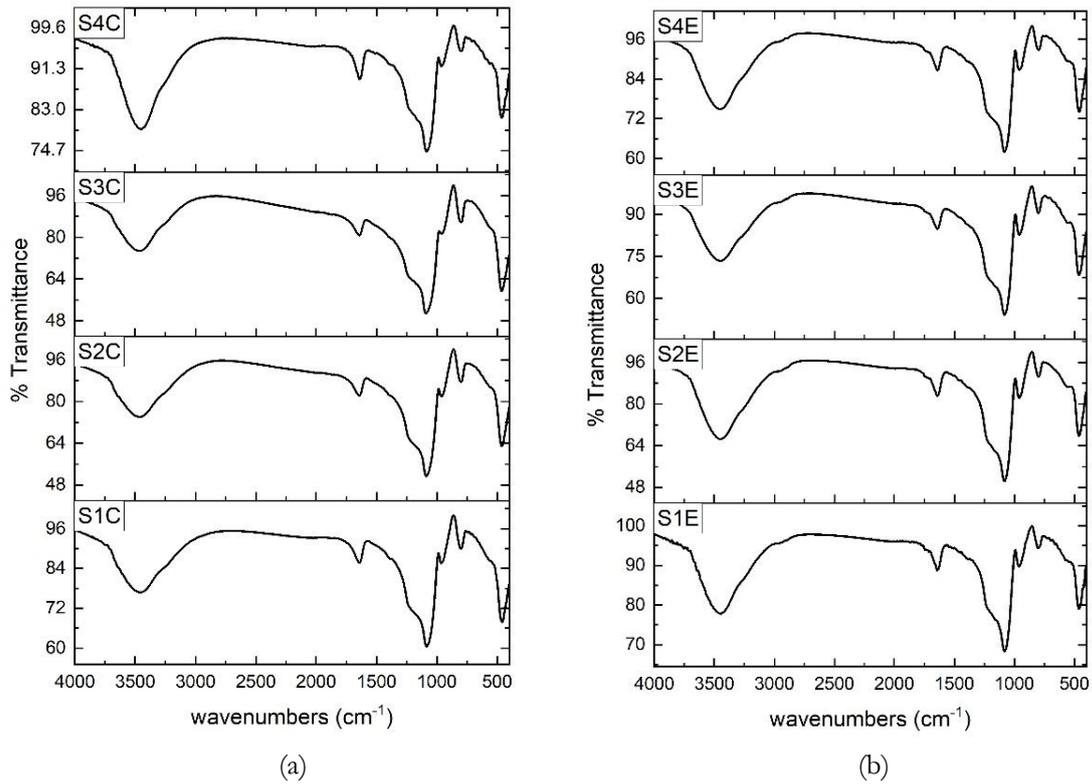


Fig. 3. FTIR spectra of amine-modified SBA-16 with amine concentration variation using (a) calcination and (b) solvent extraction de-templating techniques.

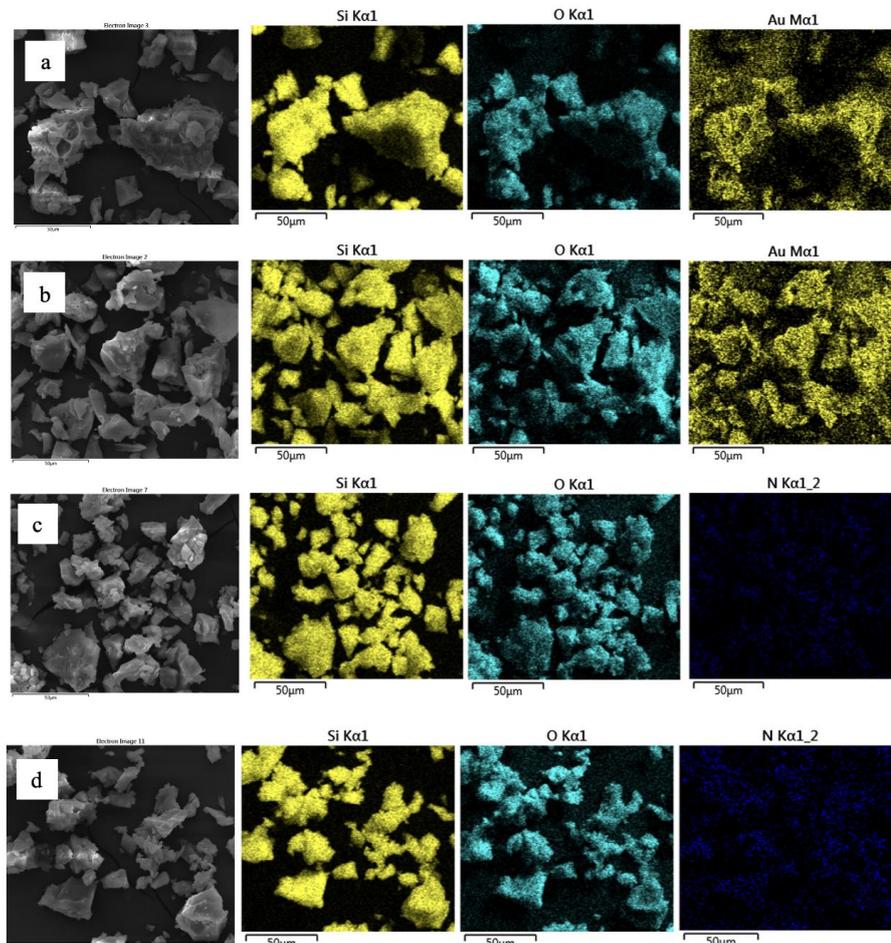


Fig. 4. Images of elemental mapping of materials (a) S1C, (b) S1E, (c) S4C, and (d) S4E.

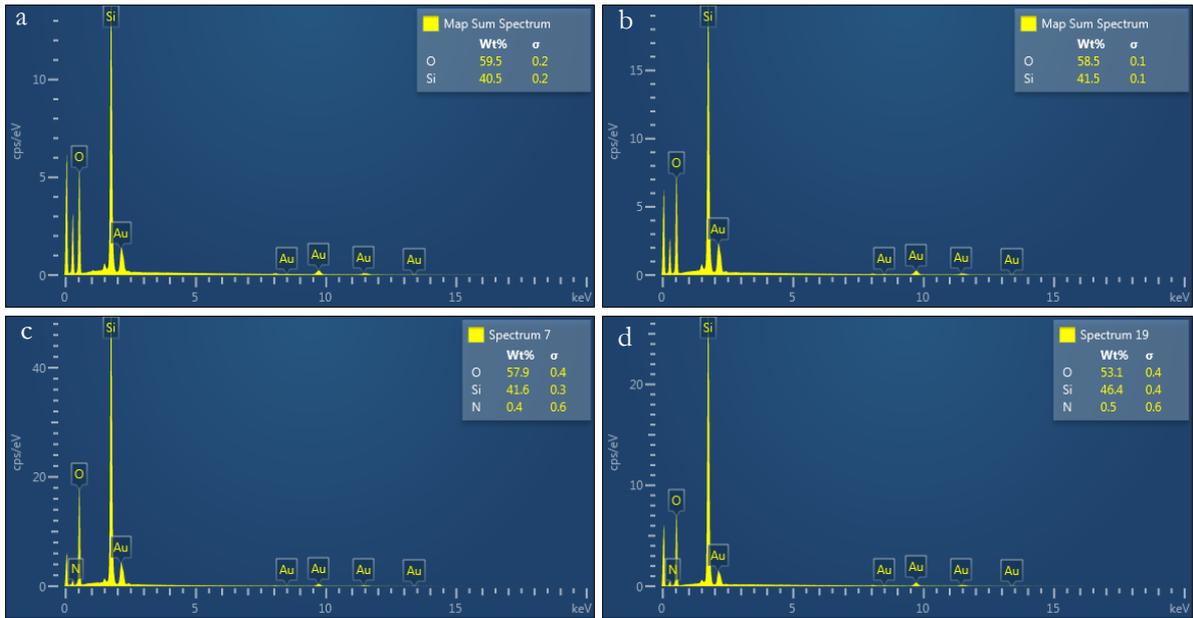


Fig. 5. EDS of amine-modified mesoporous silica (a) S1C, (b) S1E, (c) S4C, and (d) S4E.

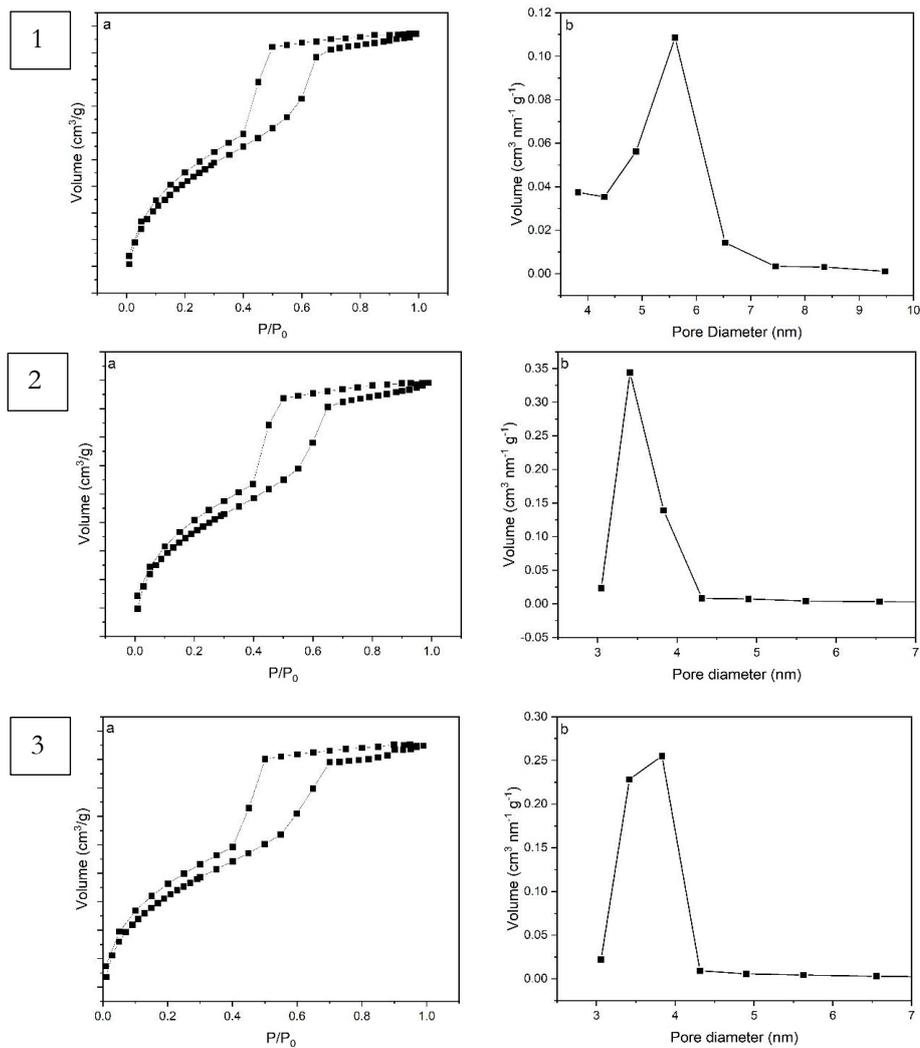


Fig. 6. Nitrogen adsorption isotherm profile and pore distribution of (1) S1C, (2) S4C, and (3) S3E.

Table 3. Uranium adsorption by amine-modified SBA-16 compared to similar investigations.

Material	Uranium uptake (mg-U/g-adsorbent)	Condition	Remark
SBA-16 (S1C)	8.82	Room temperature; reaction time: 1 h; volume of solution: 50 mL; pH: 5-6; natural seawater loaded with 143 ppm uranium, amidoxime ligands	This work
SBA-16 (S1E)	1.63		
Amine-SBA-16 S3C	17.81	Room temperature; reaction time: 1 h; volume of solution: 50 mL; pH: 5-6; natural seawater loaded with 143 ppm uranium, amidoxime ligands	This work
S4C	24.48		
S3E	5.70		
S4E	2.70		
Amine-porous aromatic framework	40	Room temperature; reaction time: 20 h; volume of solution: 200 mL; initial uranium concentration: 7.05 ppm; pH: ~ 6; uranium adsorption in simulated seawater; amidoxime ligands	[30]
Amine-SBA-16	558	T: 20°C; reaction time: 30 min; volume of solution: 200 mL; initial uranium concentration: 100 ppm; pH: 6; non-seawater; 3-(2-aminoethylamino) propyltrimethoxysilane	[32]
Phosphate-amino-SBA-15	373	T: 95°C; reaction time: ~1 h; volume solution: 10 mL; initial uranium concentration: 238 ppm; pH: 5.5; non-seawater; phosphonate and amino ligands	[33]

in Table 3). As result, nitrogen gas adsorption using the BET method was performed on the selected materials to determine the properties of the prepared material on the physio-sorption isotherm. The isotherm profiles shown in Fig. 6(a) are typical isotherm IV, indicating that the prepared samples were mesoporous silica, according to the IUPAC classification standard. The framework confined mesopores filled with nitrogen gas at P/P0=0.4-0.7. Moreover, the pore distribution profiles of the prepared samples (S4C and S3E) shown in Fig. 6(b) demonstrated the success of amine-modified SBA-16 because the pore distribution decreased from 5 - 6.5 nm to 3-4 nm following amine loading in SBA-16.

### 3.6. Preliminary adsorption test

In the preliminary adsorption investigation, the performance of amine-modified SBA-16 to adsorb uranium (VI) in natural seawater compared to other studies is shown in Table 3. The presence of primary amine induced higher uranium (VI) uptake for all template withdrawal treatments. This result aligns with the previous study by Li et al. (2017) on the adsorption of uranium (VI) from aqueous solutions using an amidoxime-modified porous aromatic framework [30]. The de-templating process demonstrated that the calcination treatment exhibited higher uranium (VI) adsorption than the solvent extraction treatment, signifying that the de-templating treatment affected not only the functional group arrangement (Figs. 1 - 3) but also the adsorption capacity.

These results are in agreement with the study of Barczak (2018) that calcination presented better adsorption uptake than solvent extraction in L-histidine adsorption [27]. In contrast to the earlier analysis by SEM-EDS, although the nitrogen content of the S4E sample was higher, the adsorption performance was not, due to the possibility of uranium adsorption by both silanol and amine groups in the S4C sample [31].

At a high amine concentration embedded in SBA-16, the sample can adsorb uranium very well in a short reaction time. However, compared to other amine group compounds, the uranium uptake in this study was lower, although a direct comparison may not be appropriate here because the initial uranium concentration, volume of solution, reaction time and temperature, effect of stirring, etc., were different across different investigations. Nonetheless, it can be concluded that the presence of the same amine groups on SBA-16 prepared by the calcination de-templating process was satisfied to be an emerging uranium adsorbent. The features of the prepared samples were reported that they had a low reduction of specific surface area (<30.5%) (see Table 2). The modified and removed templates had no effect on the basic form of the prepared materials. Regarding the mesoporous silica material as an adsorbent candidate, the specific surface area can elevate the adsorption capacity and maintain simultaneous adsorption against U(VI) species. Furthermore, the selected treatment, calcination, can solve the problem of template elimination without disturbing the basic form of the material as cubic mesoporous silica.

This study serves as a starting point for further development of the novel adsorbent for effective uranium recovery from natural seawater and aqueous solutions from, for instance, contaminated areas or industrial mining.

#### 4. Conclusions

Amine-modified mesoporous silica SBA-16 materials were successfully prepared using calcination and solvent de-templating processes. Using synchrotron radiation in LXR and SAXS analyses, the mesoporous phase and ordered structure of the samples were explored and confirmed as SBA-16-NH<sub>2</sub>. The effect of amine loading concentration for both calcination and solvent extraction de-templating processes showed that the higher concentration decreased the minor diffraction and scattering. The quantitative decoration information of the samples using FTIR, and SEM-EDS analyses demonstrated that the amine groups were uniformly deployed on SBA-16. In the preliminary uranium adsorption test, SBA-16-NH<sub>2</sub> using the calcination de-templating process and 1.5M of amine groups resulted in satisfactory performance. In summary, the novel modified mesoporous silica is a new promising adsorbent candidate for the removal or harvest of uranium from natural seawater, contaminated areas, or industrial mining.

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