Effect of sonication frequency in synthesis of silica aerogel-activated carbon nanocomposite

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Abstract. The silica adsorption capacity can be improved by composing it with activated carbon. The study aims to know the effect of sonication frequency in the nanocomposite silica aerogel-activated carbon synthesis using sol-gel method with TMCS (trimethylchlorosilane) and HMDS (hexamethyldisilazane) as modifying agents. Synthesized nanocomposites were further characterized by means of functional groups analysis using FTIR (Fourier Transform Infrared Spectrophotometry) method, morphological analysis using SEM (Scanning Electron Microscopy) method, and surface area analysis using BET (Brunauer-Emmet-Teller) method. The results of functional group analysis using FTIR shows that nanocomposite has a group of Si-OH, Si-O-Si, Si-C, C-H, C=O, C–O, the peaks around of 3300 cm⁻¹, 1051 cm⁻¹ - 1180 cm⁻¹, 1253 cm⁻¹, 2960 cm⁻¹, 1649 cm⁻¹, 1417 cm⁻¹; morphological analysis using SEM indicates that nanocomposite synthesis with 42 kHz frequency sonication has a smaller particle size than 35 kHz frequency, where are the surface area analysis using BET method obtained 674.897 m² / g at frequency of 42 kHz and 486.909 m² / g synthesis at frequency of 35 kHz.

1. Introduction
Silica aerogel is classified as a type of aerogel made from silica with low density property, large surface area and low thermal conductivity [1]. Synthesis of silica aerogel was obtained by using sodium silicate extracted from bagasse ash [2], brown rice husk [3], and rice husk ash [4]. Silica aerogel with a large surface area is utilized as an adsorbent [5]. However, the stability of silica against humid air is not good, thus affecting its adsorption power [6]. Activated carbon as a universal adsorbent has a large surface area, pore volume and large pore diameter. However, the active side of activated carbon limits its adsorption power [7]. The adsorption capacity of silica and activated carbon is improved through both composites [8]. Activated carbon modifies the structure of silica aerogel, limits the contraction of aerogel, and strengthens the framework of silica aerogel [9].

Silica aerogel-activated carbon composites combine the polar-inorganic properties of silica aerogel and non-polar-organic from activated carbon; thus, the composite is able to increase the adsorption ability. Givianrad and co-workers synthesized silica aerogel-activated carbon nanocomposites by using a mixture of TMOS, methanol, MTMS, and NH₄F solution [8]. Mixing was performed by using the help of a magnetic stirrer for 30 minutes. The results of the mixture in the form of gel plus activated carbon were stirred by using a 20000 rpm homogenizer for 30 minutes. Drying gel was stored at room temperature for 5 days. The synthesis product was applied as a heavy metal waste adsorbent with an adsorption capacity reaching 60%. Adsorbents utilizing activated carbon have an adsorption capacity of 50% and adsorbents utilizing silica aerogel have an adsorption capacity of 30%. However, the synthesis
of both adsorbents requires a long time since the addition of activated carbon into gel causes the active carbon to not properly stick to silica [5].

Sonication is considered as one of the effective techniques in mixing, reaction processes, and breakdown of materials with the help of high energy at ultrasonic wavelengths. Synthesis of mesoporous silica from rice husk ash along with sonication as a substitute for mixing with magnetic stirrer, indicated results such as large surface area, increased pore volume [4] and large adsorption power [3]. Synthesis by sonication method produces cavitation bubbles which will create nanoscale diameter particles and homogeneous size distribution of nanoparticles [10]. Sonication produces shock waves which will cause cavitation bubbles, separate particle agglomeration, and produce particle dispersion [11]. Frequency indicates the number of shock waves that occur, resulting in the formation of cavitation bubbles, clot separation, particle dispersion, and accelerated synthesis.

Sonication method with sonication frequency has advantages, such as 1) shorter synthesis, 2) greater particle surface area, 3) larger pore volume, and 4) more homogeneous pore-size. This study aims to determine the effect of sonication frequency on the synthesis of silica aerogel-activated carbon nanocomposites. The synthesis was conducted by the sol-gel method, using bagasse ash as a source of silica.

2. Research Material and Method
The basic ingredients used are bagasse ash, obtained from PG. Krebet Baru II Malang, Malang Regency. The utilized chemicals in this study include: Pure Analysis (pa), such as: NaOH (Merck), Activated Carbon (Merck), Cation exchange resins, TMCS (Merck), HMDS (Merck), NH₄OH (Merck), HCl (Merck), aqua demineralization (Hydrobatt), universal indicator paper (MN), Whatman No. 40 filter paper, and aquadest. The tools used include 42 kHz ultrasonic batch (Branson 1510), 35 kHz ultrasonic batch (Sharp), analytic balance sheet (Durascale Dab-200), magnetic stirrer (Cimarec), oven (Memmert), FTIR (Shimadzu IR-Prestige 21), SEM (FEI-INSPECT-S50), and BET (Quantachrome).

Bagasse ash was sifted and roasted to produce dry bagasse ash. Bagasse ash of 10 grams was added with 60 mL of 2N NaOH in 250 mL Erlenmeyer, then stirred with a magnetic stirrer and heated to boiling for 1 hour. The mixture was cooled to room temperature and filtered with Whatman 40 filter paper and Buchner filter. Sodium silicate was mixed by using a cation exchange resin (pH 2) in a ratio of 1:3, stirred by using a magnetic stirrer for 30 minutes and was filtered to produce silicate acid filtrate.

The synthesis step was carried out in ultrasonic batches with frequencies of 35 kHz and 42 kHz at 10- and 20-minutes time variations. Silica acid of 10 mL was added by activated carbon as much as 0.03 grams, stirred in an ultrasonic bath for 10 minutes. TMCS was added into silica acid by modifying agent as much as 0.3 mL, stirred for 10 minutes, added with 0.6 mL HMDS, and stirred for 10 minutes. If no gel has been formed, NH₄OH was added 1N dropwise. This method was repeated for variations in frequency and time.

Then the gel was processed at 40 °C for 18 hours and 60 °C for 1 hour. The formed gel was washed by using aquademineral to neutral pH, then the gel was dried at 80 °C for 24 hours to obtain Silica Aerogel-activated Carbon (SAC) nanocomposite.

SAC nanocomposite produced was characterized by: (a) FT-IR (Fourier Transform Infrared Spectrophotometry) to determine the functional groups; (b) SEM (Scanning Electron Microscopy) to determine surface morphology; and (c) surface area analysis using BET (Brunauer-Emmet-Teller) method.

3. Result and Discussion

3.1. Silica Aerogel-activated Carbon (SAC) Nanocomposite
In figure 1 FT-IR spectra show the formation of nanocomposites in the presence of broad absorption of silanol (Si-OH) groups in an area of about 3300 cm⁻¹, siloxane (Si-O-Si) regions around wave numbers 1051 cm⁻¹ and 1180 cm⁻¹. Si - C at wave number 1253 cm⁻¹, group C - H at wave number around 2960 cm⁻¹. The absorption area indicates that the Si - OH condensation becomes Si - O and is modified to Si
- CH\textsubscript{3} in the presence of a modifying agent. The functional group is identical to the functional group in the aerogel silica. The C = O group in the absorption region is around 1649 cm\textsuperscript{-1}, C-O at 1417 cm\textsuperscript{-1}, the group is identical to the functional group in activated carbon. This analysis shows the successful synthesis of aerogel silica nanocomposites-activated carbon.

![Figure 1. FT-IR Spectra of Silica Aerogel-Activated Carbon Nanocomposite.](image)

3.2. **Surface morphology of silica aerogel-activated carbon (SAC) nanocomposite**

Figure 2 indicates the surface morphology of SAC nanocomposite which is the result of SEM magnification for 100,000 times at frequencies of 35 kHz and 42 kHz. The surface morphology of SAC nanocomposites presents a round-like cotton shape with homogeneous size distribution.

The particle size of SAC nanocomposite synthesized with sonication at a frequency of 35 kHz is bigger than the size of the nanocomposite particles synthesized at the frequency of 42 kHz, see figure 2 (a) and 2 (b), respectively. The surface morphology of SAC at 42 kHz frequency appears homogeneous and small, demonstrating that the sonication shock wave was able to separate the clumping of particles (agglomeration).

3.3. **Effect of sonication frequency on nanocomposite characteristics**

Physical properties of SAC nanocomposite include surface area and pore volume. The surface area is determined by BET method and pore volume is determined by BJH (Barret-Joyner-Hallenda) method. The data of surface area and pore volume are shown in Table 1.

Sonication frequencies at 35 kHz and 42 kHz affect surface area and pore volume. Frequency indicates the number of shock waves that occur, producing cavitation bubbles which are able to separate lumps and disperse particles. Utilization of greater frequencies results in shorter synthesis times. Overall, the sonication frequencies which produce (from the largest to smallest) SAC nanocomposite surface area are: 42 kHz for 10 minutes, 35 kHz for 20 minutes and 35 kHz for 10 minutes. The data indicates that the sonication method has an energy limit, yet a maximum impact on the continuity of the reaction chemistry. Conversely, if the limit is exceeded, the effectiveness of the chemical reaction will reduce.
Figure 2. SEM SAC Nanocomposite (a) 35 kHz frequency (b) 42 kHz frequency.

Table 1. Physical properties of SAC nanocomposites.

| Frequency (kHz) | Time (minute) | $S_{BET}$ (m$^2$/g) | Pore volume (cm$^3$/g) |
|----------------|--------------|----------------------|------------------------|
| 35             | 10           | 486.909              | 0.377                  |
| 35             | 20           | 507.206              | 0.431                  |
| 42             | 10           | 674.897              | 0.631                  |
| 42             | 20           | 485.948              | 0.397                  |

Figure 3. Adsorption-desorption curves of nanocomposites (a) synthesis at a frequency of 35 KHz (b) synthesis at a frequency of 42 KHz.

SAC nanocomposite adsorption-desorption type by using nitrogen gas is presented in Figure 3 (a) and (b). The curve has similarities with typical type IV isotherms according to IUPAC classification, initially the slow gas absorption is caused by stronger intermolecular interaction of adsorbate than the interaction between adsorbate and adsorbent. This type applies to porous material. In addition, particles from the synthesis have mesoporous-sized pore diameters.

4. Conclusion

Synthesis of SAC nanocomposite can be performed by sonication at frequencies of 35 kHz and 42 kHz and synthesis time of 10 minutes and 20 minutes. The results of SAC nanocomposite FTIR indicate potential existence of Si - OH, Si - O – Si, C – H groups (identical functional groups in aerogel silica) and C = O, C - O groups (identical to activated carbon functional groups). SEM image of nanocomposite depicts that synthesis of SAC nanocomposite with sonication frequency of 42 kHz has smaller particle
size than the results of synthesis with 35 kHz with for 10 minutes. This result proves that sonication shock waves can separate agglomeration. Synthesis of SAC nanocomposite at a frequency of 42 kHz requires a shorter synthesis time than that with a frequency of 35 kHz. Longer synthesis time (20 minutes) indicates smaller surface area of SAC nanocomposite. However, sonication method has energy limits that still have a maximum impact on the sustainability of chemical reactions. If the limit is exceeded, the effectiveness of chemical reactions with sonication frequency will reduce. Sonication frequency influences surface morphology, particle size distribution, surface area, and pore volume. Based on the type IV adsorption-desorption curve, SAC nanocomposite from the synthesis has a mesoporous-sized pore diameter.

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