Effect of Sonication Time on Characteristics of Synthesized Silica Aerogel Activated Carbon Nanocomposite Based on Bagasse Ash

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Abstract. The purpose of this research was to identify the effect of sonication time on the characteristics of silica aerogel activated carbon (SA-AC) nanocomposite produced based on bagasse ash. SA-AC nanocomposites was synthesized by sol-gel method at ambient pressure. The silicic acid solution was mixed with activated carbon and the surface modifying agent (TMCS and HDMS). The mixture was then put in an ultrasonic bath at the varying sonication time of 5, 10, 15, and 20 seconds on frequency of 42 kHz. SA-AC nanocomposites were characterized by using FTIR, SEM, and BET. The results showed that SA-AC is formed, indicated by the wave number FTIR spectra of Si-O-Si (1076.28 cm⁻¹), Si-C (1253.73 cm⁻¹), C-H (2960.73 cm⁻¹), C-O (1087.85 cm⁻¹), C=C (2113.98 cm⁻¹), and C=O (1942.32 cm⁻¹). SA-AC nanocomposites synthesized by sonication assistance has a smaller agglomerate than that of without sonication. The largest surface area of SA-AC nanocomposite of 677.719 m²/g and the biggest pore volume of 0.6338 m³/g is obtained when the nanocomposite is synthesized at sonication time of 10 seconds.

1. Introduction
Silica aerogel is one of the adsorbents with large specific surface area, low density, hydrophobes, and high thermal stability. Therefore, silica aerogel is more effective at absorbing heavy metals compared to xerogel and hydrogel silica. Nazriati et al. [1], reveals that synthesized silica aerogel has a surface area of 540 to 1114 m²/g, pore volume of 0.75 to 2.16 cm³/g, pore size of 3.39 to 7.38 nm and contact angle of 140 °C. The silica aerogel was synthesized by the sol-gel method from baggase ash silica derived from sugar factory waste. Besides silica aerogel, activated carbon also has a large surface area that can be used as an adsorbent. However, activated carbon does not have enough functional groups to adsorb heavy metals economically. Therefore, several methods for modifying the surface of activated carbon are introduced chemically or physically [2],[3]. One of them is by making a nanocomposite[4]. By combining the two adsorbents, it is hoped that the new nanocomposite adsorbents can be produced with greater adsorption capacity. The adsorption capacity of nanocomposite is higher than silica aerogel and activated carbon [5][6]. The capacity of nanocomposite of activated carbon and silica aerogel can eliminate more than 60% Cd metal on the optimum experimental conditions [7].

Other method is needed to increase the surface area of nanocomposites. One method that might be used is nanocomposite synthesis using ultrasonic, or better known as the sonication method. Sankar et al. [8] reported that there were the effect of sonicacion time on the characteristics of silica nanoparticles derived from brown rice husk. The results obtained an increasing in the specific surface area of...
nanoparticles. The synthesis of nanoparticles used sonication time variations 0, 10, 30, and 50 seconds. Where the specific surface area without ultrasonic (0 seconds) 201.45 m²/g increased significantly to 271.22 m²/g at 50 seconds sonication time. The synthesized nanoparticles had an increasing surface area with increasing sonication time. Sonication method in synthesis material is produces cavitation waves which make the particles size smaller, so it has a large surface area [9][10][11][12]. Accordingly, synthesis of nanocomposite of SA-AC using ultrasonic assistant is needed to increase the surface area of the resulting product.

The sonication method can be used to replace conventional stirring using a magnetic stirrer in the synthesis of activated carbon silica nanocomposites with a sol gel method. The cavitation energy of the ultrasound in making the nanocomposite is also need to know the effect on its specific surface area. This method is one of the easiest, cheapest, and the most effective tools to provide energy for environmentally friendly reactions called Green Technique and having relatively faster synthesis times [13][14].

2. Materials and Method

The materials used in this study were bagasse ash, NaOH (p.a Merck), HCl 37% (p.a Merck), activated carbon, cation exchange resin, NH₄OH (p.a Merck), trimethylchlorosilane (TMCS) p.a, hexamethyldisilazane (HMDS) p.a, and aquades. Equipments used include glassware, hot plates, magnetic stirrer (Cimarec), oven (Memmert), vacuum pump (Ulvac Sinkukiko DA-20D), analytical balance (Durastale Dab-200), Ultrasonic (BranSonic), FTIR (Shimadzu IR-Prestige 21), SEM (FEI-INSPECT-S50), dan BET (Nova Touch LX4 Quantachrome).

Synthesis of SA-AC nanocomposites was started by extracting sodium silicate from bagasse ash using NaOH 2 N solution for 1 hour. The sodium silicate solution that has been obtained was then mixed with cation exchange resin to produce a silicic acid solution. A 10 mL silicic acid solution was mixed with 0.03 g of activated carbon. The mixture was put in an ultrasonic bath with sonication time variations of 5, 10, 15, and 20 seconds with a frequency of 42 kHz. Subsequently, the surface modifying agent was added in the form of trimethylchlorosilane (TMCS) as much as 0.3 mL and hexamethyldisilazane (HMDS) as much as 0.6 mL. The addition of modifying agent was carried out by drop while stirred in an ultrasonic bath with sonication time variations of 5, 10, 15, and 20 seconds. The formed hydrogel was then aged at 40 °C in 18 hours and 60 °C in 1 hour for tissue strengthening. The hydrogel was then washed using demineralized water until the neutral pH and it was filtered. The hydrogel obtained was drained at 80 °C in 24 hours to get the SA-AC nanocomposite.

The SA-AC nanocomposite produced was analyzed to determine its characteristics. The analysis was used several instruments such as functional group analysis using the Fourier Transform Infra Red (FTIR) instrument, nanocomposite surface morphology analysis using Scanning Electron Microscopy (SEM) instruments, and specific surface area analysis using the Brunauer-Emmet-Teller (BET) instrument.

3. Results and Discussion

FTIR spectra of SA-AC nanocomposites with each sonication time of 5, 10, 15, and 20 seconds is then compared with standard wave number to determine the functional groups contained in the synthesized SA-AC nanocomposite. The SA-AC nanocomposite FTIR spectra at every sonication time of 5,10, 15, and 20 seconds can be seen in Figure 1.
Figure 1. FTIR Nanocomposite Spectra of SA-AC at sonication time of 5, 10, 15, and 20 seconds.

Based on the spectra in Figure 1, there are several typical absorption bands. The FTIR spectra of the nanocomposite SA-AC at sonication time of 5, 10, 15, and 20 seconds show an absorption band at wave number of 1076.28 cm\(^{-1}\) indicating the presence of Si-O-Si vibration. It shows that condensation of silanol (Si-OH) into siloxan (Si-O-Si) has occurred. While the absorption band at wave number of 1253.73 cm\(^{-1}\) indicates the presence of Si-C vibration in the Si-CH\(_3\) functional group of SA-AC nanocomposite. It indicates that the nanocomposite has been successfully modified due to a modifying agent. In addition, the successful modification of nanocomposites is shown by the absorption band at the wave number of 2960.73 cm\(^{-1}\) which indicates the C-H vibrations of CH\(_3\).

The difference between FTIR spectra of SA-AC nanocomposite and silica aerogel is shown by the absorption band at wave numbers of 1942.32 cm\(^{-1}\) and 2113.98 cm\(^{-1}\) indicating the vibrations of C = O and C = C. In addition, there is an absorption band on waves around 1087.85 cm\(^{-1}\) which indicates the presence of C-O vibrations. Vibration at wave numbers of 1087.85 cm\(^{-1}\), 1942.32 cm\(^{-1}\), and 2113.98 cm\(^{-1}\) is also present in the active carbon spectrum. It is related to the functional groups of C-O, C = O, and C = C that are typical functional groups possessed by activated carbon. In addition, the SA-AC nanocomposite absorption band synthesized at sonication time of 5, 10, 15, and 20 seconds has the similarity wave number of peaks. It shows that SA-AC nanocomposites were successfully formed at sonication time of 5, 10, 15, and 20 seconds.

Morphology of SA-AC nanocomposites was analyzed using SEM as presented in Figure 2. It shows that the morphology of SA-AC nanocomposites synthesized by sonication assistance has smaller agglomerates than that of without sonication. It can be related to the cavitation process generated from ultrasonic waves that propagate in the liquid medium. The energy caused by the collapse of cavitation will reduce the size of the agglomeration of material formed. The shock waves of sonication can separate agglomeration resulting in a smaller particle size. Characterization of the surface area used adsorption and desorption N\(_2\) with BET method and the measuring pore volume used BJH method. The data of BET and BJH method were presented in Table 1.
Figure 2. SEM images of (a) SA-AC nanocomposites without sonication and (b) Nanocomposites with sonication.

Table 1. BET Analysis of SA-AC Nanocomposite.

| Sample       | $S_{BET}$ (m$^2$/g) | Pore volume (cm$^3$/g) |
|--------------|----------------------|------------------------|
| NC SA-AC TU  | 509.139              | 0.5280                 |
| NC SA-AC 5 s | 509.940              | 0.5675                 |
| NC SA-AC 10 s| 677.719              | 0.6338                 |
| NC SA-AC 15 s| 435.682              | 0.4705                 |
| NC SA-AC 20 s| 485.948              | 0.3969                 |

Data at Table 1 shows that the surface area of the SA-AC nanocomposite synthesized at sonication time of 10 seconds has the largest surface area of 677.719 m$^2$/g and pore volume of 0.6338 m$^3$/g. The surface area of the nanocomposite is increasing when it is synthesized at optimal time of sonication. Ultrasonic waves can prevent agglomeration or clumping of particles [15]. It is also in line with Suslick's statement [16] that the sonication induces particle size and tends to be more homogeneous and becoming smaller which is eventually leads to the size of the stable nanoparticles and avoid clumping. At the optimum sonication time, the surface area becomes larger because the particle size is getting smaller. After passing the optimum sonication time, however, the surface area of nanocomposite becomes smaller because of agglomeration.

The phenomena of adsorption and desorption type of N$_2$ gas in the BET method can be seen in Figure 3. All nanocomposite samples synthesized at sonication time of 5, 10, 15, and 20 seconds showed the type IV of isotherm. It indicates that the SA-AC nanocomposites has pores in the range of 2 to 50 nm and the adsorbent was a mesoporous material.
Figure 3. The Adsorption Isotherm BET of composites at various sonication time of (a) 5 seconds (b) 10 seconds (c) 15 seconds (d) 20 seconds.

4. Conclusions
Silica aerogel-activated carbon nanocomposites have been successfully synthesized using ultrasonic assistant. The nanocomposite synthesized by varying the sonication time of 5, 10, 15, and 20 seconds at a frequency of 42 kHz produced mesoporous materials. The surface area of SA-AC nanocomposite synthesized at sonication time of 10 seconds has the largest surface area of 677.719 m²/g and the biggest pore volume of 0.6338 m³/g. The longer sonication time resulted on the smaller surface area as well as pore volume of SA-AC nanocomposites.

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