SYNTHESIS OF HYBRID SPONGY NANOCOMPOSITE MATERIALS BASED ON Al_2O_3 AND STEARIC ACID TO RECOVER WASTE OIL IN WATER

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ABSTRACT

The spongy nanocomposite materials based on Al_2O_3 hybridized with stearic acid were synthesized by a hydrothermal method combined with a sol-gel combustion method. The characteristics of the materials were determined by standard methods such as Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). A 0.03 M NH_3 solution and a 0.05 M stearic acid solution were used to synthesize materials. The synthesis yield of Al_2O_3 nanoparticles and stearic acid hybridized Al_2O_3 spongy nanocomposites reached 96.5 % and 97.6 %, respectively. The effects of the variation of NH_3 concentrations, steric acid concentrations, and sintering temperature on the absorbability of the nanofoams were investigated. The hybrid nanomaterials were used to treat 2 types of waste oil from motorcycle engine and cooking. The results showed that 1 g of hybrid nanocomposite foams absorbed 5 mL of waste oil. This indicates that the steric acid-hybridized Al_2O_3 spongy nanomaterials could be applied for the treatment of oil pollution.

Keywords: *Nanocomposite foam, nanomaterial, stearic acid, Al_2O_3, waste oil.*

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1. INTRODUCTION

Oil spills and waste oil pollution are accidents that occurs during the exploitation, storage, transportation and use of oil. Oil pollution and waste oil not only negatively affect an economy, but also seriously affect an ecological environment. Recently, along with rapid socioeconomic development, Vietnam's petroleum industry has been also strongly developed. It is estimated that around 11 million tons of oil and oil products have been consumed every year. Moreover, Vietnam is located on the international maritime route of oil transportation from the Middle East to Japan in amount of up to 30 million tons per year. This implies that tens of millions of tons of oil are being circulated on the territory of Vietnam every year and therefore the risk of oil spills is very high. The fact shows that oil spill accidents have consecutively occurred for many years. For example, the accidents of the Neptune Aries in 1994 in Ho Chi Minh city, the Formosa One in 2001 in Ba Ria - Vung Tau, the My Dinh ship in 2004 in Cat Ba sea, and dozens of other small accidents in the whole country and in the petroleum industry [1-3]. In addition, around 1.5 million liters of cooking oil is consumed in Vietnam every

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year. A rate of 10% - 20% of the amount is disposed after use, implying 150,000 to 300,000 liters of waste cooking oil is discharged to the environment every year [4].

In order to recover waste oil and treat oil pollution, mechanical methods using offshore oil booms, shoreline oil booms, floating barrier and vacuum equipments have been often used. Besides, there are many other treatment technologies such as chemical dispersion, biodegradation, in-situ combustion, and adsorption. The adsorption methods may be considered as more appropriate solutions for the recovery of waste oil since these methods minimize potential negative impacts on the environment [5-9].

Most of adsorbents using for oil spill treatment that were synthesized from clay, perlite, and glass wool had low adsorption capacity. Although polyurethane spongy materials had high adsorption capacity, they were very bulky. Moreover, their chemically compatibility with different oils was not high and therefore the oil treatment was not thorough [10-12]. In this work, spongy nanocomposite materials based on stearic acid-hybridized Al_2O_3 were synthesized to apply for the recovery of waste oil in water by a hydrothermal method combined with a sol-gel combustion method. The effects of NH_3 concentrations, steric acid contents, and sintering temperature on the characteristics and waste oil absorbability of the hybrid nanocomposites were investigated.

2. MATERIALS AND METHODS

2.1. Materials

Aluminum nitrate nonahydrate $Al(NO_3)_3.9H_2O$ (white solid, ≥ 99.5% purity, China), ammoniac solution (20 – 25% concentration, Vietnam), stearic acid (white solid, ≥ 98% purity, Indonesia), tergitol (≥ 99% purity, Malaysia), n-hexane (colorless liquid, ≥ 99.5% purity, China), double distilled water

Waste oil was collected from a motorcycle engine with a black color and high viscosity. Waste cooking oil was collected from the kitchen of a restaurant which has a brownish color.

2.2. Synthesis of stearic acid-hybridized Al_2O_3 nanocomposite foams

Spongy nanocomposite materials based on Al_2O_3 hybridizing with stearic acid were synthesized by a hydrothermal method combined with a sol-gel combustion method via two processes as presented in figure 1.

The synthesis procedure includes two steps, namely the synthesis of Al_2O_3 nanofiblers and stearic acid/Al_2O_3 spongy nanocomposites. Al_2O_3 nanoparticles were synthesized via the slow addition of NH_3 solutions with various concentrations of 0.1 M, 0.3 M and 0.5 M into a 25 mL of a solution containing 15 g of $Al(NO_3)_3$ until pH = 6. A suspended mixture was generated and continuous stirred for 1 h. After that, the mixture was centrifuged at a speed of 4.500 rpm for 5 min to obtain a precipitate part which was transferred to an autoclave for a hydrothermal process at 170^0C for 24 h. Subsequently, the product of the hydrothermal process was mixed with 5 g of tergitol. Finally, the mixture was sintered at 450 – 600^0C for 5 h to form Al_2O_3 nanoparticles.

Stearic acid/Al_2O_3 spongy nanocomposites were synthesized by the addition of steric acid solution in a suspension of Al_2O_3 nanoparticles. Briefly, 1 g of Al_2O_3 nanoparticles was ultrasonicated in 50 mL of distilled water for 5 min to generate a suspended solution. Then, various volumes in the range of 50 mL – 150 mL of a 0.05 M stearic acid solution were injected in the Al_2O_3 suspension during a vigorous shaking to form milky spongy nanocomposite materials which were purified by using a filter paper.

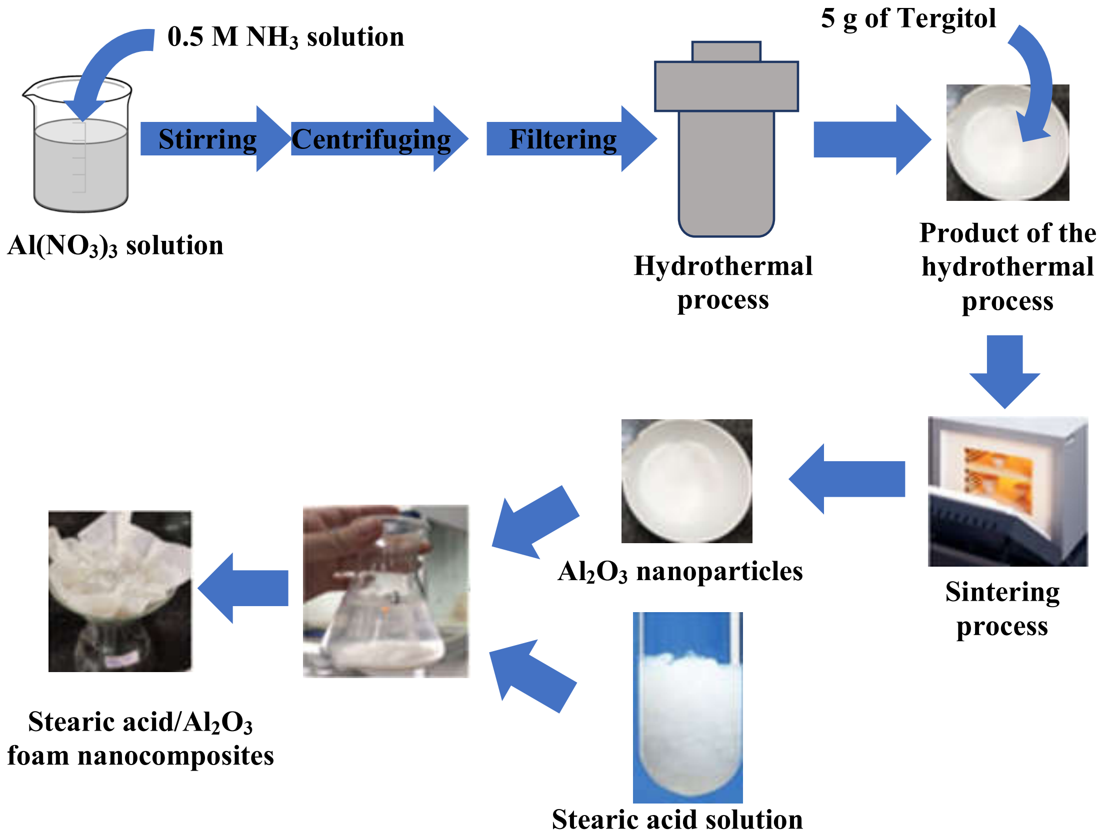

Figure 1. Schematic diagram illustrating the synthesis procedure of spongy nanocomposites based on Al_2O_3 hybridized with stearic acid.

2.3. Structure characterization of the hybrid foams

The structure characterization of the function groups of Al_2O_3 nanoparticles and stearic acid-hybridized Al_2O_3 nanocomposites was analyzed by a Fourier-transform infrared spectroscopy (FTIR) using Bruker Tensor spectrometer (Institute of Geography, VAST). The surface structure morphology of materials was determined by using a Jeol JMS 6490 Scanning Electron Microscopy (SEM).

The experimental procedure for the density determination of the nanocomposite was carried out according to TCVN 6039-1: 2015 (ISO 1183-1:2012).

2.4. Evaluation of the absorbability of the hybrid foams to waste oil

The waste oil absorbability of hybrid foams was evaluated using a static model, which was performed at the laboratory of Faculty of Environment, Ha Noi University of Nature Resources and Environment. The detail practical procedure was carried out as follows. Firstly, various volumes in the range of 1 mL to 6 mL of waste oil were added into beakers containing 50 mL distilled water, then

1 g of stearic acid/Al_2O_3 spongy nanocomposites was added to each beaker. Waste oil in water was immediately adsorbed on the spongy nanocomposites. The waste oil adsorbed nanocomposites were separated by using filter cloth or glass wood, which were dried and weighed for the determination of adsorption yield of the materials.

For the preparation of a blank sample, 1 mL of waste oil was added into a beaker containing 50 mL distilled water, then the solution was flowed through the layer of filter cloth or glass wood. Water oil adsorbed on the spongy nanocomposites was recovered via a simple mechanical compression method. All experiments were repeated three times.

3. RESULTS AND DISCUSSION

3.1. Effects of synthesis conditions on the properties of hybrid nanocomposite foams

3.1.1. Effects of the concentration variation of NH_3 solutions on the formation of Al_2O_3 nanoparticles

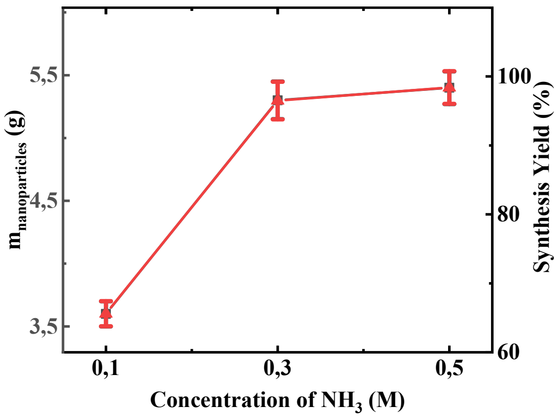

Figure 2. The effects of NH_3 concentrations on Al_2O_3 nanoparticle formation.

The effects of NH_3 concentrations on the formation of Al_2O_3 nanoparticles were detailed in Figure 2. NH_3 solutions with concentrations of 0.1 M, 0.3 M and 0.5 M were used for synthesis processes while other conditions were similar as described in section 2.2.

The obtained results showed that NH_3 concentration impacted the mass and size of Al_2O_3 nanoparticles. The formation yields of Al_2O_3 nanoparticles increased during the increase in the concentrations of NH_3 solutions. When the synthesis process achieved a theorical yield of 100%, it would generate 5.49 g of Al_2O_3 nanoparticles. It means a 0.5 M NH_3 solution could be used to synthesize the nanoparticles with a yield of 98.4%, which was higher than the yield of synthesis processes using lower NH_3 concentrations. However, low NH_3 concentrations could form the nanoparticle with smaller and more uniform sizes. It may be explained by the fact that the size of $Al(OH)_3$ precipitates formed from low concentration NH_3 solutions were smaller and more uniform, whereas $Al(OH)_3$ formed from a high NH_3 concentration tended to accumulate a large size. Therefore, the shape of Al_2O_3 nanoparticles synthesized from a high NH_3 concentration was heterogeneous. From the result, 0.3 M NH_3 solutions were used for further experiments.

3.1.2. Effects of the variation of sintering temperature

strongly impacted on the properties and waste oil adsorption capability of nanomaterials. Various temperatures in the range of 450^{0}C to 600^{0}C were used to synthesis spongy nanocomposites while other experimental conditions were fixed as described in section 2.2. The spongy nanocomposites were utilized to adsorb a waste oil sample containing 2 mL of motorcycle waste oil in 50 mL of distilled water.

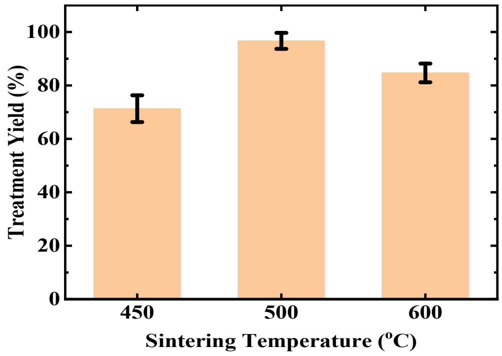

Figure 3. Effects of sintering temperature variation on the waste oil adsorption capability of spongy composites

The temperature of sintering processes Figure 3 shows the yield of waste oil treatment using stearic acid-hybridized Al_2O_3 spongy nanocomposites. The results indicated that the nanocomposites synthesized under the sintering temperature of 500^0C could adsorb waste oil with the highest yield of 96.7%. This may result from the effects of temperature on the spongy structure of stearic acid/Al_2O_3 nanocomposites.

3.1.3. Effects of the volume variation of stearic acid solutions

The effects of stearic acid content on the waste oil treatment yield of spongy nanocomposites were evaluated by using various volumes of stearic acid to synthesize the spongy nanocomposites. The synthesis yield and treatment yield of different nanomaterials are presented in figure 4.

The results show an increasing treatment yield with an increasing stearic acid volume from 50 mL to 150 mL. However, the highest synthesis yield was achieved 97.6% for a stearic acid volume of 100 mL. This probably comes from the difference between the ratios of stearic acid to Al_2O_3 nanoparticles, which altered the structure, size and spongy properties of the nanocomposites. Importantly, the experiments helped us to determine the optimal conditions of spongy nanocomposites, namely a NH_3 concentration of 0.3 M, a sintering temperature of 500^0C, and a 0.05 M stearic acid volume of 100 mL.

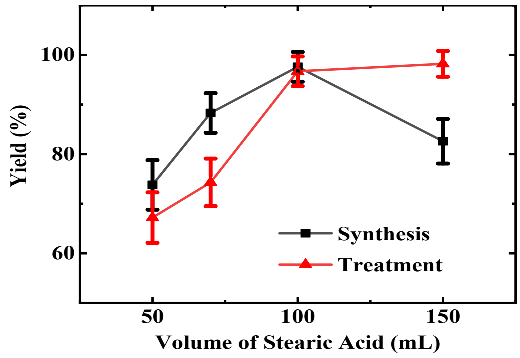

Figure 4. Synthesis yield and waste oil treatment yield of spongy nanocomposites synthesized from various volumes of stearic acid solutions

3.2. Characteristics of hybrid nanocomposite foams

3.2.1. Bond features of hybrid nanocomposite foams

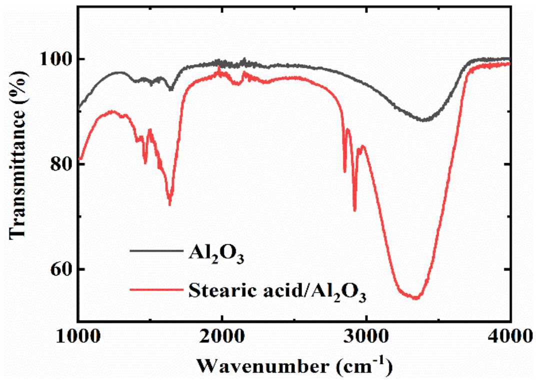

Figure 5. Fourier-transform infrared spectra of Al_2O_3 nanoparticles and stearic acid-hybridized Al_2O_3 nanocomposites

The bond features of Al_2O_3 nanoparticles and stearic acid-hybridized Al_2O_3 nanocomposites were investigated using a Fourier-transform infrared spectroscopy method. Figure 5 shows that both Fourier-transform infrared spectra of Al_2O_3 nanoparticles and stearic acid-hybridized Al_2O_3 spongy nanocomposites exhibited absorption bands at the same wavenumbers around 1560 and 3450 cm^{-1}, which were attributed to Al-O-Al bonds and O-H bonds in H_2O molecules absorbed on the nanoparticles, respectively. Moreover, the spectrum of the spongy nanocomposites displayed various absorption bands at 2911 and 2844 cm^{-1} relating to the asymmetric and symmetric covalent vibrations of C-H bonds of stearic acid. Significantly, the characteristic band of C=O bonds of stearic acid at 1694 cm^{-1} was not observed on the spectrum, implying that stearic acid molecules created strong bonds with Al_2O_3 via a chemical process. This could probably impact the surface of materials, which formed hydrophobic and lipophilic characteristics of the stearic acid-hybridized Al_2O_3 nanocomposites.

3.2.2. Surface structures of hybrid nanocomposite foams

The surface structure of stearic acid-hybridized Al_2O_3 spongy nanocomposites was imaged by using a scanning electron microscope, which was presented in Figure 6. The SEM images indicate that the surface structure morphology of the hybrid nanocomposites was relatively spongy. The addition of stearic acid made Al_2O_3 particles tend to bind together via stearic acid molecules, resulting in the formation of a multidimensional spongy structure with high porosity.

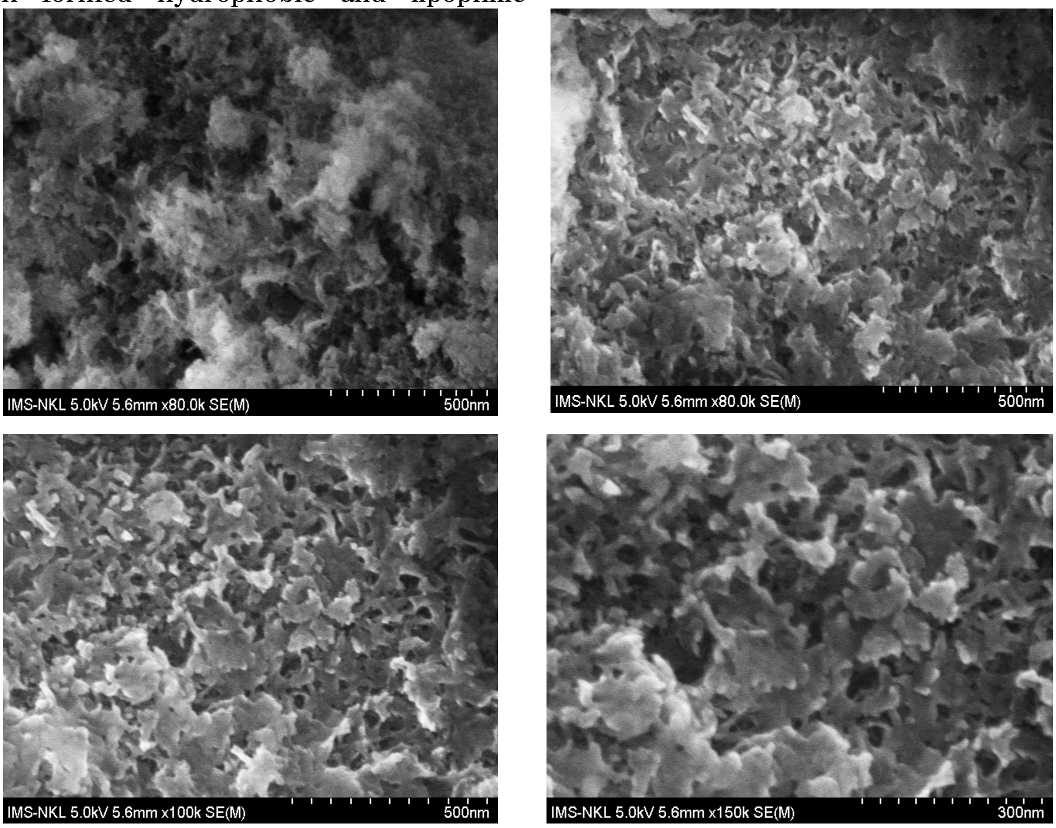

Figure 6. SEM images of spongy nanocomposites based on stearic acid-hybridized Al_2O_3

3.2.3. Density of hybrid nanocomposite foams

The density of acid-hybridized Al_2O_3 nanocomposites was determined to be 0.74 g/cm^3. The low density of the hybrid nanocomposites indicated the spongy structure of the materials, which was consistent with the surface structure analysis by SEM imaging. This result also implies that the hybrid composites could be float on water, which facilitates the treatment of waste oil floating on water since the density of waste oil is also lower than water.

3.3. Evaluation of the absorbability to waste oil of hybrid nanocomposite foams

The waste oil absorbability of stearic acid-hybridized Al_2O_3 spongy nanocomposites was evaluated by the addition of 1 g of the nanocomposites to beakers containing various volumes of waste oil in 50 mL distilled water. The results of experiments showed that the waste oil in water was immediately absorbed by the spongy nanocomposite (Figure 7).

Figure 7. Experimenting on the waste oil absorption capability of spongy nanocomposites based on Al_2O_3 hybridizing with stearic acid

When the spongy nanocomposites absorbed waste oil were separated by a filter cloth, there were no trace of waste oil in transparent filtrates for the initial volumes of waste oil in the range of 1 – 5 mL. However, there was a small amount of waste oil in the filtrate when the initial volume of waste oil was 6 mL. It implies that the spongy nanocomposites were saturated with waste oil. This result could allow us to state that the absorption capability of the spongy nanocomposites is around 5 mL of waste oil per 1 g of the material. Moreover, the stearic acid-hybridized Al_2O_3 spongy nanocomposites were also used to treat waste cooking oil in water. The result of experiments indicates that the nanocomposites could absorb the waste cooking oil with the absorption capability similar to their waste oil absorption capability. It implies the hybrid nanocomposites can be applied to treat different waste oil types.

4. CONCLUSIONS

We successfully synthesized spongy nanocomposite materials based on the hybridization of Al_2O_3 with stearic acid by using a hydrothermal method and a sol-gel method. The optimal conditions were investigated for the synthesis procedure of the hybrid spongy nanocomposites, namely a NH_3 concentration of 0.5 M, pH = 6, a 0.05 M stearic acid volume of 100 mL, and a sintering temperature of 500^{0}C. The characteristics of the hybrid nanocomposites were determined by FTIR spectroscopy, SEM imaging. The results indicated the nanocomposites had multidimension spongy structure with a high porosity, which was consistent with the low density of the materials (0.74 g/cm^3). The nanocomposites were utilized to absorbedly treat waste oil in water with a maximum absorption capability of 5 mL/1 g. This result should open the various applicability of hybrid nanomaterials for the recovery and treatment of spilled oil and waste oil in water and can be applied for the treatment of oil pollution.

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