SYNTHESIS OF HYDROPHOBIC MARSHMALLOW GEL FOR THE SEPARATION OF ORGANIC SOLVENT IN WATER

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TÓM TẮT

TỔNG HỢP VẬT LIỆU MARSHMALLOW GEL SIÊU KỴ NƯỚC SỬ DỤNG ĐỂ THU HỒI CÁC DUNG MÔI HỮU CƠ TRONG NƯỚC

Bài báo đề cập quy trình tổng hợp đơn giản và dễ dàng để điều chế marshmallow gel siêu kị nước sử dụng để thu hồi các dung môi hữu cơ trong nước. Vật liệu marshmallow gel siêu kỵ nước được đặc trưng bằng các kỹ thuật hiện đại như phân tích nhiệt (TGA), kính hiển vi điện tử truyền qua (SEM) và phổ hồng ngoại rắn (FT-IR). Vật liệu marshmallow gel tổng hợp đã cho thấy khả năng hấp thụ siêu việt đối với các dung môi hữu cơ như xăng, dầu, hexane, toluen, xylene. Hơn nước, các dung môi này được thu hồi trong nước bằng vật liệu marshmallow gel mà không làm thay đổi cấu trúc vật liệu
Keywords: *Marshmallow gel, supper hydrophobic, separation, organic solvent.*

1. INTRODUCTION

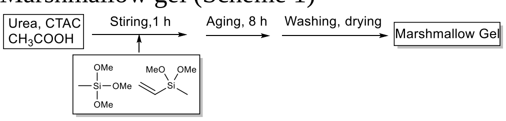
Over the last decade, petroleum production and refining have been some of the most critical industries globally, with the consumption of over 80 million barrels of oil per day. An oil spill is an accident that occurs during oil processing, storage, transportation, and use. It seriously affects the ecological environment, especially the marine system, and negatively affects the economy. The number of accidents increased with industry development, including the Neptune Arie of Ho Chi Minh City oil spill (1994), Formosa One of Vung Tau (2001), and Ham Luong 05. Due to the seriousness of the eviction of oil, scientists have paid more attention to the separation of oil and water. Numerous studies have reported hydrophobic porous materials and their application as oil/water separation media [1]. In addition, other materials have been investigated and studied, such as carbon-based materials, metal oxide, biomass nanofiber, organic polymer, and hydrophobic aerogel [2-7] so far. Polydimethylsiloxane (PDMS) or fluorocarbon-coated materials [8-11], and the design of a biomimetic rough surface, through etching techniques, to enhance hydrophobicity [12-16] are also widely reported. However, these materials have problems, such as complicated, lengthy processes and high costs. In 2011, Hayase and co-workers investigated hydrophobic polymethylsilsesquioxane (PMSQ) materials, consisting of transparent aerogels and xerogels with mesoporous to microporous monoliths created by controlling phase separation in the sol-gel process [17]. They have a hydrophobic surface due to methyl groups directly bonded to silica atoms. This flexible network structure allows the material to spring back after compression. In the following year, they also reported blendable marshmallow-like porous gel derived from a co-pressor system of Methyltrimethoxylsilane and dimethyl-dimethoxy silane in the same way as PMSQ gel. The marshmallow-like gel shows compression properties like PMSQ and very soft materials and high sound absorption properties due to their weak network. The flexibility and hydrophobia indicate that marshmallow-like gel can be used as a sponge as a sorption media to remove unwanted organic compounds quickly. Herein, this study reported the outstanding capability of these materials for the separation of organic solvents in water.

2. EXPERIMENTAL

2.1. Preparation and characterization

Glacial acetic acid (≥ 99%), urea (≥ 99%), n-hexadecyltrimethylammonium chloride (CTAC) (≥ 98%), vinyl methyl dimethoxy silane (VMDMS) (97%), methyl trimethoxy silane (MTMS) (98%), xylene, toluene, hexane was purchased from Sigma Aldrich. Gasoline (RON 95) and petroleum were purchased from the gas station. All the chemical reagents were used as received without further purification.

First, 0.80 g of CTAC, 5.0 g of urea, and 15 mL of 5 mM aqueous acetic acid were mixed in a glass sample tube. Then 0.021 mol of MTMS and 0.014 mol of VMDMS were added simultaneously under vigorous stirring at ambient temperature, and stirring was continued for 60 min until the solution was homogeneous. The obtained sol was transferred into a tightly sealed container and placed in a forced convection oven at 80 °C for nine hours to complete gelation and aging. The obtained gels were washed with methanol by soaking/squeezing them by hand several times to remove the residual surfactant and other chemicals. The washed samples were dried under the ambient condition to obtain Marshmallow gel (Scheme 1)



Scheme 1. Facile synthesis of Marshmallow gel

The IR spectra were recorded by FT-IR 8101M Shimazu, and UV-DRS spectra were measured on the Jaco V-530 apparatus. A scanning electron microscope (JSM-6060S, JEOL, Japan) was employed to observe the microstructure.

2.2. Organic solvent separation

10 ml solvents or mixtures of organic solvent and water were prepared (9/1), and then marshmallow gel was put in these mixtures. After removing the marshmallow gel, the mix volume was calculated to detect the adsorption amount.

3. RESULTS AND DISCUSSIONS

3.1. Catalyst characterization

The marshmallow gel can easily prepare within a day, even on a large scale. It also can be formed in any shape desired.

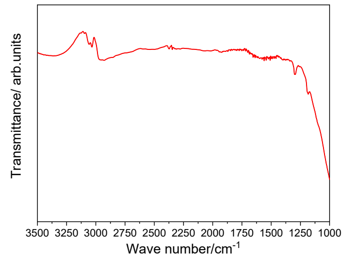


Figure 1. IR spectra of marshmallow gel

Figure 1 shows the IR spectra of the target material. It contains Si-O-Si asymmetric stretching at 1200 cm^{-1} (polycyclic oligomers) as well as C-H (methyl groups) asymmetric deformations at 1280 and 1400 cm^{-1}. The CH_2=CH- asymmetric stretching was also observed at 3000 cm^{-1}. It suggests that the marshmallow gel was successfully prepared.

To observe the shape and size of the material, the SEM was also measured and shown in fig. 2. The results show that the marshmallow gel has excellent mono-dispersion with macropores while the average size is about 5 μm.

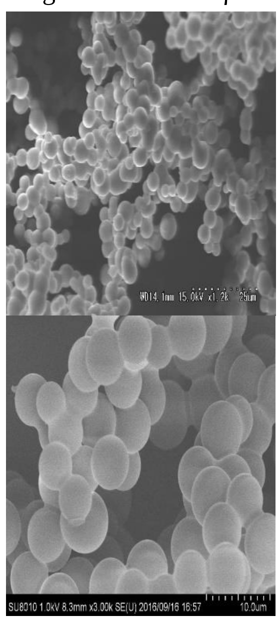


Figure 2. SEM image of marshmallow gel

To evaluate its thermal stability, TG analysis was conducted and shown in figure 3. The results show that the material was stable until 380ºC, where a methyl group and vinyl group are broken at high temperatures.

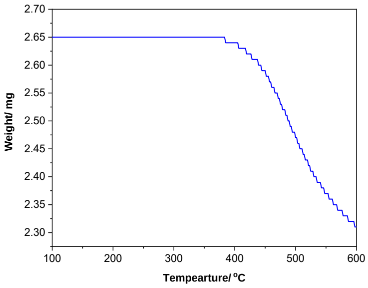


Figure 3. TG curve of marshmallow gel

In addition, the marshmallow gel has a low density (ca. 0.12 g cm^{-3}, which corresponds to a porosity of > 92%) and superhydrophobicity (figure 3). The hydrophobicity is caused by the rough geometrical surface, derived from a macroporous structure presumably formed by spinodal decomposition and by the many methyl groups and vinyl groups exposed.

3.2. Separation of Solvent

To evaluate the material as an oil/ water (9/1) separation media, marshmallow gel was used for the adsorption of some organic solvents in water, such as hexane, gasoline, and petroleum. The data is shown in figure 5. Over twenty repetitions, the marshmallow gel showed stable performance and excellent adsorption for all solvents, and no damage was observed. We also performed a gasoline removal test using this material like a sponge. All the gasoline was successfully separated from water easily and quickly, even though there was a larger quantity of liquid that could be absorbed at once.

Figure 4. The hydrophobic property of marshmallow gel

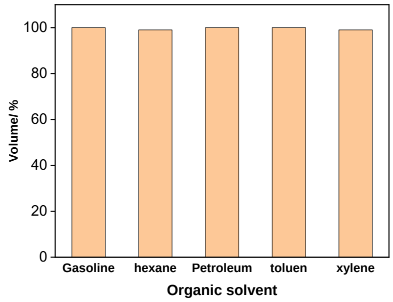


Figure 5. Adsorption of solvent by marshmallow gel

It also is very interestingly, after adsorption solvent, the volume of marshmallow gel is increased, then decreased during solvent evaporation, and finally springs back. Figure 6 shows the hexane adsorption of marshmallow gel. After the hexane adsorption, the material volume increased by 37% compared to the original one. However, the volume of the material decreased by nearly half during solvent evaporation and sprang back after drying.

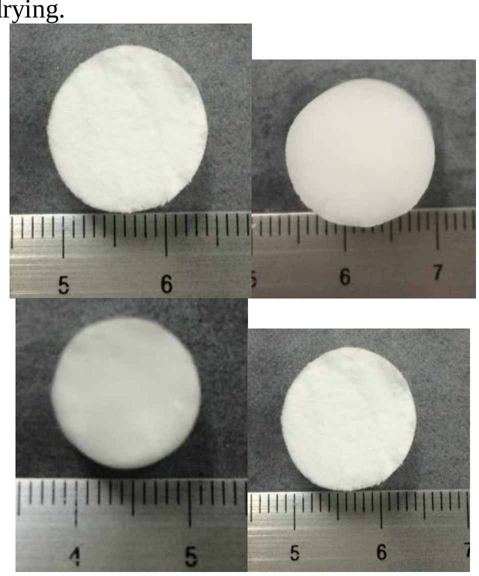


Figure 6. Adsorption of hexane over Marshmallow gel: a) marshmallow gel; b) after deep in hexane; c) during drying, d) completely dry

4. CONCLUSION

In this study, the supper hydrophobic marshmallow gel was prepared via a simple method using alkylated silica as starting materials in the presence of CTAC. The target marshmallow gel was characterized by various modern techniques, including SEM, FT-IR, and TGA. The Marshmallow gel has shown an excellent ability to remove the organic solvent in water.

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