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Study on optimizing the expansion process of vermiculite mineral as an adsorbent material

Nguyen Van Huy[1], Khuat Hoang Binh[1], Nguyen Minh Viet[4], Tran Van Chinh[1], Nguyen Thi Hoai Phuong[2], Vu Tri Thien[1], Le Minh[3], Nguyen Thi Hong Phuong[3], Nguyen Khanh Toan[3], Vu Thu Hang[3], La Duc Duong[1,*]

[1] *Institute of Chemistry - Materials, Institute of Military Science and Technology, 17 Hoang Sam, Hanoi, Vietnam*
[2] *Joint Vietnam-Russia Tropical Science, Vietnam*
[3] *School of Chemistry and Life Sciences, Hanoi University of Science and Technology, Vietnam*
[4] *The VNU-Key Laboratory of Advanced Materials for Green Growth (KLAMAG-HUS), University of Science, Vietnam National University, Hanoi*
** Email: duc.duong.la@gmail.com*

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ABSTRACT

Vermiculite (VER) is a type of clay mineral abundant in reserves, with low cost and environmental friendliness. There are many chemicals used to expand VER such as HCl, H_2SO_4, etc. In this study, vermiculite was expanded using mixed methods using microwave irradiation with H_2O_2. Factors affecting the expansion process of vermiculite minerals such as VER:H_2O_2 ratio, H_2O_2 concentration, drying temperature, drying time, microwave time, soaking time were investigated and optimized. VER material was determined to be optimally expanded at a VER:H_2O_2 ratio of 1:6, with 30% H_2O_2 concentration, soaking for 60 minutes, drying at 60 °C for the first time, 1 minute /5 times of microwave irradiation, and drying at 120 °C for the second time. By the volume measurement method, the expansion coefficient of VER significantly increased compared to its initial state before modification, with the expansion coefficient increasing by 14 times. The results on the absorption capacity of expanded VER for some solvents and chemicals showed that the synthesized material has good absorption capacity for some organic solvents and chemicals, with adsorption capacities ranging from 10 to 30 times.

Introduction

Vermiculite (VER) is the geological name given to a group of hydrated laminar minerals that are aluminum-iron-magnesium silicates, resembling mica in appearance [1]. Vermiculite is a clay mineral with a structure similar to montmorillonite ($(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O$), with a tendency to swell in the presence of water and with a high ion exchange capacity. Vermiculite is of supergene (chemical weathering) and/or hydrothermal (water and temperature action together) origin, produced from the alteration or substitution of phlogopite, biotite, and chlorite, among other mafic micas (volcanic origin) in various types of rock [2]. This clay mineral occurs in both macroscopic and microscopic categories, the first one being formed predominantly in natural deposits, and it can be found in four rock types: (1) ultramafic and mafic; (2) gneiss and schist; (3) carbonate rocks; and (4) granitic rocks [3]. Vermiculite is a clay silicate

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with particles smaller than 2 µm and a crystalline structure formed by layers of type 2:1. Interlayer minerals such as mica and biotite have potassium atoms in their constitution, but in vermiculite, the interlayer has water molecules and magnesium [4]. The expanded of vermiculite (VER) in this study has been successfully investigated through the following process: The optimal VER material was determined at a ratio of 1:6, 30% H_2O_2 concentration, 60 minutes of soaking, drying at 60°C for 90 minutes in the first time, microwave treatment for 1 minute/5 times, and drying at 120°C for 60 minutes in the second times. The use of H_2O_2 helps the material to absorbent evenly. During the expansion process with microwave treatment, H_2O_2 undergoes thermal decomposition into H_2O and releases gas, which aids in the expansion of the material. This process results in a VER material with a higher expansion coefficient (k = 14). The expanded VER has a porous structure with a significantly larger specific surface area compared to the original material. Furthermore, it was evaluated for its adsorption capacity towards certain organic solvents and toxic chemicals. The expanded VER shows a significant increase in adsorption capacity compared to the raw VER. In the future, modified vermiculite is expected to be a versatile adsorbent material for removing dyes [5] and metal cations [6] from aqueous solutions. Additionally, vermiculite is a promising material for selective adsorption of saturated hydrocarbons such as petroleum [7,8].

Materials and methods

Chemicals

Raw vermiculite (4-8 mm, Viet Nam), H_2O_2 (30%). KOH, NaOH, Ethyl acetate, n-Hexane, Benzen, Toluene, Xylene, Cyclohexane (Xilong, China).

Preparation of vermiculite

1 gram of the sample was spread in a glass Petri dish (diameter=120mm) containing 6mL H_2O_2 solution then soaked for 60 minutes and then placed in a convection oven at 60 °C in 90 minutes. Next, the dish was heated by microwave 1 minute/5 times. Finally, the materials were dried at 120 °C in 60 minutes and then stored in a desiccator before usage.

Adsorption capacity

The adsorption capacity of the expanded vermiculite (VER) was tested with approximately 10 types of chemicals and toxic organic solvents. The detailed experimental procedure is as process: Approximately 0.1 g of expanded VER material was weighed and then completely immersed in a 15 mL glass vial containing 5 mL of the chemical and organic solvent solution and allowed to adsorbent for 60 minutes. Immediately after the adsorption period, the weight of the adsorbed samples (M_{abs}) was measured. The dry weight (M_{dry}) was determined after drying at 120°C for 60 minutes. The adsorption capacity was calculated using the following formula:

$$\text{Adsorption capacity (g g}^{-1}\text{)} = M_{abs} - M_{dry} / M_{dry}$$

Expansion ratio (k)

The expansion degree of the expanded vermiculite (VER) was evaluated by measuring the change in volume. To obtain the initial volume of the sample (V_0), 0.3172 g of raw VER was placed into a graduated cylinder. The volume after expansion (V) was also measured using the same graduated cylinder. The expansion ratio (k) was calculated by relationship of $k = V/V_0$. To minimize errors when measuring volume, the material was carefully dropped into the graduated cylinder to avoid excessive compression and ensure uniform sample size during measurement. The determination and calculation of the expansion ratio (k) followed the same procedure for assessing the expansion behavior of the material.

The morphology and structure of the expanded VER were observed using Scanning Electron Microscopy (SEM). The chemical composition was analyzed by X-ray Fluorescence (XRF), while the crystalline structure of the material was characterized by X-ray Diffraction (XRD). The pore size distribution and surface area were determined using Nitrogen adsorption (BET method).

Results and discussion

Characterization of Material Properties

XRD analysis

The X-ray diffraction (XRD) analysis results are shown in Figure 1. The characteristic peak of the initial vermiculite (VER) appears at 25.02°, with a sharp peak. Additionally, there are several other weaker diffraction peaks, which correspond to trace amounts of impurities present in the raw VER mineral. After expansion with H_2O_2, there is virtually no significant difference in the diffraction pattern, indicating that the crystal structure remains essentially unchanged.

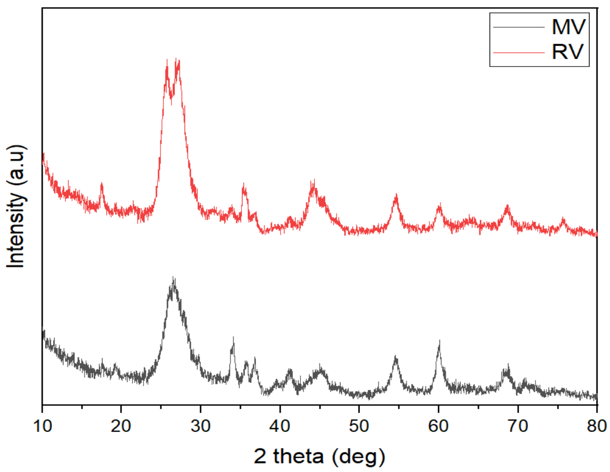

Figure 1. X-ray diffraction pattern of Vermiculite raw (RV) and expanded (MV)

SEM Analysis

The SEM analysis results are presented in Figures 2a and 2b. The VER mineral before (2a) and after expansion (2b) were magnified up to 50,000 times. The results show a significant change in morphology before and after expansion. After expansion with H_2O_2, a relatively large number of thin, uniform layers with a more compact structure appear compared to the raw VER. In conjunction with the microscope analysis, the external appearance of the VER material before and after expansion with H_2O_2 is clearly observable in Figures 2c and 2d.

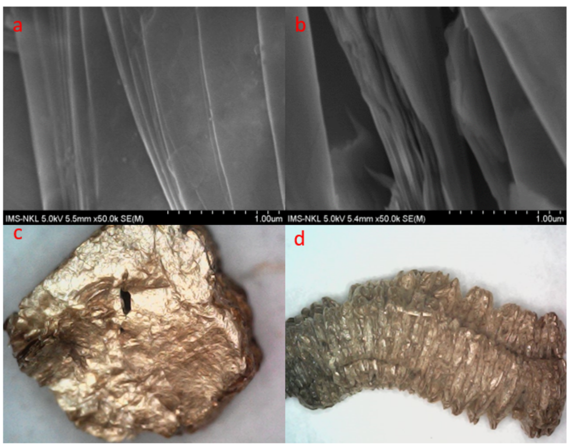

Figure 2. SEM and Microscope analysis images of raw Vermiculite (a,c); Vermiculite expanded (b,d)

In addition, the chemical composition analyzed by XRF is presented in Table 1. The components obtained are consistent with previous reports.

Table 1. Chemical compositions of Vermiculite analyzed by XRF.

Oxdie	Ratio (%)
MgO	10.296
Al_2O_3	12.887
SiO_2	33.625
K_2O	10.949
CaO	2.210
TiO_2	4.234
MnO	0.230
Fe_2O_3	25.569

BET analysis

The expanded VER sample has a specific surface area of 42.5013 m^2/g and a pore volume of 0.0832 cm^3/g, which is higher than that reported in previous studies, where the surface area was 3.57 m^2/g and the pore volume was 0.015 cm^3/g . Based on these results, it can be concluded that the properties of the expanded VER have been improved compared to those reported in earlier studies. Therefore, with its larger surface area, expanded VER offers significant advantages in surface adsorption applications.

Factors Affecting the Material Expansion Process

Ratio VER : H_2O_2 , concentration H_2O_2

Results in Figure 3, it can be observed that at a concentration of 30%, the ratio of 1:6 is the optimal condition after surveying various concentrations and ratios. If the concentration of H_2O_2 exceeds 30%, it will break down the internal structural layers of the mineral and reduce the expansion efficiency of the material.

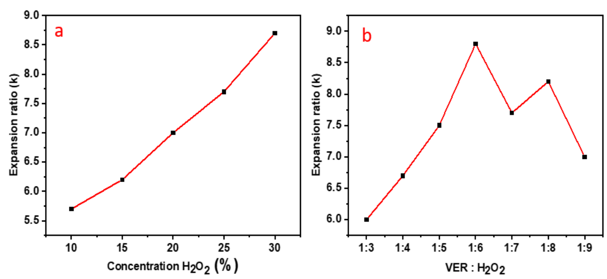

Figure 3. Expansion ratio k at concentration H_2O_2 (a), ratio (b) different

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Times, temperature

Temperature and drying time are critical factors that directly influence the material expansion process. If the temperature is too low or too high, the expansion ratio (k) will not be optimized. In this study, the highest expansion ratio (k) was obtained at 60°C for 90 minutes. The purpose of microwave treatment is to evaporate H_2O_2; therefore, if the microwave exposure time is too long, H_2O_2 will undergo thermal decomposition, and the resulting H_2O product will affect the material expansion process. Among various microwave exposure and soaking times, 3 minutes of microwave treatment and 60 minutes of soaking resulted in the optimal expansion ratio (k) (Figures 4c,d).

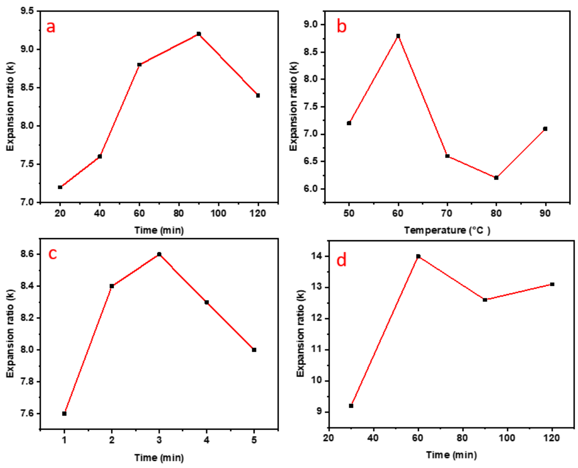

Figure 4. Expansion ratio (k) at drying time (a); temperature (b); microwave time (c); soak time (d)

Adsorption capacity with some evironments and chemicals

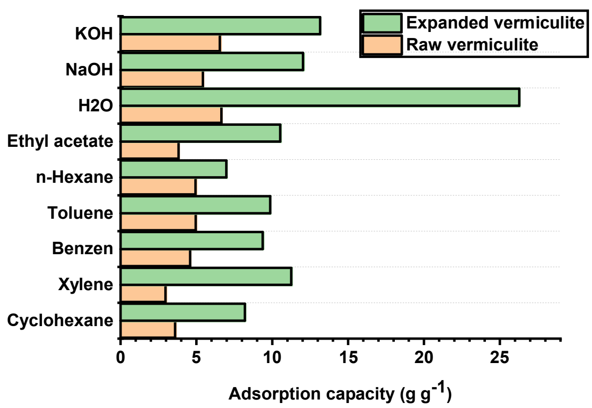

Figure 5. Adsorption capacity of Vermiculite raw and expanded

The adsorption capacity of expanded VER was tested for several organic solvents and chemicals with different chemical properties, including KOH, NaOH, Ethyl acetate, n-Hexane, Toluene, Benzene, Xylene, and Cyclohexane. Figure 5 shows the superior adsorption performance of the modified VER compared to the unmodified material. The expanded VER samples exhibited an adsorption capacity ranging from 8.7 g g^{-1} to 28.8 g g^{-1}, which is significantly higher than that of the original VER material, which had an adsorption capacity ranging from 3.4 g g^{-1} to 7.5 g g^{-1}.

Conclusions

The VER material expanded with H_2O_2 combined with the microwave method has been successfully studied at the optimal ratio of 1:6, using 30% H_2O_2 concentration, soaking for 60 minutes, drying at 60°C for 90 minutes, followed by microwave treatment for 1 minute/5 times, and drying at 120°C for 60 minutes. When compared to the raw VER, the expanded VER shows better adsorption capacity for organic solvents and toxic chemicals due to its larger surface area. These results suggest that VER, expanded using the H_2O_2 method in combination with microwave treatment, is a promising and highly potential adsorbent for mitigating large-scale hazardous chemical spills, offering advantages such as low cost, thermal stability, chemical inertness, and mechanical durability.

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