PREPARATION OF FILTER AIDS BASED ON LAM DONG DIATOMITE

Mai Thanh Phong*, Tran Doan Minh Dang

Faculty of Chemical Engineering, Hochiminh City University of Technology 268 Ly Thuong Kiet Str., Dist. 10, Hochiminh City, Vietnam

*Email: *mtphong@hcmut.edu.vn*

Received: 4 November 2011; Accepted for publication: 26 May 2012

ABSTRACT

Diatomite from Dai Lao valley, in Lam Dong province was selected for investigation of its possible application in preparation of filter aids. For this purpose, diatomite ore was leached in acids to enrich SiO_2 and reduce impurities, and then calcined at high temperatures in order to improve the material characteristics for use in filtration. The leaching was conducted in a hot 6M H_2SO_4 solution (90 – 95 ^oC) for a time period up to 36 h. To examine effects of temperature, the calcination temperature was varied in the range 900 – 1250 ^oC. The physical, chemical, thermal and micro–structural features of the raw and the calcined diatomite were determined to compare them with those of the commercial filter aids currently used. It is shown that the Lam Dong diatomite can successfully be used for preparation of filter aids.

Keywords. Lam Dong diatomite, diatomaceous earth, XRD, DTA-TG, SEM, filter aids.

1. INTRODUCTION

Diatomaceous earth is a non–metallic mineral raw material composed of skeletal remains of single-cell water plants (algae), known as diatomite. The skeletal diatomite, microscopically viewed, have quite complex structures with numerous fine microscopic pores, cavities and channels and, therefore, large specific surface area and high absorption capacity. Owing to these characteristics, diatomaceous earth can be used as adsorption auxiliary material for filtration. In some regions, deposits of diatomaceous earth are sufficiently thick and pure to be exploited and processed for certain purposes. Common industrial uses for diatomite include filtration of sugar syrup, whiskey, wine, fruit juice, water, mineral or vegetable oils and pharmaceuticals. Especially, it is suitable for production of filtering compounds used in breweries [1].

In Vietnam, diatomite reserves are approximately 165.5 million tons. One of the two largest deposits is in Lam Dong province with a capacity of about 8 million tons [2]. The annual production of beer in Vietnam is about 2 billion liters. Lam Dong has sufficient resources of diatomaceous earth to meet the needs of domestic breweries, but there is no organized production of beer filter aids. Many deposits of diatomaceous earth can be found at several localities in Dai Lao valley where the reserve is largest and some elsewhere such as in Dinh

Trang Thuong, Tan Trung ward. According to market analysis, the annual consumption of diatomaceous earth filter aids by breweries in Vietnam is completely covered by imports from other countries, mainly from China. Therefore, diatomaceous earth from Lam Dong was selected for this study. The objective of this study is to investigate preparation of filter aids based on diatomite collected from Lam Dong.

2. MATERIALS AND METHODS

This study focused on the production of filter aids from a low grade diatomite powder by hot-acid leaching and straight calcinations.

2.1. Geological characteristics of deposits

Diatomaceous earth was explored on Dai Lao valley in Lam Dong province, Vietnam. Lam Dong diatomite was white, gray or brown, porous and light - weight. In cases of higher contamination level, the thickness of the gray earth layer is in the range of 0.6 – 1.0 m and it is found close to the upper layers of coal. The thickness of the white diatomaceous earth bed is in the range of 3 – 6 m and it is found above upper coal layers. White diatomaceous earth is considered to be the raw material of the highest quality. Resources of white diatomaceous earth are almost negligible in comparison to those of the gray one, so the investigation was focused on gray diatomaceous earth in Lam Dong.

2.2. Sample preparation

The tests were performed with 350 kg of diatomaceous earth obtained from the Dai Lao valley deposit, in Lam Dong. The method of mechanical and thermal sample preparation consisted of the following phases: natural draught drying, ore crushing and cutting, screening, leaching with acids, washing – filtration, plant drying, calcinations, disintegration process and particle - distribution size analysis.

2.3. Material characterization

Characterization of the samples was made by chemical and mineralogical analyses, determination of physical and thermal properties and microstructure analysis.

Chemical compositions of samples were determined by X-ray fluorescence (XRF). Particle size distribution was performed by particle – distribution size analysis equipment – Microtrac S3500. X – Ray diffraction analysis (XRD) was carried out in a Philips X-ray diffractometer type Philips PW - 1820/00 using monochromatic CuKα radiation. Loss on ignition and the influence of temperature was determined by DTA – TG method on STA 409 PC – NETZSCH equipment. The surface structure and inner structure were determined by Scanning Electron Microscope (SEM).

2.4. Leaching diatomite

The sample was wet ground in an attrition mill for 1 h using alumina balls. The slurry was dried at 105 ^oC for 2 – 3 h, then screened through a sieve of 0.25 mm apertures and leached in 6M H_2SO_4 solutions at 90 – 95 ^oC. For leaching, 10 g of diatomite was charged into 200 ml of the solution, and then stirred continuously at 500 rpm using a magnetic stirrer. A thermostat was used to keep the reaction medium at constant temperature. After 6 h, the solid product was filtered and washed with distilled water. This 6 h – leaching stage was repeated from one to five times.

2.5. Preparation of filter aids

The diatomite after the treatment with acid was used to prepare filter aids by calcinations in the temperature range from 900 ^oC to 1250 ^oC. The selected temperatures are 900 ^oC, 1000 ^oC, 1100 ^oC and 1250 ^oC. Process of calcination was conducted in an electric furnace and heating time was 90 minutes. High temperature is necessary to strengthen skeletal, increase porosity, and remove degradable impurities of diatomite.

3. RESULTS AND DISCUSSION

An open skeletal structure was investigated in low-grade diatomite at different leaching periods. Later, the powders were shaped and sintered at relatively high temperature and their microstructure was determined.

3.1. Characterization of Lam Dong diatomite

Chemical compositions of initial diatomite are presented in Table 1.

Table 1. Chemical composition of diatomite from the Dai Lao deposit, Lam Dong

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	L.O.I
52.9	22.9	5.32	0.43	0.26	0.51	1.25	0.15	19.8

Based on chemical analyses data, it can be seen that the Lam Dong diatomite has low content of SiO_2 and therefore higher contents of other present oxides such as Al_2O_3, Fe_2O_3. Hence, diatomaceous earth from Lam Dong is considered as raw material of average quality with the content of SiO_2 about 52.9 %. It is also evident that Fe_2O_3 content in the sample is quite high, which can affect beer quality. Loss of ignition (L.O.I) is considerable in the Lam Dong diatomite due to high content of coal as shown in table 1.

The thermal treatment of Lam Dong diatomite in terms of TG-DTA is given in Fig. 1 from the DTA curves, the surface and hygroscopic water removal was seen as an endothermic pattern in the heating stage, and transition from amorphous to crystallized form was seen as a weak exothermic pattern in the cooling stage. From the TG curve, it is seen that diatomite lost 4.31% of its surface humidity at 200 °C. With the increase of temperature, weight loss continued up to 1199.3 °C and 11.88 % weight loss occurred owing to the degradation of montmorillonite, kaolinite and impurities. The weight did not change at 1200 °C when the temperature was held constant for duration of 1 h. After this period, a weight loss of 0.6% was observed with a weak exothermic reaction in the cooling stage reflected by the occurrence of crystolbalite which proved the establishment of stronger crystal bonds.

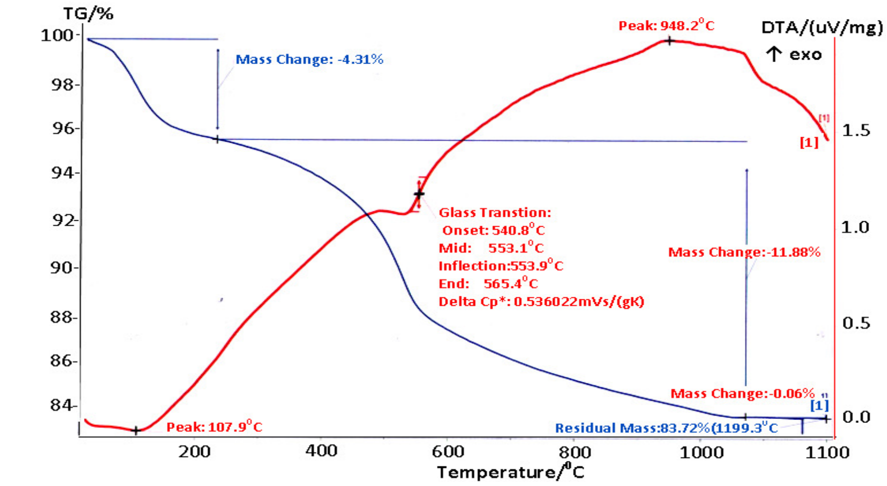

Fig. 1. The results of TG – DTA analysis of raw Lam dong diatomite

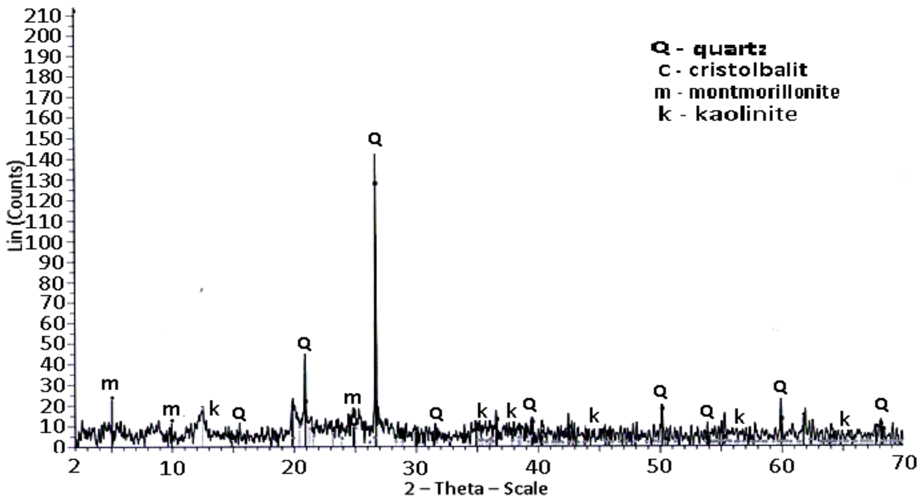

Figure 2. The XRD pattern of raw Lam Dong diaotmite

The diffractogram of the raw Lam Dong diatomite is presented in Fig. 2. The X-ray diffraction analysis shows that the sample mostly consist of amorphous phases with traces of quartz, montmorillonite, kaolinite and some clay minerals like kaolinite, montmorillonite, etc. Mineralogical analyses show that content of skeletons and shells are approximately 80 % while the rest are impurities of organic and inorganic origin.

Microstructure analyses provide reliable information about shape, structure, porosity and size of diatomaceous earth particles. Scanning electron microscopes (SEM) of raw Lam Dong diatomite are presented in Fig. 3.

On the surface of diatomaceous earth, insignificant content of the impurities originating from coal can be noticed. The impurities are outside pores, so during the calcinations, complete combustion of coal is obtained.

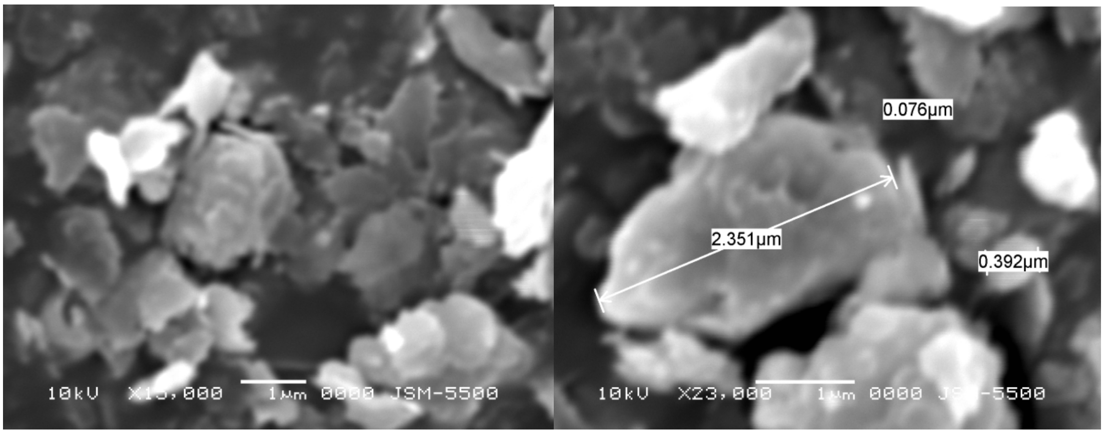

Figure 3. Scanning electron microscopes of raw Lam Dong diatomite

Microphotographs presented in Fig. 3a-b show the morphological shape and size of diatomaceous earth particles of the Lam Dong diatomite. The presence of various shapes of diatomaceous earth (cylindrical and plateaus particles) together with small particles of impurities (small shales and plates) and broken diatomite, too, could be noticed in Fig.3a. Considerable content of small crystals (impurities) such as quartz, montmorillonite, kaolinite are detected on the surface of diatomaceous earth and this sample belongs to gray diatomaceous earth.

3.2. Leaching in acid

Table 2. Chemical composition of the leached diatomite

Assay	Raw D.E	Leaching times					
		6h	12h	18h	24h	30h	36h
SiO_2	52.9	61.3	70.6	75.3	79.0	81.7	86.9
Al_2O_3	22.9	17.3	12.1	10.9	7.90	6.73	4.10
Fe_2O_3	5.32	3.50	1.79	1.58	1.10	0.89	0.53
CaO	0.43	0.66	0.01	0.01	0.03	0.04	0.01

The raw diatomite powder was treated in 6M H_2SO_4 solution at 90 – 95 °C to reduce some metal oxides and organic minerals. The chemical composition after the treatment is shown in table 2.

Based on the chemical composition shown in Table 2, the treatment of raw diatomite for 36 h resulted in the highest SiO_2 level, while levels of Al_2O_3 and Fe_2O_3 are lowest. However, the chemical compositions resulted from the treatment for at least 18 h are acceptable for filter aids manufacture.

3.3. Preparation of filter aids

In order to analyze effects of treatment temperature on filter aid properties, the diatomite, which was already leached for 36 h, was selected to be calcined at different temperatures to obtained filter aids. The obtained filter aids were chemically and physically characterized. The results are shown in table 3.

From data shown in table 2 and 3, it is seen that the SiO_2 content of the diatomite was increased significantly upon high temperature calcination. SiO_2 content of the diatomite calcined at 1000 °C, 1100 °C, and 1250 °C is almost more than 90 %. It is also seen that the calcined diatomites have considerably low Fe_2O_3 and CaO contents.

Table 3 also shows that the density of the calcined diatomite is about 2.2 to 2.3 g/ml. It is in good agreement with what of filter aids that has been studied previously [1 - 3] and the current market [4]. The surface area of the calcined diatomite decreases as calcination temperature increases. This could be due to the diatom structure shrinks.

Table 3. Physical and chemical index of filter aids from Lam Dong diatomite

Index / Model	Chemical Index				Physical Index			
	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	Specific surface area (BET), m^2/g	Density (g/ml)	Humidity %	Particle size, µm
Filter aid 1 900 °C	89.6	4.32	0.56	0.02	62.0	2.31	0.68	<74
Filter aid 2 1000 °C	92.3	4.52	0.57	0.02	44.2	2.23	0.48	<74
Filter aid 3 1100 °C	93.2	4.57	0.59	0.02	14.8	2.29	0.35	<74
Filter aid 4 1250 °C	94.1	4.57	0.59	0.02	0.87	2.31	0.32	<74

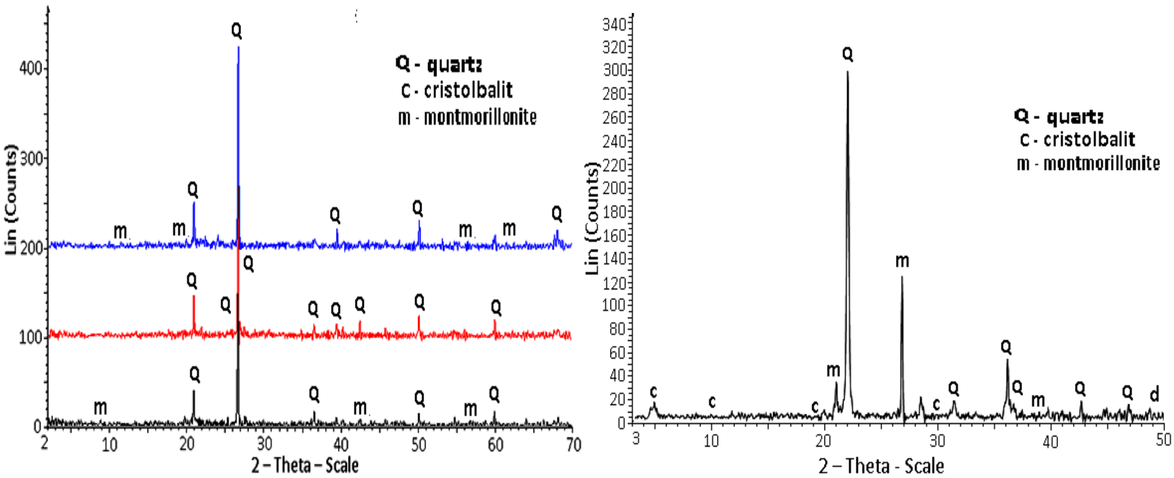

Figure 4. XRD of filter aids from Lam Dong diatomite: (a) – 900 °C; (b) – 1000 °C; (c) – 1100 °C; (d) – 1250 °C

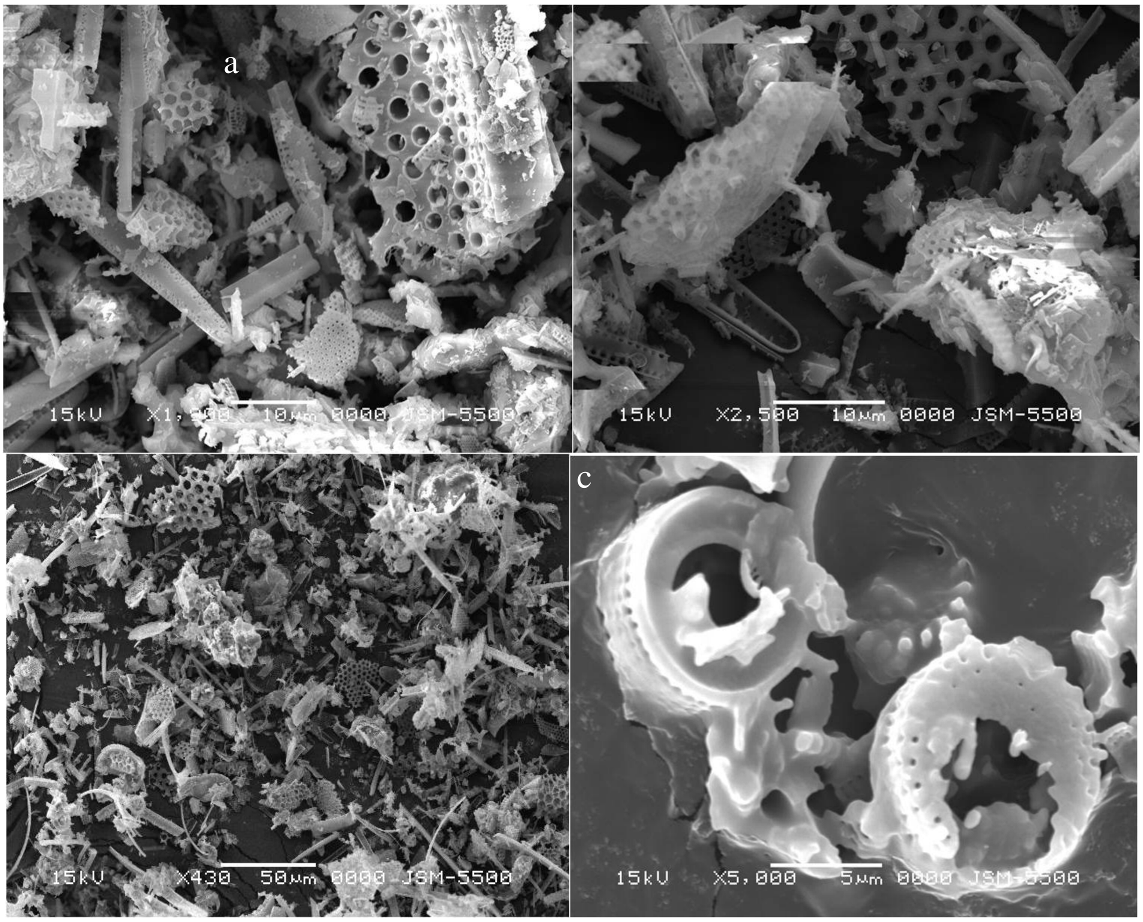

Figure 5. SEM images of the diatomite calcined at different temperatures: (a) – 900 ^oC; (b) – 1000 ^oC; (c) – 1100 ^oC; (d) – 1250 ^oC

Phase analysis was performed to determine the mineral content of the raw and the calcined diatomite utilizing an XRD instrument (Fig. 4). Finally, scanning electron microscopy (SEM) was used to determine diatom frustules using a SEM instrument (Fig. 5).

In the XRD patterns, extensive amorphous structure was seen in sections between 10 and 30° of 2-theta. Besides the intensive peaks of quartz, many weak peaks due to montmorillonite (Fig. 4a–c) and cristolbalite (Fig. 4d) minerals were observed. This shows that the quartz has been transformed into cristolbalite. Compared to the XRD pattern of the raw diatomite, it can be seen that kaolinite was almost removed by calcination. That is also obviously seen from chemical compositions of the raw and the calcined diatomite shown in Table 2 and 3. Comparison of XRD results of both raw and calcined diatomite shows that raw diatomite had irregular structure but became more regular upon heat treatment.

SEM images in Fig. 5 show the morphological shape and size of the calcined diatomites. The presence of various shapes of the diatomite (cylindrical, elongated and plateaus particles) and broken diatomites, too, could be noticed. It can be seen that plateaus particles were almost broken. In some images, particles became aggregated to coarser size. It also can be noticed that the higher calcination temperature, the more particles broken and the more minerals melted (Fig. 5b-d). At the calcination temperature of 1250 ^oC, parts of pores on particles were filled with melted minerals. This is in good agreement with the specific surface area of the filter aids obtained by different calcinations shown in table 3.

5. CONCLUSION

Diatomite collected from Lam Dong was characterized and investigated to prepare filter aids. The characterized results show that Lam Dong diatomite has low quality for filter aid manufacture. SiO_2 content was low (about 53 %), while impurities were high.

6M H_2SO_4 solution at about 90 - 95 ^oC was very good to enrich SiO_2 and reduce impurities. After treatment in 6M H_2SO_4 solution for 24 h or more, the diatomite can be used for calcination to produce filter aids. The obtained results also shows that after calcination the diatomite became more chemically stable by increasing the SiO_2 content and decreasing impurities.

Microstructure and physical analyses shows that calcination at too high temperatures could make particles broken and minerals melted, hence specific surface area decreased. 900 ^oC was the most suitable calcination temperature among temperatures investigated.

REFERENCES

1. Sanja Martinovic, Milica Vlahovic, Tamara Boljanac, Ljubica Pavlovic - Preparation of filter aids based on diatomites, Int. J. Miner. Process. **80** (2006).
2. Phạm Cẩm Nam, Trần Thanh Tuấn, Lâm Đại Tú, Võ Đình Vũ - Xác định các đặc tính của nguyên liệu Diatomite Phú Yên bằng FT-IR, XRF, XRD kết hợp với phương pháp tính toán lý thuyết, Tạp chí Khoa học và Công nghệ, Đại học Đà Nẵng **2** (31) (2009).
3. Nezahat Ediz, Smail Bentli, Lknur Tatar - Improvement in filtration characteristics of diatomite by calcinations, International Journal of Mineral Processing **94 (**2010) 129-134.
4. Tousheng Diatomite enterprise, product introduction.
5. Attorney, Agent, or Firm-Robert M. Krone; Joseph J. Keylley - Method of preparing diatomite for repid calcinations, Unites States Patent, 1982.
6. Breese R. O. Y, Diatomite, in Carr, D. D., and others, eds. - Industrial minerals and rocks (6th ed.): Littleton, CO, Society for Mining, Metallurgy, and Exploration, Inc. 1994, pp. 397-412.
7. British Geological Survey - Industrial minerals laboratory manual – DIATOMITE, Technical Report WG/92/39 – Mineralogy Petrology Series.
8. Durham D. L., Diatomite, Brobst D. A., and Pratt W. P., eds. - United States minerals resources: U.S. Geological Survey Professional, 1973, pp. 820-19.
9. Emilio Gahin a, Isabel Gonzilez, Eduardo Mayoral, Adolfo Miras - Properties and applications of diatomitic materials from SW Spain, Applied Clay Science **8** (1993).
10. Kunwadee Rangsriwatananon, Aphiruk Chaisena, Chutima Thongkasam - Thermal and acid treatment on natural raw diatomite influencing in synthesis of sodium zeolites, J. Porous Mater **15** (2008) 499–505.
11. Osman Şan, Remzi Gören, Cem Özgür - Purification of diatomite powder by acid leaching for use in fabrication of porous ceramics, Int. J. Miner. Process **93** (2009) 6-10.

12. Richard B. Nielsen, Irvine Charles J. Vogelsang - Cerritos, both of Calif, Diatomaceous earth filter aid and method for its manufacture, United States Patent, 1980.
13. S. Akin, J. M. Schembre, S. K. Bhat, A. R. Kovscek - Spontaneous imbibition characteristics of diatomite, Journal of Petroleum Science and Engineering **25** (2000).
14. Silvia Cristina Alves França, Eng. Química, D. Sc., Adão Benvindo da Luz, Eng. de Minas, D. Sc., M. T. Millqvist - Beneficiation of brazilian diatomite for filtration application industry, SME Annual Meeting, 2002.
15. Wen-Tien Tsai, Chi-Wei Lai, Kuo-Jong Hsien - Characterization and adsorption properties of diatomaceous earth modified by hydrofluoric acid etching, Journal of Colloid and Interface Science **297** (2006).

TÓM TẮT

NGHIÊN CỨU CHẾ TẠO CHẤT TRỢ LỌC TỪ KHOÁNG DIATOMITE LÂM ĐỒNG

Mai Thanh Phong*, Trần Doãn Minh Đăng

Khoa Kỹ thuật Hóa học, Trường Đại học Bách Khoa – ĐHQG TP.HCM

*Email: *mtphong@hcmut.edu.vn*

Công trình đã nghiên cứu việc chế tạo chất trợ lọc từ khoáng diatomite lấy từ mỏ Đại Lào, tỉnh Lâm Đồng. Với mục tiêu này, khoáng diatomite thô lấy từ mỏ Đãi Lào trước hết được làm giàu SiO_2 và giảm thiểu các tạp chất bằng dung dịch axit, sau đó được thiêu kết ở nhiệt độ cao để cải thiện một số đặc tính cho phù hợp với chất trợ lọc. Quá trình làm giàu SiO_2 được thực hiện với dung dịch H_2SO_4 6 M nóng (90 - 95 ^oC) trong khoảng thời gian tối đa là 36 giờ. Để khảo sát sự ảnh hưởng của nhiệt độ thiêu kết, quá trình thiêu kết đã được tiến hành ở các nhiệt độ khác nhau trong khoảng 900 – 1250 ^oC. Các đặc tính vật lý, hóa học, nhiệt và vi cấu trúc của diatomite trước và sau khi xử lí xác định và được so sánh với các đặc tính của chất trợ lọc thương mại. Kết quả cho thấy rằng, khoáng diatomite Lâm Đồng có chất lượng trung bình và có thể sử dụng để sản xuất chất trợ lọc.

Từ khóa: Diatomite Lâm Đồng, chất trợ lọc, XRD, DTA-TG, SEM.