

Study of the Adsorption Possibility of SO_x and NO_x Using Porous Diatomite Ceramic

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Abstract : In this work, a porous diatomite ceramic filter (PDCF) was synthesized and then modified with acid and alkali for the adsorption of H₂S and NH₃. PDCF was characterized by XRF, SEM, TGA, XRD and EDS. Sintering temperature exhibited significant effect on the density and compression strength, and PDCF at 1,100 °C is the best sample due to its excellent adsorption performance and sufficient compressive strength. In addition, NaOH and H₃PO₄ can greatly alter surface properties, such as increased surface area and porosity, and produce a large number of reactive sites and functional groups that significantly improved adsorption performance. As a result, PDCF was very suitable for adsorption of H₂S and NH₃. Therefore, PDCF is expected to remove SO_x and NO_x, pollutants in diesel engines.

Key Words : Diatomite ceramic, Adsorption, H₂S, NH₃

1. Introduction

Nowadays, the pollution of volatile organic compounds (VOCs) has been attracting more and more attention in the world due to its toxicity and harm to human health.¹⁻⁵⁾ Exhaust pollution from diesel engine contributed a lot to VOCs pollution, especially nitrides and sulfides.⁶⁾ Many technical methods has been used for the removal of diesel engine exhaust, such as activated carbon adsorption, catalytic oxidation, UV oxidation, bio-trickling filter, bio-reactors, etc..^{7,8)} However, these methods are either costly or may result in secondary pollution emissions and operational difficulties. Therefore, a

low-cost and efficient removal method is urgently required for the removal of diesel engine exhaust to protect the environment and people's health.

Diatomite, also known as diatomaceous earth, is a siliceous sedimentary rock composed of a fossilized skeleton of diatoms. It is usually a white powder with a low density and particle size ranging from 2 μm to 200 μm. The typical chemical compositions of diatomite are 80~90% silica, 2~4% alumina, 0.5~2% iron oxide and other impurities like metals and organic components.⁹⁾ Due to its high porosity, large specific surface area, high thermal and chemical stability, good mechanical properties, and low cost, make it suitable for application in the

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removal of air pollutant. Thus, in this study, diatomite was used to prepare porous diatomite ceramic for the adsorption of air pollutants. In order to improve the adsorption performance, the prepared porous diatomite ceramic was modified with acid and alkali. Acid and alkali treatment can significantly alter the surface properties of diatomite ceramic, such as increasing surface area and porosity, producing a large number of reactive functional groups, resulting in greatly improving adsorption performance.^{10,11)}

To our best knowledge, so far, studies on the removal of air pollutant using porous diatomite ceramic modified with acid and alkali has been hardly reported. In this work, H₂S and NH₃ gases were chosen as adsorbates (engine exhaust) for the adsorption test. H₃PO₄ and NaOH were selected as catalyst to modify the prepared porous diatomite ceramic filter (PDCF). The specific objectives of this work were a) the investigation of effect of sintering temperature and molding pressure on the mechanical properties and porosity, b) the investigation of adsorption efficiency of porous diatomite ceramic filter (PDCF) modified with acid and alkali. This study was expected to expand the utilization of diatomite for the adsorption of engine exhaust.

2. Materials and experimental method

2.1 Preparation of sample and adsorption experiments

The diatomite powder purchased from Linjiang Imerys Diatomite Company Co., Ltd. China was used to prepare porous diatomite ceramic and the preparation process was as follows: First, diatomite powder was mixed with PEG (polyethylene glycol 4,000; 18.6 wt.%) for 10 minutes using a stirrer; second, the diatomite slurry was distributed on a

plate then oven dried at 60°C for 1.5 hours; third, the dried diatomite was gridded into powder, and 3.0 g dried power was injected into a square mold (35 × 35 mm) then pressed at different pressure of 2, 5 and 8 MPa; finally, the prepared sample was heated in air to 600°C at a heating rate of 10°C/min for 2 hours to remove the PEG binder, then the binder-free sample was subsequently sintered at a temperature range of 900 to 1,400°C with a heating rate of 30°C/min for 1 hour.

Prepared porous diatomite ceramic filter (PDCF) was modified with H₃PO₄ (85.0%) and NaOH (98.0%) through the following steps: First, two different catalyst solutions were prepared by mixing 40 wt.% catalyst (NaOH or H₃PO₄) with 20 wt.% distilled water and 40 wt.% binder. Second, the prepared PDCF sample was immersed into catalyst solutions for 2 minutes then naturally dried for 24 hours. The modified samples were defined as H₃PO₄/PDCF (for NH₃ adsorption) and NaOH/PDCF (for H₂S adsorption), respectively. Prior to adsorption experiment, the dried sample was oven dried again at an optimized temperature of 90°C for 20 minutes.¹²⁾

An enclosed chamber (0.1 m³) was designed as experimental apparatus as shown in Fig. 1(a). 0.5 liter of H₂S (H₂S 4.02% and N₂ balance) gas was injected into the chamber to set up the initial concentration of 200 ppm for the adsorption experiment by NaOH/PDCF sample. When it comes to NH₃, a certain amount of NH₃ (28.0~30.0%, 48.8 μL) liquid was put on the hot pad and heated them for 15 minutes to have an initial concentration of 200 ppm for the adsorption experiment by H₃PO₄/PDCF sample. Then, the electric fan was operated at a flow velocity of 4.8 m/s. The concentration of toxic gases was measured at 30 min, 60 min and 120 min using a syringe type detector with a gas tube as shown in Fig. 1(b).

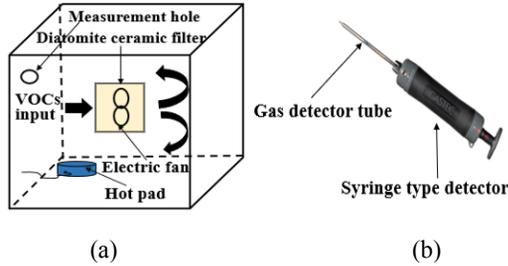


Fig. 1 Schematic diagram of (a) the experimental apparatus, and (b) syringe type detector

2.2 Analytical methods

XRF (X-Ray Fluorescence Spectrometer, SHIMADZU (Japan), XRF-1700) was used to identify the chemical composition of diatomite. XRD ((X-Ray Diffractometer, Rigaku (Japan), Ultima IV) was used to analyze the crystal structure of raw diatomite. FE-SEM (Field Emission Scanning Electron Microscope, TESCAN (Czech), MIRA 3 LMH In-Beam Detector) was employed to observe the surface morphology of raw diatomite and PDCF samples. Thermo Gravimetric Analyzer (Perkin Elmer (U.S.A), TGA 7, Pyris 1) was employed to perform the thermal gravimetric analysis of raw diatomite. EDS (Energy Dispersive X-ray, TESCAN(Czech), VEGA II LSU) was used to determine the key element of catalyst and adsorbed air pollutants. The compression strength of sintered samples was determined by using universal testing machine at a rate of 0.5 mm/min. The density of sintered samples was determined by calculating the dimensional volume and mass of samples. All experiments and analyses were performed at least twice and the averages were reported in the results section.

3. Results and discussion

3.1 Characterization of diatomite

Table 1 shows the chemical composition of raw diatomite. As expected, diatomite mainly comprises

of silica (92.43%) as well as other metal oxides. According to Martinoyic et al.,¹³⁾ if the silica (SiO_2) content is greater than 85%, the diatomite is considered to be a high-purity diatomite, suitable for development of a commercially available celite filter. Fig. 2(a) shows the FE-SEM image of diatomite and it is clearly that the diatomite consists mainly of plates and broken particles, and the plate exhibits an inherently highly porous structure. The information regarding density and textural properties of the diatomite powder is provided in Table 2.

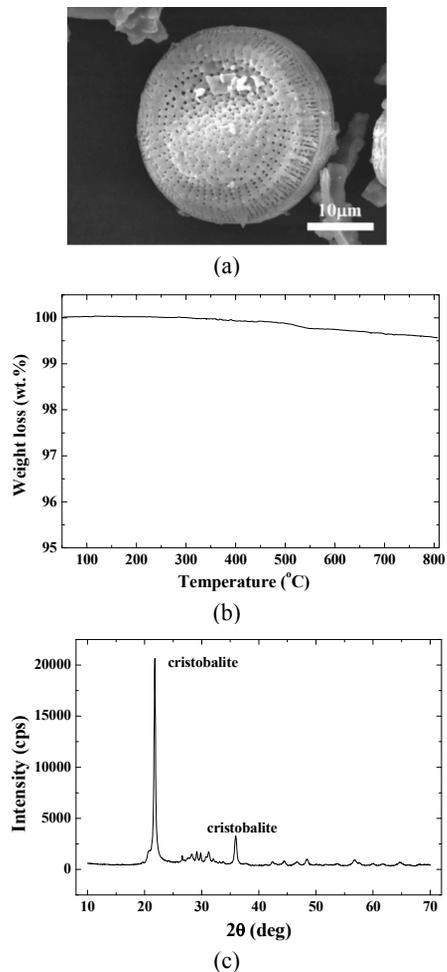


Fig. 2 (a) the FE-SEM image of as-received diatomite, (b) the TGA curve of diatomite, and (c) X-ray diffraction pattern of diatomite

Table 1 Chemical composition of diatomite

Compound	Diatomite (wt.%)
SiO ₂	92.43
Na ₂ O+K ₂ O	3.00
Al ₂ O ₃	1.63
Fe ₂ O ₃	1.50
SO ₃	0.36
CaO	0.30
MgO	0.21
TiO ₂	0.10
Cl	0.47

Table 2 Textural properties of diatomite powder

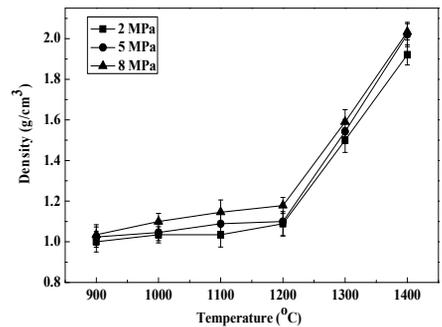
Adsorbent	Diatomite
Density (g/cm ³)	0.2 ~ 0.6
Specific Surface area (m ² /g)	19 ~ 65
Pore Volume (cm ³ /g)	0.4 ~ 1.4
Half pore width (Å)	500~8,000

TGA curve in Fig. 2(b) shows that no significant change in the weight loss was found, which indicated that diatomite does not contain volatile impurities. In addition, The XRD pattern of diatomite in Fig. 2(c) shows that the diatomite is mainly composed of cristobalite. High-temperature calcination treatment is able to transform the original amorphous silica of diatomite into cristobalite without significant shape change. Due to its excellent chemical and thermal stability, cristobalite is superior to amorphous silica in many applications.¹⁴⁾

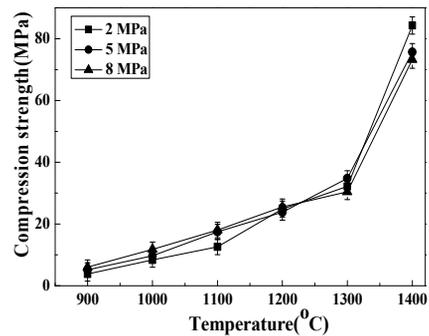
3.2 Effect of sintering temperature and molding pressure on density and compressive strength of diatomite ceramic filter

As can be seen from Fig. 3(a), as the temperature increased, the density of PDCF increased, but the density suddenly increased greatly since 1,200°C. This was due to the low temperature (<1,200°C) can not cause the sintering, thereby it still retained inherently highly porous structure of diatomite as

shown in Fig. 4(I)(a), and (b). When the temperature increased to 1,100°C, the diatomite particle began to partially melt, and the liquid phase accumulated (formation of cristobalite) in this region as shown in Fig. 4(I)(c). Furthermore, with the increase of temperature, the liquid phase continued to expand until it completely covered the surface of diatomite ceramic at 1,400°C as shown in Fig. 4(I)(d), (e) and (f). This indicated that the sintering of diatomite occurred at around 1,200°C, and the sharp condensation of diatomite particle during sintering caused a significant increase in density. Roccket et al.¹⁵⁾ reported that the formation of cristobalite was occurred at about 1,500°C. But, in this study, the sintering temperature was found to be



(a)



(b)

Fig. 3 Density and compressive strength of diatomite ceramic filter as a function of sintering temperature, (a) Density and (b) Compression strength.

around 1,100~1,200°C, which is less than 1,500°C. This could be due to impurities (such as Na₂O, K₂O, Al₂O₃, etc.) promoted low temperature eutectic reactions and the formation of liquid phase. A similar phenomenon was also found in other studies,^{16,17)} in which it was reported that the eutectic reaction of diatomite sintering occurred at around 1,150°C (close to 1,100°C in this study). This was further confirmed by the EDS analysis

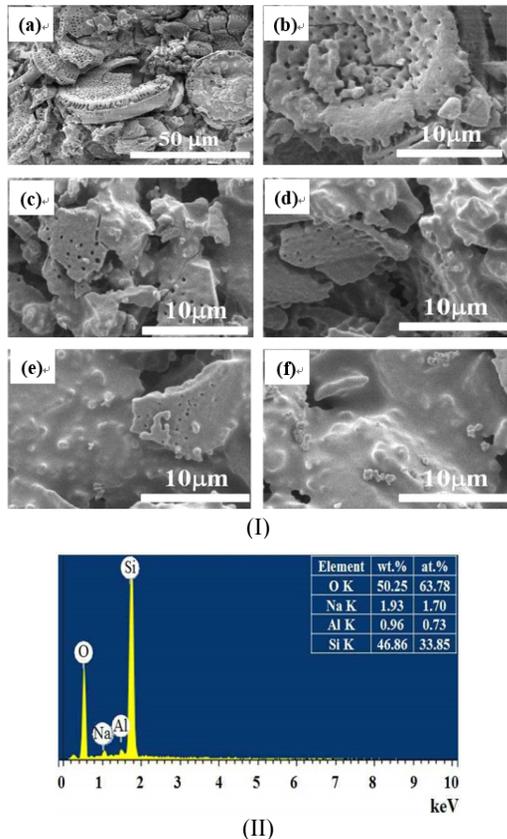


Fig. 4 (I) of FE-SEM images of the fractured surfaces of the diatomite ceramic filter at different sintering temperatures of: (a) 900°C, (b) 1,000°C, (c) 1,100°C, (d) 1,200°C, (e) 1,300°C and (f) 1,400°C, and (II) of sintered diatomite ceramic filter at a molding pressure of 2 MPa and sintering temperature of 1,100°C.

(Fig. 4(II)), in which the presence of peaks of Na and Al at 1,100°C demonstrated that the metal oxides did facilitate the low temperature eutectic reactions. On the other hand, a result similar to density behaviour was obtained for the variation of compression strength as a function of temperature as shown in Fig. 3(b). That is, with the increase of temperature, the compression strength increased. In addition, it can be seen that the modeling pressure had a light effect on the density, i.e. the greater the modeling pressure, the greater the density as shown in Fig. 3(a). no significant changes in compression strength as a function of modeling pressure was found as shown in Fig. 3(b).

3.3 Adsorption of H₂S and NH₃ by diatomite ceramic filter

Fig. 5 shows the adsorption results of H₂S and NH₃ by diatomite ceramic filter. It can be seen that as the sintering temperature increased, the adsorption rate decreased, and only NaOH/PDCF at 1,000°C and 1,100°C can completely remove H₂S within 120 min as shown in Fig. 5(a). Similar results were also found for adsorption of NH₃ by H₃PO₄/PDCF as shown in Fig. 5(b). This was due to the lower the sintering temperature, the lower the density, meaning the more porosity was retained. This was consistent with the effect of temperature on the density above mentioned. However, the lower the sintering temperature, the lower the compression strength. Akhtar et al.¹⁸⁾ reported that if the compressive strength of diatomite ceramic is 18 MPa, that is sufficient for water and air filtration. Therefore, considering the adsorption performance and compression strength, the diatomite ceramic filter sintered at 1,100°C was regarded as optimized sample due to its high compressive strength (around 20 MPa see Fig. 3(b)) and good adsorption performance.

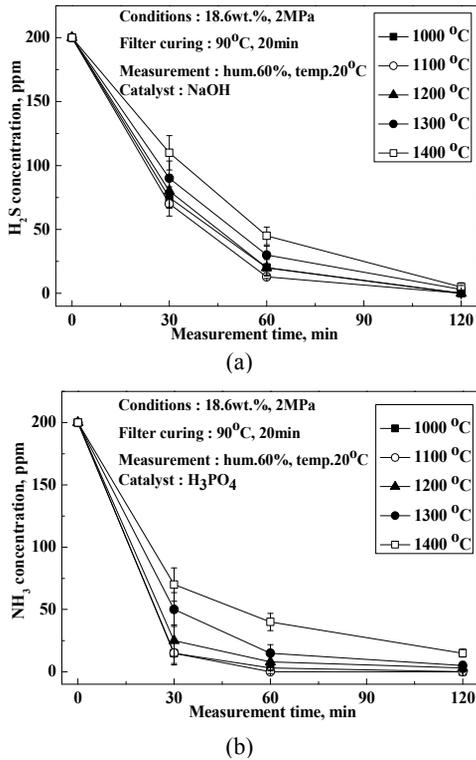


Fig. 5 Adsorption results of (a) H₂S by NaOH/PDCR, and (b) NH₃ by H₃PO₄/NaOH

In order to investigate the effect of NaOH and H₃PO₄ on the adsorption performance of H₂S and NH₃, SEM-EDS analysis was performed to observe the surface of PDCF modified with NaOH and H₃PO₄, and identify the adsorbed air pollutant molecules. Based on the above analysis, PDCF at 1,100°C was selected as a sample for SEM-EDS analysis as shown in Fig. 6(a), and the bimodal porous structure of inter-particle pores and intra-particle pores was obviously observed, which is beneficial for the adsorption. After modification with NaOH and H₃PO₄, the peaks of Na and P were determined, indicating the presence of NaOH and H₃PO₄ on the PDCF as shown in Fig. 6(b) and (d). Acid or base leaching led to the dissolution and erosion of diatomite particle, producing a large number of reactive sites and functional groups and

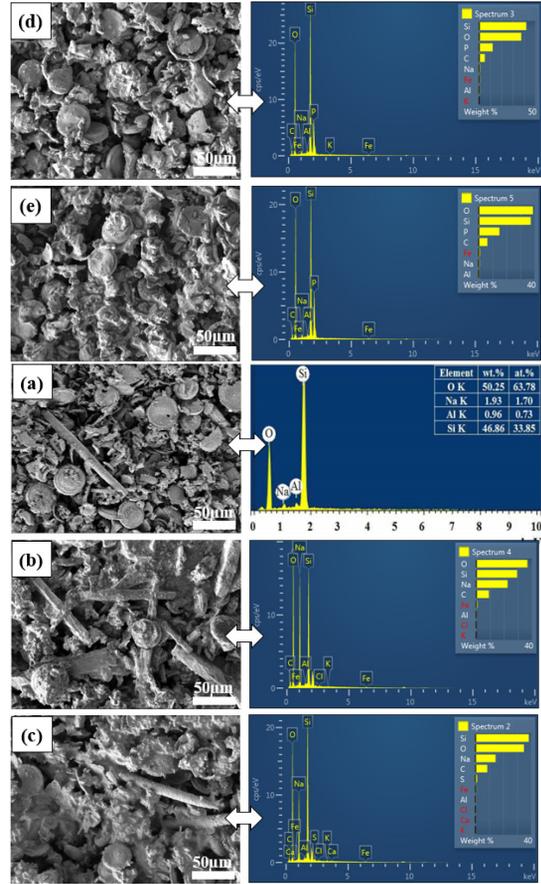


Fig. 6 SEM-EDS of (a) PDCF at 1,100°C, (b) NaOH/PDCF, (c) H₂S adsorbed NaOH/PDCF, (d) H₃PO₄/PDCF and (e) NH₃ adsorbed H₃PO₄/PDCF

making the surface very rough and irregular, increasing surface area as shown in Fig. 6(b) and (d). Similar findings were found in other study,¹⁹⁾ which reported that chemical activation can alter surface properties, such as increasing surface roughness and irregularities, and creating more new pores, increasing their pore properties and surface area. After adsorption of H₂S and NH₃, a peak of "S" (around 2 wt.%) was identified as shown in Fig. 6(c), showing the presence of adsorbed H₂S on NaOH/PDCF. Correspondingly, the bimodal porous structure was covered obviously by air pollutant

molecules on the SEM image as shown Fig. 6(c). Similar phenomenon was also found in the SEM image of Fig. 6(e), which indicated that the NH_3 molecules were adsorbed and attached on the surface of $\text{H}_3\text{PO}_4/\text{PDCF}$.

4. Conclusions

In this study, preparation of diatomite ceramic filter was conducted by using diatomite powder and PEG at different sintering temperatures of 900~1,400°C. The XRF, SEM, EDS, TGA and XRD analysis were carried out to characterized the diatomite powder, the results showed that diatomite has good properties for capturing air pollutant. Also, the analysis of compressive strength and density indicated that sintering temperature is most important parameter for diatomite sintering, and impurities of metal oxides play a major role in promoting the sintering of diatomite. In addition, NaOH and H_3PO_4 can greatly alter surface properties, such as increased surface area and porosity, and produced a large number of reactive sites and functional groups that significantly improve adsorption performance.

Author contributions

H. G. Kim; Investigation, Resources, K. W. Nam; Methodology. Writing-review & editing.

References

1. S. K. Song, Z. H. Shon, Y. H. Kang, K. H. Kim, S. B. Han, M. S. Kang, J. H. Bang and I. B. Oh, 2019, "Source apportionment of VOCs and their impact on air quality and health in the megacity of Seoul", *Environmental Pollution*, Vol. 247, pp. 763-774. (<https://doi.org/10.1016/j.envpol.2019.01.102>)
2. J. H. Lim, K. H. Kim, S. W. Kim, M. H. Lee and S. G. Oh, 2015, "A Study on the exhaust gas characteristics of the vehicle gasoline according to the ambient temperature", *Journal of the Korea Society For Power System Engineering*, Vol. 19, pp. 47-53. (<https://doi.org/10.9726/kspse.2015.19.6.047>)
3. D. H. Yoo, 2015, "Reduction of Nitrous Oxide Emission by EGR Method on Diesel Engine", *Journal of the Korea Society For Power System Engineering*, Vol. 19, pp. 16-21. (<https://doi.org/10.9726/kspse.2015.19.3.016>)
4. K. H. Kim, S. W. Kim, M. H. Lee, S. G. Oh and S. H. Lee, 2014, "The Study on the Assesment Greenhouse Gases and Air Pollutants of Diesel Vehicle according to Ambient Temperature and Driving Condition", *Journal of the Korea Society For Power System Engineering*, Vol. 18, pp. 77-83. (<https://doi.org/10.9726/kspse.2014.18.6.077>)
5. S. D. Lee, K. H. Kim, H. S. Lee and S. H. Jung, 2013, "Optimization of NOx Emission with Blends of Bio-diesel Oil and Diesel Fuel Using Design of Experiments", *Journal of the Korea Society For Power System Engineering*, Vol. 17, pp. 149-155. (<https://doi.org/10.9726/kspse.2013.17.6.149>)
6. I. Yildiz, E. Acikkalp, H. Caliskan and K. Mori, 2019, "Environmental pollution cost analyses of biodiesel and diesel fuels for a diesel engine", *Journal of Environmental Management*, Vol. 243, pp. 218-226. (<https://doi.org/10.1016/j.jenvman.2019.05.002>)
7. A. Berenjian, N. Chan and H. J. Malmiri, 2012, "Volatile Organic Compounds Removal Methods: A Review", *American Journal of Biochemistry and Biotechnology*, Vol. 8, pp. 220-229. (<https://doi.org/10.3844/ajbbsp.2012.220.229>)
8. C. K. Seo and J. Y. Bae, 2015, "De-NOx Characteristics of V2O5 SCR according to the Ratio of TiO2 Crystal Structures", *Journal of the Korea Society For Power System Engineering*,

- Vol. 19, pp. 26-32.
(<http://dx.doi.org/10.9726/kspse.2015.19.6.026>)
9. S. E. Ivanov and A. V. Belyakov, 2008, "Diatomite and its applications", *Glass and Ceramics*, Vol. 65, pp. 48-51.
(<https://doi.org/10.1007/s10717-008-9005-6>)
 10. A. K. Panda, B. G. Mishra, D. K. Mishra and R. K. Singh, 2010, "Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin clay", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 363, pp. 98-104.
(<https://doi.org/10.1016/j.colsurfa.2010.04.022>)
 11. J. Zhang, Q. W. Ping, M. H. Niu, H. Q. Shi and N. Li, 2013, "Kinetics and equilibrium studies from the methylene blue adsorption on diatomite treated with sodium hydroxide", *Appl. Clay Sci.* Vol. 83-84, pp. 12-16.
(<https://doi.org/10.1016/j.clay.2013.08.008>)
 12. S. Wang, H. Nam, H. Kim and K. Nam, 2016, "Cocoa activated carbon to remove VOCs (TMA, H₂S)", 13th International Symposium on the Genetics of Industrial Microorganisms (GIM2016 WUHAN), 2016:277.
 13. S. Martinovic, M. Vlahovic, T. Boljanac and L. Pavlovic, 2006, "Preparation of filter aids based on diatomites", *Int. J. Miner. Process.*, Vol. 80, pp. 255-260.
(<https://doi.org/10.1016/j.minpro.2006.05.006>)
 14. F. Akhtar, P. O. Vasseliev and L. Bergström, 2009, "Hierarchically porous ceramics from diatomite powders by pulse current processing", *J. Am. Ceram. Soc.* Vol. 92, pp. 338-343.
(<https://doi.org/10.1111/j.1551-2916.2008.02882.x>)
 15. T. J. Rockett and W. R. Foster, 1956, "Phase relations in the system boron oxide-silica", *J. Am. Ceram. Soc.* Vol. 48, pp. 75-80.
(<https://doi.org/10.1111/j.1151-2916.1965.tb11803.x>)
 16. A. Šaponjić, M. Stanković, J. Majstorović, B. Matović, S. Ilić, A. Egelja and M. Kokunešoski, 2015, "Porous ceramic monoliths based on diatomite", *Ceramics International*, Vol. 41, pp. 9745-9752.
(<https://doi.org/10.1016/j.ceramint.2015.04.046>)
 17. F. Akhtar, Y. Rehman and L. Bergström, 2010, "A study of the sintering of diatomaceous earth to produce porous ceramic monoliths with bimodal porosity and high strength", *Powder Technology*, Vol. 201, pp. 253-257.
(<https://doi.org/10.1016/j.powtec.2010.04.004>)
 18. W. T. Tsai, K. J. Hsien and C. W. Lai, 2004, "Chemical Activation of Spent Diatomaceous Earth by Alkaline Etching in the Preparation of Mesoporous Adsorbents", *Ind. Eng. Chem. Res.*, Vol. 43, pp. 7513-7520.
(<https://doi.org/10.1021/ie0400651>)