

Manipulating surface wettability and oil absorbency of diatomite depending on processing and ambient conditions



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ABSTRACT

In this study, a diatomite sample, which is a natural inorganic mineral with inherently high water and oil absorption capacity, was subjected to grinding before surface modification. Afterwards, the diatomite surface was modified via facile methods using a fluorocarbon (FC) chemical and stearic acid (SA) in addition to the sol–gel fluorosilanization (FS) process. The water and oil wettability, and oil absorbency properties of the unmodified and modified diatomites were investigated in addition to diatomite characterizations such as chemical content, surface area, particle size distribution, morphology, and modification efficiency. It was revealed that the wettability was changed completely depending on the surface modification agent and the media used, while the oil absorbency property surprisingly did not change. On the other hand, the oil absorbency was worsened by the grinding process, whereas the wettability was not affected.

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1. Introduction

Diatomaceous earth (DE) or diatomite, being a natural amorphous silica, is classified as the only biologically based natural mineral. It is a siliceous sedimentary mineral compound formed from the microscopic skeletal remains of unicellular algae-like plants called diatoms. There are known to be well over 100,000 different species, each possessing a unique morphology [1]. Diatoms range from approximately 1 μm to several mm in diameter. When aquatic diatoms die, they sink and collect on ocean and lake floors to form a material known as “diatomaceous earth” [2]. This residue is mined and used, for example, as an insulating material, abrasive,

filter, paint filler, and pesticide carrier. The high porosity and low density of diatomite make it ideal for industrial applications; however, its full potential has far from been realized.

Diatomite, being cheap and abundant in nature and possessing a high sorption ability and surface area, could be used for metal ions removal from contaminated wastewaters [3–7]. Owing to its high oil and water absorption capacity, diatomite could also be used for combating marine oil spills. However, the water-loving (hydrophilic) and oil-loving (oleophilic), i.e., amphiphilic, structure of diatomite should be modified beforehand properly for a selective oil absorbency, especially for recovering watery oil from marine oil spills.

Hydrophobic surface modification of organic or inorganic materials has been an effective way to synthesize absorbents for oil removal [8–11]. In such cases, the sol–gel method and subsequent hydrophobic treatment has been the method of choice due to its easiness and efficiency [12]. Hydrophobic and oleophilic silica particles and aerogels have been synthesized by using perfluorinated silane coupling agents via the sol–gel method [13–20]. In addition, nanowire membrane [21], mesh films [22–27], filter papers [28,29], sponges and foams [9,30–33], polymer composites [8,34–37], microsphere [38], and surface-modified magnesium carbonate [39] have been generated for separating oil from water. Based on the related studies [13–20], the diatomite surface was fluorosilanized via the sol–gel process and/or plasma treatment for the purpose of making superhydrophobic structure [40–42].

In this study, the diatomite used was subjected to a grinding process before surface modification and its oil absorption

Abbreviations: RDE, raw diatomite; GDE, ground diatomite; FS, fluorosilane; FC, fluorocarbon; SA, stearic acid; RDEFS1, raw diatomite modified with 1 wt% FS; RDEFS10, raw diatomite modified with 10 wt% FS; RDEFC1, raw diatomite modified with 1 wt% FC; RDEFC10, raw diatomite modified with 10 wt% FC; RDESA1, raw diatomite treated with 1 wt% SA; RDESA10, raw diatomite treated with 10 wt% SA; GDEFS1, ground diatomite modified with 1 wt% FS; GDEFS10, ground diatomite modified with 10 wt% FS; GDEFC1, ground diatomite modified with 1 wt% FC; GDEFC10, ground diatomite modified with 10 wt% FC; GDESA1, ground diatomite treated with 1 wt% SA; GDESA10, ground diatomite treated with 10 wt% SA; γ_{OA} , surface tension of the oil–air interface; γ_{WA} , surface tension of the water–air interface; γ_{OW} , surface tension of the oil–water interface; θ_{OW} , contact angle of oil-in-water; θ_{O} , contact angle of oil-in-air; θ_{W} , contact angle of water-in-air.

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property was investigated. Afterwards, for providing a selective oil absorbency property, the ground/unground diatomite surfaces were modified with three different chemicals. Considering the literature, the diatomite was surface modified with a fluorosilane by a sol-gel process, which involves high chemical cost, complex preparation processes, and difficulty in scalable fabrication. Additionally, diatomite was treated with a fluorocarbon chemical and a saturated fatty acid by using facile methods in comparison to the fluorosilane modification. Afterwards, the surface properties of the diatomite samples in relation to water and oil wettability and absorbency were evaluated in different mediums in addition to characterizations such as chemical content, surface area, particle size distribution, morphology, and modification efficiency.

2. Experimental

2.1. Materials

A flux calcined type of diatomite was obtained from Imerys (Celite 281, Istanbul, Turkey), designated as RDE. Trimethoxy(3,3,3-trifluoropropyl)silane ($\geq 97\%$, Sigma Aldrich), Orgaguard[®] FC 6000 (fluorocarbon compound containing six carbon atoms, conc. 33% Organik Kimya, Istanbul, Turkey) [43] and stearic acid ($>95\%$, Sigma-Aldrich) were used as surface modification agents.

2.2. Methods

2.2.1. Grinding

Considering the literature that indicates an inverse proportionality between particle size and surface area [44,45], the RDE was subjected to a grinding process for the purpose of enhancing specific surface area and thus to increase the absorption capacity of diatomite. Deniz [46] showed that diatomite could be ground easily although it contains a high amount of silicon dioxide (SiO_2), meaning that there would be no problem in terms of the grinding process.

The diatomite samples were dry ground in a Fritsch Pulverisette 5 planetary ball-mill at 400 rpm using balls with a 5 mm diameter. The material of the mortars and balls was zirconium oxide. The milling process was conducted in time intervals of 2-min milling, followed by a 4-min break to avoid excessive heating of the mortar and sample. We decided to use an effective grinding time of 16 min according to the preliminary grinding tests.

2.2.2. Fluorosilane (FS) surface modification

The modifier amount was set to 1 and 10 wt% based on our previous studies. A 95/5 ethanol/distilled water solution was prepared and its pH was adjusted to 4 with acetic acid (CH_3COOH , 15%). A certain amount of trimethoxy(3,3,3-trifluoropropyl)silane was added to the solution and stirred for 24 h in a dark room for the hydrolysis of the silanol groups. Afterwards, diatomite was added slowly and the slurry was left overnight; it was continuously stirred at ambient conditions for deposition of fluorofunctional silane onto the diatomite. The slurry was washed twice with ethanol and subsequently dried at 100°C for 3 h [47].

2.2.3. Fluorocarbon (FC) surface modification

Either 0.33 ml (1 wt%) or 3.3 ml (10 wt%) fluorocarbon compound was added to 90 ml of distilled water containing 10 g of RDE and stirred for 15 min using a magnetic stirrer. The slurry was repeatedly washed with distilled water and then centrifuged at 4000 rpm for 9 min. Then the slurry was dried and cured at 110°C for 5 min [43].

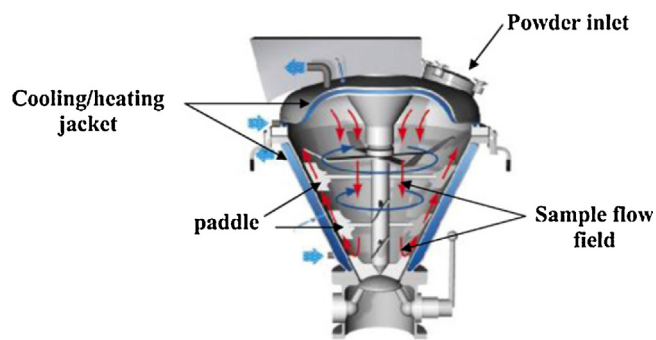


Fig. 1. Schematic diagram of a Cyclomix high shear mixer [43].

2.2.4. Stearic acid (SA) surface treatment

Diatomite was surface treated with stearic acid (1 and 10 wt%) in dry state in a Cyclomix 5 (Hosokawa Micron, The Netherlands) high shear mixer. This instrument can be used in the drying, coating, mixing, agglomeration, and densification of particulate materials and has a nominal volume capacity of 5 L. The mixer has four pairs of flat-bladed impellers placed from the bottom to the top (Fig. 1). Related details can be found elsewhere [48]. The diatomite surface coating was carried out at 80°C for 15 min with a rotation speed of 1500 rpm. After completing the coating process, a quick cooling to room temperature and discharging were carried out.

2.3. Characterization

2.3.1. X-ray fluorescence and X-ray diffraction analyses

Elemental analysis of the specimen was carried out using a Panalytical-Axios Advanced wavelength dispersive X-ray fluorescence spectrometer.

Diatomite samples were analyzed using a Bruker AXS Advance D8 diffractometer (Cu $\text{K}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$, generator voltage = 40 kV, current = 30 μA). Samples were scanned in 2θ ranges from 1° to 60° at a rate of $1^\circ/\text{min}$. The raw data were transformed into an XRD spectrum using Bruker Evaluation Software Version 7.0.

2.3.2. BET analysis

The specific surface area of the diatomite samples was determined using multi-point measurements on a Micromeritics Gemini VII 2390 instrument by the Brunauer, Emmett and Teller (BET) gas adsorption method. The samples were dried at 150°C for 24 h and degassed at 200°C for 5 h under vacuum prior to measurement.

2.3.3. Particle size analysis

Particle size and particle size distribution analyses were performed on a Mastersizer 2000 laser diffraction particle size analyzer (Malvern, UK) from wet dispersions. A microvolume (200 mg) sample feeder collected triplicate measurements in 2-s intervals. The obscuration limits were set to 5–15%.

2.3.4. SEM analysis

The surface morphology of the diatomite was studied employing a ZEISS EVO scanning electron microscope (SEM) in VP mode operating with an accelerating voltage of 25 keV. In addition to the morphology analysis, EDX chemical composition analysis was carried out on the surface-modified diatomite samples.

2.3.5. FTIR analysis

The chemical structure of the raw and surface-modified diatomite samples was investigated using a Perkin Elmer Spectrum

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