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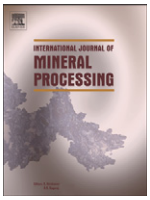

Effect of acid treatment on the chemical composition and the structure of Egyptian diatomite

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ABSTRACT

In this study Egyptian diatomaceous earth from Kasr El-Sagha locality in El Fayium province, Egypt was used. A highly purified diatomite has been prepared successfully by using a two stage process. In the first stage, samples of Egyptian diatomite were subjected to several mechanical techniques (attrition scrubbing and hydrocyclone classification) to remove most of the accompanied gangue minerals like inorganic carbonate, silica sand, and clay. The fraction with a particle size of −45 μm was then submitted to a thermo-chemical treatment. This second stage started with a calcination of the diatomite samples at 1023 K for 1 h. Three modified forms of diatomite were then prepared by hot acidification of the calcined diatomite samples with aqua regia (5 M HCl + 5 M HNO_3), 5 M sulphuric acid or 5 M hydrochloric acid. The refined products were characterized by X-ray diffraction, X-ray fluorescence, low temperature nitrogen adsorption, mercury intrusion and scanning electron microscopy. Silica materials with high purity (>96 wt.% SiO_2) and an accessible and interconnected mesopore structure could be obtained. Additionally, all samples displayed a large amount of macropores of about 1 μm diameter and a broad distribution of larger interstitial macropores. The treatment with hydrochloric acid led to products with a specific surface area between 120 and 150 $m^2\ g^{-1}$ and 63 wt.% of amorphous phase.

1. Introduction

Diatomite or diatomaceous earth refers to fossil deposited diatoms: The accumulation of amorphous silica remains of dead diatoms formed fine grained siliceous sedimentary rock after thousands of years. The major component of all types of diatomite is biogenic amorphous silica featuring high porosity, low density, low thermal conductivity, high melting point and chemical inertness (Stoermer and Smol, 1999). These properties make diatomite a promising candidate for a broad spectrum of applications such as filter aids, fillers, adsorbents and catalyst supports (Stoermer and Smol, 1999).

There are two different types of diatomite deposits in Egypt. The first type was deposited in the form of sedimentary rock of the Eocene epoch. This diatomite sediment is mainly present in the El Fayium depression, about 180 km from Cairo. The second type was formed along the bank of Nile River and is known as Nile diatomite. The fresh water diatomite of the tertiary period is usually associated with volcanic rocks and present in the El Fayium area. The Nile and El Fayium diatomites include the fresh water species. Both are formed by the diatoms deposited in marine and fresh water environments (Al-Wakeel, 2009).

Many studies have been published about the physical treatment of raw Egyptian diatomite, especially those from the El Fayium depression in a large area extending from Wadi El Rayan to the south east of Gabel Elow El-Masakheet locality (Swedan, 1972; Ibrahim and Selim, 2010, 2011, 2012; Ibrahim, 2012; Hassan et al., 1999). There are almost six main diatomite deposits in El Fayium locality. Some of these diatomite ores are embedded either in clayey matrix like Demia—yellow diatomite or in clayey calcitic—matrix like Kom-Osheem deposit and El-Berka deposit. The other diatomite ores are embedded in a mainly calcitic matrix like El-Masakheet diatomite, Demia—grey deposit, and Kasr El-Sagha diatomite. The only diatomite deposit that contains appreciable amount of gypsum is the Kasr El-Sagha diatomite (Table 1).

The studies of the Egyptian diatomite species in the El Fayium region showed that they contain water soluble salts, carbonate, sandy and clay fractions. The impurities have a notable influence on the application of diatomite. However, it should be mentioned that the Egyptian diatomite ores vary in grade from high, moderate to low ranks (Ibrahim and Selim, 2011; Hassan et al., 1999; Zalat, 2002). This leads to variations in the

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Table 1
Generalized chemical composition of different diatomite deposits in El Fayium.

Diatomite types	Constituent wt.%					
	SiO_2	Fe_2O_3	Al_2O_3	SO_3	CaO	LOI
Kom-Osheem	53.6	6.3	8.6	0.4	14.4	16.7
Berka	55.7	3.7	8.9	0.3	14.6	16.8
El-Masakheet	54.9	0.8	2.1	0.5	16.5	25.2
Demia—yellow	64.5	2.3	10.7	1.5	1.8	19.2
Demia—grey	59.5	4.5	2.2	0.4	13.5	19.9
Kasr El-Sagha	38.2	2.7	3.9	2.0	26.4	26.8

physic-chemical properties. A recent study on the Gabel Elow El-Masakheet diatomite (El Fayium region) reports that the diatomite ore with the particle size of −25 μm is suitable for use as filter aid due to its high silica content of about 96 wt.% and a BET specific surface area of 195 $m^2\ g^{-1}$ (Ibrahim and Selim, 2011). In contrast, the Kom-Osheam diatomite (El Fayium region) contains only 74 wt.% SiO_2 for the fraction with particle size in the range between −45 and +10 μm. A combined mechanical/thermal/acid treatment is necessary to improve its properties for further industrial applications such as production of mesoporous materials (Selim et al., 2010).

The objective of this study is to subject selected samples of Egyptian diatomite, from El Fayium depression in Kasr El-Sagha locality, to a defined thermal and chemical leaching treatment with inorganic acids in order to assess the impact of the individual treatments on various parameters which are important for practical applications of the materials. In addition to crystallinity, purity and particle morphology, the textural properties of the treated diatomite are in the focus of this investigation. For this purpose low temperature nitrogen adsorption is combined with mercury intrusion. Finally, new applications of these materials are discussed.

2. Experimental

2.1. Materials

The diatomite raw material was obtained from Kasr El-Sagha locality in El Fayium governorate, Egypt.

Sulphuric acid (H_2SO_4, 96%, reagent grade) was obtained from ACROS ORGANIC, Germany. Nitric acid (HNO_3, 65%, reagent grade) and hydrochloric acid (HCl, 37%, reagent grade) were purchased from Prolabo, EC.

2.2. Methods

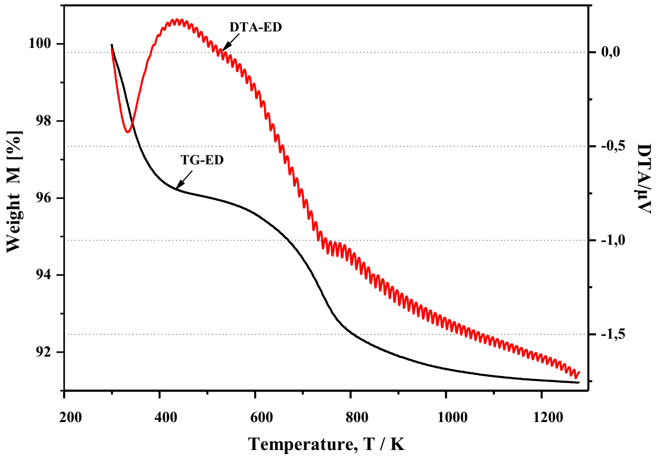

Fig. 1. DTA/TG profiles of the ED sample obtained after mechanical processing with an average diameter of −45 μm. TG curve (y axis on the left-hand side) and DTA curve (y axis on the right-hand side).

A representative diatomite sample was gently and completely crushed with hammers to obtain a fraction with a particle size of −5 mm. The crushed product was afterwards subjected to attrition scrubbing in a closed circuit with double deck vibration screening to reject the over-screen fraction with a particle size of +74 μm. The product fraction of −74 μm was then directed to a 3" (3 inch) hydrocyclone classifier (7.08 cm Sprout Bauer Andriz, Sprout Bauer, Inc., Muncy, PA, USA) to remove the silt fraction with a particle size of +45 μm (Table 2). The silt was defined as a coarse granular material of the size somewhere between sand and clay. The silt contained mostly quartz and feldspar and its particle sizes ranges between 4 and 63 μm.

The semi quantitative analysis (determined by XRD) of original Kasr El-Sagha diatomite with the fraction of −45 μm showed the following composition: quartz 16.7 wt.%, kaolinite 22.5 wt.%, calcite 41.0 wt.%, albite 7.5 wt.% and gypsum 12.3 wt.%. The fraction formed about 60.7 wt.% of the overall sample (Table 2). Additionally, the sample was leached with 1 M HCl at 323 K to remove calcite and gypsum from the fraction of −45 μm.

The resulting diatomite rich product with a particle size of −45 μm is abbreviated as ED (Egyptian diatomite). This fraction was subjected to a calcination in a ceramic crucible at 1023 K for 60 min (heating rate of 10 K min^{-1}) and then cooled down to room temperature inside the muffle furnace (type N 11/H, Nabertherm, Germany). The sample was denoted as ED-1023 K.

The first acid leached sample was obtained by treating the calcined diatomite with aqua regia (sample designation ED-AR). Aqua regia (AR) was prepared by adding three volumes of 5 M hydrochloric acid to one volume of 5 M nitric acid. The second sample (designated as ED-H_2SO_4) was treated with 5 M sulphuric acid. The third sample (designated as ED-HCl) was treated with 5 M hydrochloric acid. The leaching process was carried out for 24 h at a solid to liquid ratio of 1:25 (g/ml), a stirring speed of 1000 rpm (mechanical stirrer, RW 20, Janke& Kunkel GmbH & Co. KG IKA-Labor Technik, Staufen, Germany) and a temperature of 368 K. A 1000 ml three-neck round bottom glass was used for the acid treatment.

Table 2
Refining results for the Kasr El-Sagha diatomite original sample.

Process	wt.%	Constituent wt.%				
		SiO_2	Fe_2O_3	Al_2O_3	CaO	LOI[a] + OI
Original sample	100	38.2	2.7	3.9	26.4	28.8
Attrition scrubbing:						
Over Screen, +74 μm fraction	7.0	94.3	0.8	–	2.6	2.3
Hydrocyclone classification:						
7.62 cm hydrocyclone UF fraction +45–74 μm	32.3	35.0	2.1	2.6	28.3	32
7.62 cm hydrocyclone OF fraction −45 μm	60.7	44.6	2.7	3.9	26.4	22.4

[a] LOI = loss on ignition; OI = other inorganic oxides.

Table 3
Particle size analysis of the untreated and treated Egyptian diatomite samples. Each value is the average of three individual samples with their standard deviations.

Product	Average particle diameter *dp* in μm				
	ED	ED-1023K	ED-AR	ED-H_2SO_4	ED-HCl
[a]dp_{10}	3.5 ± 0.3	3.3 ± 1.3	4.3 ± 0.8	5.7 ± 0.8	2.9 ± 0.4
[a]dp_{50}	12.8 ± 0.6	13.2 ± 0.8	15.6 ± 0.7	16.0 ± 1.3	10.0 ± 1.2
[a]dp_{90}	29.6 ± 0.5	31.2 ± 1.5	32.5 ± 0.9	39.3 ± 1.1	18.3 ± 0.8

[a] dp_{10}, dp_{50}, dp_{90} are the average particle diameters at 10%, 50% and 90% of the cumulative size distribution of the analyzed powder.