IMPROVEMENT OF FILTRATION PROPERTIES OF GHIDIRIM DIATOMITE (REPUBLIC OF MOLDOVA)

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Abstract. The aim of the study was to modify the diatomite from Ghidirim village (Ribnita distinct, Republic of Moldova) with the purpose of using it as filter material. The initial diatomite was modified by alkaline treatment with sodium carbonate and the filtering capacity was evaluated by suction filtration method. The treatment of diatomite by sodium carbonate resulted in an increased filtration rate, recording the most pronounced filtering capacity for diatomite treated with 20% solution of sodium carbonate.

Keywords: diatomite, alkaline treatment, filtration rate.

Introduction

Diatomite, also known as diatomaceous earth or kieselguhr, is a fine sedimentary rock of biogenetic origin. Its main component is amorphous hydrated silica ($SiO_2 \cdot nH_2O$) [1,2]. Diatomite is a silica mineral formed from the fossilized skeletal remains of microscopic singlecelled aquatic plants called diatoms. Over 10,000 species of these microscopic algae have been recognized, each with its own distinct shape, ranging in size from below 5 microns to over 100 microns. Normally, the diatomite deposits consist of diatom shells only, but these deposits actually contain other sediments such as clay, inorganic carbonates, iron oxides, and fine sand [3]. Diatomaceous earth typically consists of 86-94% silicon dioxide (SiO_2), with a significant quantity of alumina [4].

Diatomite is wide-spread in many areas of the world and it is available in large quantities at a low cost. Due to its physical characteristics, such as high porosity (25–65%), small particles size, low thermal conductivity and specific gravity, appropriate surface area (16-70 m^2g^{-1}) and high adsorption capacity, diatomite can be applied in various industrial fields as a filter material, absorbent, anti-caking agent, thermal insulator, filler, catalyst carrier and additive for numerous other purposes [5,6].

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One of the most popular methods used to purify and modify the surface properties of diatomite is chemical treatment with alkaline agents. Typically, the alkaline agents include sodium hydroxide, sodium carbonate and potassium hydroxide. These agents are used to create more open pores. By removing impurities and organic compounds can be expected to gain a larger surface area and total pore volume in diatomite [1].

In the Republic of Moldova, the most significant deposits of diatomite are located along the Dniester River, Naslavcea - Kamenka area. Diatomite from these deposits is used exclusively in order to obtain construction materials [7]. Nevertheless, studies regarding other areas of diatomite' application are performed [8,9].

The aim of the present study was to modify the diatomite from Ghidirim village (Ribnita distinct, Republic of Moldova) with the purpose to use it as filter material.

Experimental
Modification of diatomite

The diatomite from Ghidirim village (Ribnita distinct, Republic of Moldova) was used for investigations. The diatomite samples were washed with distilled water to remove impurities,

then dried and sieved. The fraction under 0.63 mm was used for study.

The alkaline treatments were carried out with sodium carbonate solution of different concentrations (1, 5, 10 and 20%) at a solid/liquid ratio of 1:25 (7 g diatomite/175 mL solution) in the water bath (90-95°C) for an hour in reflux conditions. Further, the cooled suspension was filtered. The modified diatomite was repeatedly washed with distilled water until the pH value of eluate was equal to 7, dried at 110°C, and then calcined at 850°C for 2 hours.

Characterization of diatomite samples

Thermal analysis was performed using a Derivatograph Q-1000 analyzer. The samples were heated from room temperature up to 1000°C in a flowing air atmosphere (100 mL/min) at a heating rate of 10°C/min.

The infrared spectra (IR) of the diatomite were recorded in the range 400 – 4000 cm^{-1} using the Fourier Transform Infrared Spectrometer (PerkinElmer, Spectrum 100, USA), applying the KBr pellet technique.

The porous structure and adsorption parameters of diatomite samples were obtained from nitrogen adsorption isotherms performed at 77 K. The adsorption isotherms were measured using Autosorb-1 (Quantachrome), after degassing the samples at 200°C for 12 hours. The Density Function Theory (DFT) was used to calculate the pore volume distribution [10].

The *bulk density, specific gravity* and *oil absorption* were determined according to British Standards for diatomite [6]. Bulk density was measured by gently knocking base of measuring cylinder with certain quantity of sample. Bulk density value (g/cm^3) was calculated using Eq.(1):

$$Bulk\ density = \frac{m}{V} \qquad (1)$$

where, *m* is quantity of sample (g);
   V is the sample volume (mL).

Specific gravity was calculated from the difference in mass of pycnometer with diatomite suspension and with distilled water. Specific gravity value was determined by Eq.(2):

$$Specific\ gravity = \frac{B - A}{(B + D) - (A + C)} \qquad (2)$$

where, *A* is the mass of pycnometer (g);
   B is the mass of pycnometer with 10 g of dry diatomite sample (g);
   C is the mass of pycnometer with 10 g of dry diatomite sample and filled with distilled water (g);

D is the mass of pycnometer filled with distilled water (g).

Oil absorption value was determined by the addition of linseed oil, drop by drop, to a certain quantity of sample, until the formation of a smooth consistency paste. Oil absorption value (mL/100g) was calculated using Eq.(3):

$$Oil\ absorption = 100\frac{V}{m} \qquad (3)$$

where, *V* is the recorded volume of oil added (mL);
   m is the quantity of sample (g).

The *filtration rate* of initial and modified diatomite samples were determined using suction filtration method [11]. A 3 g sample was shaken with 50 mL of distilled water and emptied in a filtration funnel. When all initial water has filtered from the sample, a portion of 100 mL of water was added and the filtration time recorded. The filtration rate (mL/m^{2}s) was determined using Eq.(4):

$$Filtration\ rate = \frac{W_F}{F \cdot t} \qquad (4)$$

where, W_F is the volume of the filtrate (mL);
   F is the effective filter paper surface (m^2);
   t is the filtration time (s).

Results and discussion

Generally, depending on the mineralogical structure, diatomite can be characterized by formations from well crystallized forms (christobalite) to quite amorphous forms (opal). The mineral phase of the diatomite from the Ghidirim village of Republic of Moldova contains a number of clay minerals, like montmorillonite (in a mixture with insignificant quantities of slightly chloritized montmorillonite), illite and kaolinite. Diatomite also contains fine-dispersed quartz and amorphous material, the more probable sources of which are opal, amorphous alumosilicates, aluminum and iron hydroxides [12].

The chemical composition of Ghidirim diatomite includes silica (85.4%), alumina (3.0%), iron oxides (1.9%), calcium oxide (1.8%) and magnesium oxides (0.6%) [8].

Thermo-gravimetrical analysis for Ghidirim diatomite shows an intensive loss in weight in the temperature range of 50–200°C and around 800°C. The first endothermic peak at 127°C is due to the loss of absorbed water from the surface

and from open pores, while the intense loss of mass during the second endothermic peak at 800°C is the result of loss of the hydrated water (Figure 1).

Figure 2 shows the results of IR analysis of initial diatomite. The peaks at 470 and 1095 cm^{-1} may be attributed to the asymmetric stretching modes of Si–O–Si bonds; the peak at 800 cm^{-1} may be related to the stretching vibration of Al–O–Si [2,13,14]. The weak absorption peak at 695 cm^{-1} is probably due to Si–O deformation and Al–O stretching. The peaks at 3435 and 1630 cm^{-1} correspond to the stretching vibrations of sorbed water [2,13,14].

The porous structure characteristics of initial and modified samples of diatomite are presented in Table 1. Analysis of pore size distribution, obtained using DFT model, demonstrates the predominance of meso-pores in the structure, especially for samples modified with 20% solution of sodium carbonate (Figure 3).

Oil absorption test results show a good absorption capacity for the diatomite samples treated with 1% and 5% solution of sodium carbonate (Figure 4).
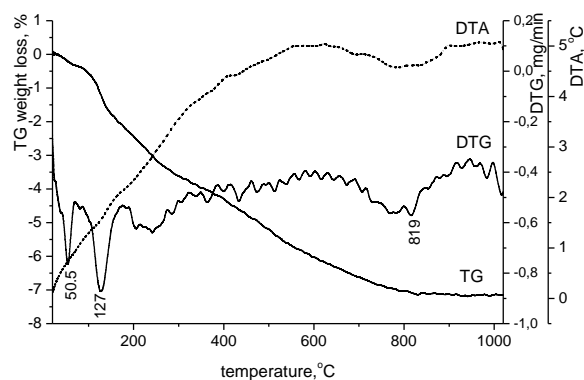

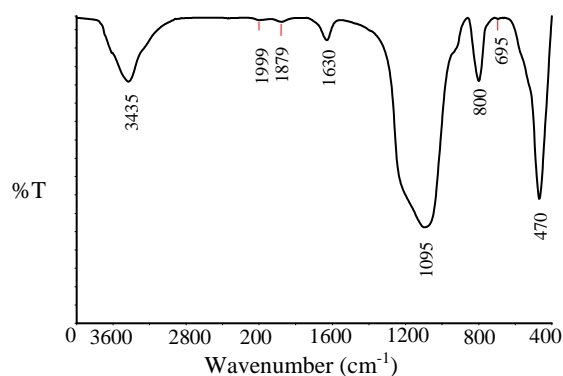**Figure 1. Thermogravimetric (TG/DTG/DTA) curves for diatomite.**

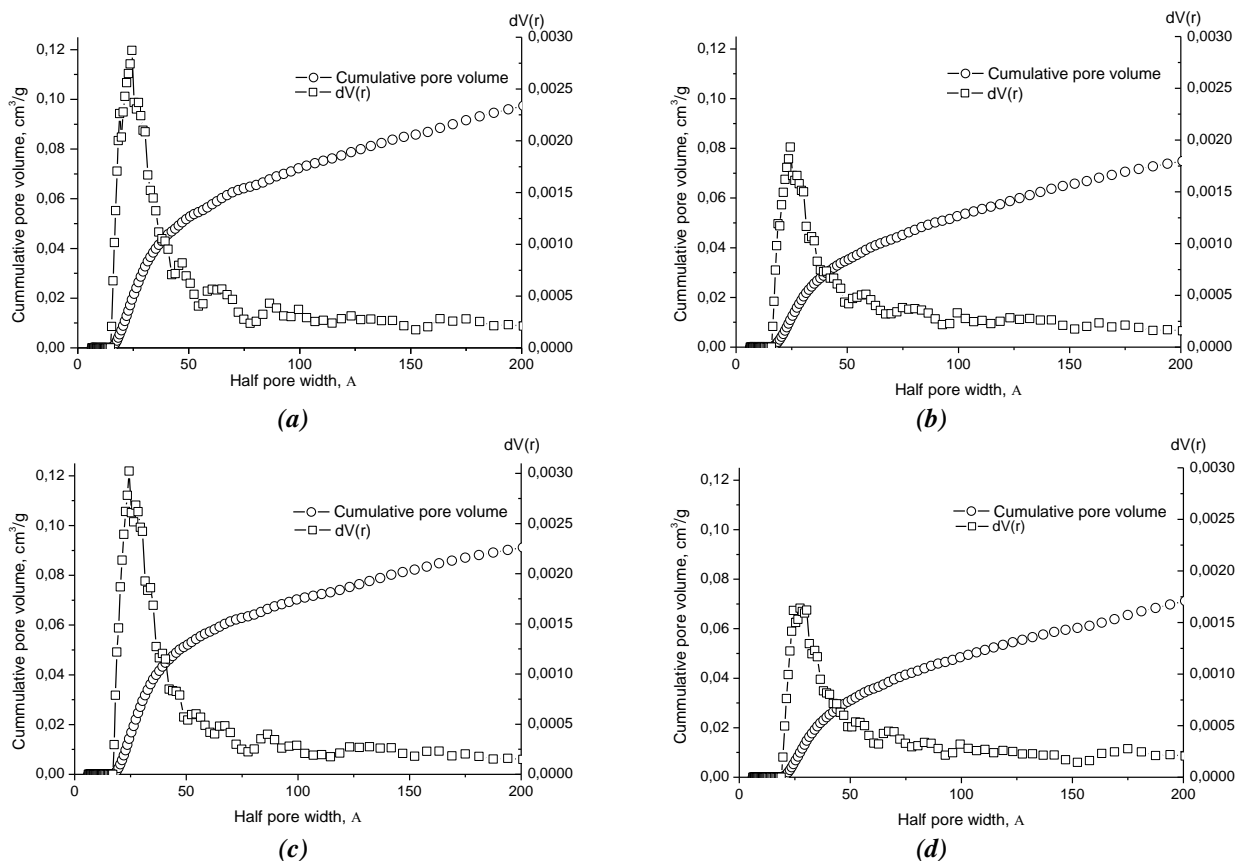**Figure 2. IR spectra of initial diatomite.**

(a)

(b)

(c)

(d)

Figure 3. Pore size distribution for initial diatomite *(a)* **and samples modified by calcination at 850°C** *(b)* **and modified with sodium carbonate solution of 10%** *(c)* **and 20%** *(d)***.**

Generally, diatomite has a low specific gravity in the range of 1.95-2.3 [15]. Values of specific gravity and bulk density for obtained samples of diatomite are listed in Table 2. Specific gravity of obtained samples is in the range of 1.96-2.2, while values of bulk density are in the range of 0.44-0.67 g/cm^3.

Filtration quality of diatomite could be significantly improved after treatment with various agents [11]. In this case, the alkaline treatment with 20% solution of sodium carbonate improved the filtering capacity of studied diatomite by about 50 times (Figure 5).

Table 1

Porous structure characteristics of diatomite samples.

Sample	Total pore volume, cm^3/g	Specific surface area, m^2/g	Half pore width, Å
Initial diatomite	0.125	49.77	24.4
Diatomite calcined at 850°C	0.106	35.07	24.4
Diatomite modified with Na$_2$CO$_3$ of 10%	0.115	45.63	24.4
Diatomite modified with Na$_2$CO$_3$ of 20%	0.101	30.15	27.4

Table 2

Values of specific gravity and bulk density for obtained samples of diatomite.

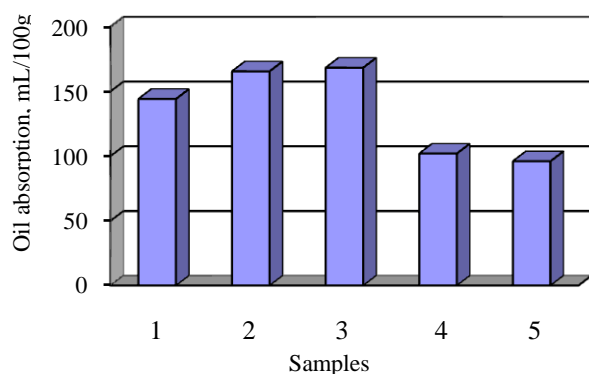| Sample	Bulk density, g/cm^3	Specific gravity
Diatomite calcined at 850°C	0.44	1.96
Diatomite modified with Na$_2$CO$_3$ of 1%	0.44	1.95
Diatomite modified with Na$_2$CO$_3$ of 5%	0.46	1.97
Diatomite modified with Na$_2$CO$_3$ of 10%	0.64	2.20
Diatomite modified with Na$_2$CO$_3$ of 20%	0.67	2.19

Figure 4. Oil absorption values (mL/100g) registered for diatomite calcined at 850°C (*1*) and samples modified with sodium carbonate solution of 1% (*2*), 5% (*3*), 10% (*4*) and 20% (*5*).
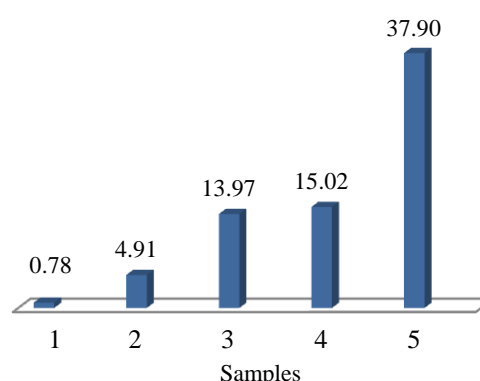

Figure 5. Values of filtration rate (mL/m^{2}s) registered for diatomite calcined at 850°C (*1*) and samples modified with sodium carbonate solution of 1% (*2*), 5% (*3*), 10% (*4*) and 20% (*5*).

Conclusions

Analysis of pore size distribution of initial diatomite and samples modified with sodium carbonate, using DFT model, demonstrates the predominance of mesopores in the structure. The meso-porous structure is more developed for the sample treated with 20% sodium carbonate solution.

Filtration quality of diatomite increased significantly after treatment with sodium carbonate. The most pronounced filtering capacity was recorded for diatomite treated with 20% solution of sodium carbonate.

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