

Acid Modification of Diatomite-Based Sorbents

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Abstract

In this work, the effect of acid pre-treatment (hydrochloric acid, HCl) and calcination of diatomite, a silicon dioxide-material from natural sources, was studied with the aim to obtain diatomite-based sorbents with specific physicochemical properties. For this, acid pre-treatments with HCl at different calcination conditions, namely HCl concentration (0.5, 1 M) and calcination temperatures (from 600 to 900 °C) were studied. Morphological features different from those of natural diatomite were obtained. It has been found that treatment of diatomite with 0.5 M HCl at 800 °C showed a specific pore volume of 0.008 cm³/g, and a specific surface area of 19.26 m²/g, while the treatment of diatomite with 1.0 M HCl showed a specific pore volume of 0.011 cm³/g, and a specific surface area of 25.57 m²/g. The performance of the acid pretreatment of diatomite for adsorption of Pb ions from water was also studied.

1. Introduction

Diatomite is a mineral of silicon dioxide consisting of fossilized skeleton remnants of microscopic single-celled aquatic plants (algae) called diatoms. Diatomite from Aktobe field of Kazakhstan can be used to remediate many environmental problems. It has a unique combination of physical and chemical properties (good absorption ability, chemical inertness and a large surface area) that makes it applicable as a sorbent for purification of water from heavy metals and ion exchange [1–3, 4].

Modern methods make it possible to purify water from heavy metals, in principle, to any depth, for example, using activated carbons. Nevertheless, the implementation of existing technological procedures is limited by its high cost associated mainly with activation or combination with other active phases in the diatomite-based sorbent production, recovery of used sorbent, and regenera-

tion. To overcome these drawbacks, it was planned to exploit ready-for-use sorbents (native solid sorbents) the performance of which could be further implemented after minimal activation treatments.

Different natural solid sorbents modification protocols are conventionally used by researchers to enhance specific diatomite properties, such as high efficiency, considerable adsorption capacity operated selectivity. Among them are: thermal activation; mechanical activation; chemical activation.

As the composition of diatomite includes minerals such as montmorillonite and kaolinite that possess a high wetting ability, it is possible to use thermal treatment (calcination) and grinding to eliminate the excess of water and amorphous contaminants. The calcination also promotes the growth of the specific surface area thus enhancing activity of the adsorbent. The work [4] reports that diatomite thermally treated at 500 °C presents an enhanced adsorption capacity for major of inorganic pollutants as cadmium (Cd), lead (Pb), mercury (Hg), etc.

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Mechanical activation requires prolonged abrasion of the sorbent in ball mills implying the use of expensive equipment. However, mechanical activation of minerals allows obtaining new materials with completely different properties, useful in the production of building materials. So, when grinding a mixture of quartz and calcium compounds, a new mineral is obtained – silicalcite, which increases the strength of concrete products due to the formation of a calcium silicate crust.

When extracting metals from the waste of concentration and metallurgy, activated by grinding the material, reagent solutions contribute to the oxidation of useful minerals to obtain metal oxides [5]. The chemical activation approaches are divided into three main groups: salt activation; alkaline activation; acid activation.

From these, the most widely used is acid activation during which one can observe: i) dissolution of a considerable part of oxides (CaO, MgO, Na₂O, FeO, Fe₂O₃, Al₂O₃ and others); ii) the increase of pore sizes; iii) the change in the chemical features of the surface (sorbents are converted in the H-form) [6, 7]. During acid activation, a complete replacement of exchangeable ions takes place with a partial replacement of Al³⁺ and Mg²⁺ ions in crystalline lattices. The crystalline lattice is preserved upon acid activation also resulting in an overall increase of the surface polarity, thus positively affecting the technological characteristics.

In [8], the authors report that the sulfuric acid treatment under controlled conditions significantly destroys the structure of pores of clay mineral due to a high content of silicon leaving the sites with the BET surface area of 10 m²/g. In the creation of more open pores, the concentration of acid is a determining factor compared to other parameters of the process (temperature, exposure).

In [9] have been studied the adsorption of sodium and chloride ions from aqueous solutions using deionized diatomite. As a result, it was established that the maximum adsorption was 50.2 mg/g, and the maximum degree of extraction, corresponding to the concentration range of 5–100 mg/l, was 53.9%.

In [10], the authors present the investigation results on textural characteristics and the adsorption performance of Mn²⁺ modified bentonite was successfully evaluated. Bentonite clay modified with Fe³⁺ and Al³⁺ which show the highest adsorption capacity at pH 2 compared with Mn²⁺ bentonite illustrate its maximum adsorption capacity at initial pH 4.

In [11] the authors present a survey about the physico-chemical properties of diatomite samples. The study shows that diatomite consists mainly of amorphous silica (opal) and a very small amount of quartz. During calcination, the molar ratio of Si/Al remains constant but hot acid treatment changed both: the structure and the chemical composition.

In order to assess the sorption capacity of heavy metal ions in comparison to untreated diatomite, natural diatomite was saturated with a microemulsion this showing the increase in Cr (III) sorption. The adsorption process depends on pH and the best results for the initial Cr (III) concentration of 1.5 g/L was obtained at pH 2.95. Following the adsorption step, a desorption process was carried out using several eluent solutions. The best results have been obtained when using concentrated hydrochloric acid as an eluent [12].

The raw and modified diatomite was effective for all pollutants, particularly, for inorganic pollutants, such as Fe: 34–68%, Cu about 65%, Pb: 55–80% [13]. In [14], the authors stated that diatomite modified with aluminium hydroxide was found as an efficient adsorbent for defluoridation of liquid and groundwater. The maximal purification of water from fluoride and adsorption capacity was 89% and 1.67 mg/g, respectively.

Natural diatomite which contains kaolinite, montmorillonite even after thermal and mechanical treatment does not possess a sufficient adsorption activity. Activation of diatomite with sulphuric acid is carried out mainly under boiling or impregnation conditions at room temperature.

The study [15] reports about yeast cells immobilization onto diatomite surface, pre-treated with polyethylenimine with the aim to increase the degree of Pb²⁺ removal from solutions. The diatomite/yeast composite biomaterial was shown to adsorb 97.8% of Cu²⁺ ions and 99.4% of Pb²⁺ ions [15].

Analysis of the scientific-technical data on the existing methods of activation of natural adsorbents confirmed the fact that the most effective among them is activation with sulphuric acid. In this work, we studied pre-treatment of natural diatomite with HCl followed by a thermal treatment to obtain diatomite-based sorbents. The obtained materials are characterized by a high ability to sorption lead ions.

In this study, the removal of Pb²⁺ ions from aqueous solutions by modified diatomite earth has been investigated. The results indicate that the maximum Pb²⁺ ions removal degree is achieved by acid modification of diatomite with 0.5 M HCl.

The object of research is a natural mineral treated by acid at different calcination conditions, namely HCl concentration (0.5, 1M) and calcination temperatures (from 600 to 900 °C) were studied.

2. Materials and methods

2.1. Raw material

Diatomite from Aktobe field of Republic of Kazakhstan was used as an initial material (Fig. 1).



Fig. 1. Map of Kazakhstan.

2.2. Acid treatment technique

25 g of powdered diatomite was suspended in 75 mL of HCl solutions at different concentrations (0.5, 1, 1.5 M) at 150 °C and heated upon mechanical stirring (200 rpm) for 60 min to remove exchangeable ions (mainly iron, titanium, aluminium). After recovered by filtration, the acid-treated diatomite was rinsed several times with water to remove free HCl traces, after that it was dried (100 °C) and ground in a mortar. The size of the particles after grinding was 707 μm. Finally, the samples were placed in a muffle furnace and calcined. Calcination of diatomite-derived materials is conducted at atmospheric pressure for 3 h at dif-

ferent final calcination temperatures (from 500 to 900 °C; the heating rate of 10 °C/min) in order to remove organic impurities. The temperature and time of calcinations were selected with the aim to activate diatomite adsorbent.

Figure 2 presents a scheme of the procedure sequence for obtaining diatomite-based sorbents.

To state the effect of different operative conditions (i.e. the HCl concentration and final calcination temperature) on the sorbent features, the physical-chemical characteristics of the activated diatomite were determined.

2.3. Morphological parameters

The morphology of the obtained modified samples has been investigated on a Quanta 3D 200i scanning electron microscope (FEI, Holland) with the ability to vary the accelerating voltage from 0.2 to 30 kV.

The phase's compositions of the materials were characterized by X-ray powder diffraction technique (DRON-4 diffractometer in digital form using copper radiation). The sampling modes are as follows: the X-ray tube voltage is 35 Kv, the tube current is 20 mA, the step of the goniometer is $0.05^{\circ}2\theta$, and the intensity measurement time at a point is 1.5 sec. During shooting, the sample was rotated in its own plane at a speed of 60 rpm.

Preliminary processing of X-ray diffraction patterns to determine the angular position and intensities of reflections was carried out using the Fpeak program. The phase analysis was performed using the Search-Match and PCPDFWIN programs with the diffractometric database.

Pb²⁺ testing procedure was conducted by Perkin Elmer Analyst 400 atomic absorption spectrometer (USA), with a spectral range of 190–870 nm, and power consumption of no more than 300W.

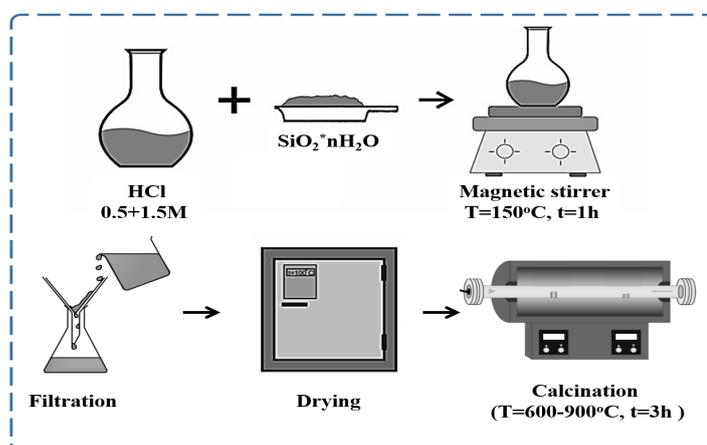


Fig. 2. A scheme of the procedure sequence for obtaining diatomite-based sorbents.

3. Results and discussion

Figure 3 presents SEM images of natural and acid-treated diatomite.

Figure 4 presents SEM images of diatomite modified with 0.5M HCl after calcination at different temperatures.

Similar morphologies were obtained by using 1.0 M HCl at the temperatures of 600, 700, 800, 900 °C (Fig. 5).

In SEM images it can be seen that the modified sorbent has a different structure compared to the initial natural diatomite (Fig. 3a).

To increase the specific surface and improvement of surface characteristics requires significant modification of the diatomite. Acid activation by adsorbents promotes the dissolution of a significant portion of oxides (CaO, MgO, Na₂O, FeO, Fe₂O₃, Al₂O₃ and etc.), an increase in pore size, and a change in the chemical nature of the surface.

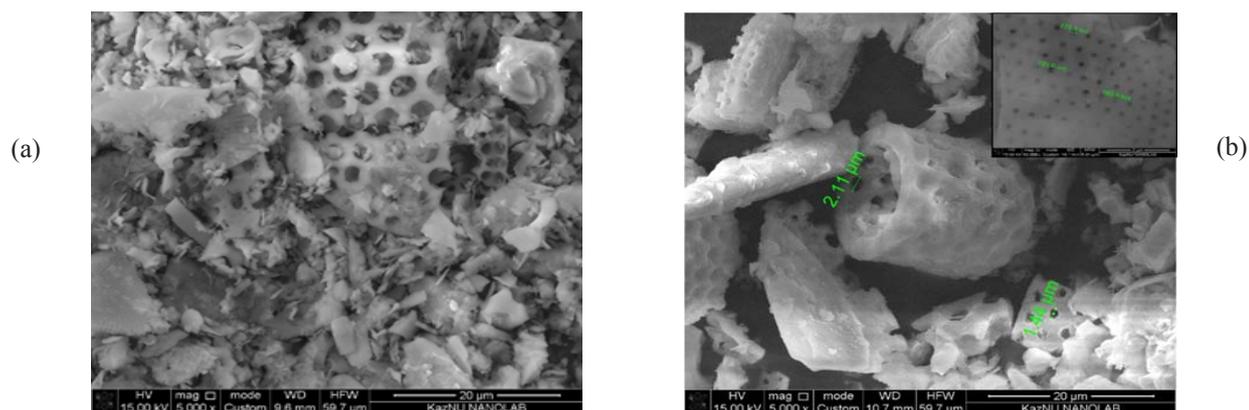


Fig. 3. SEM images of initial natural and treated diatomite (without calcination): (a) – initial natural diatomite; (b) – acid-treated diatomite (0.5 M HCl).

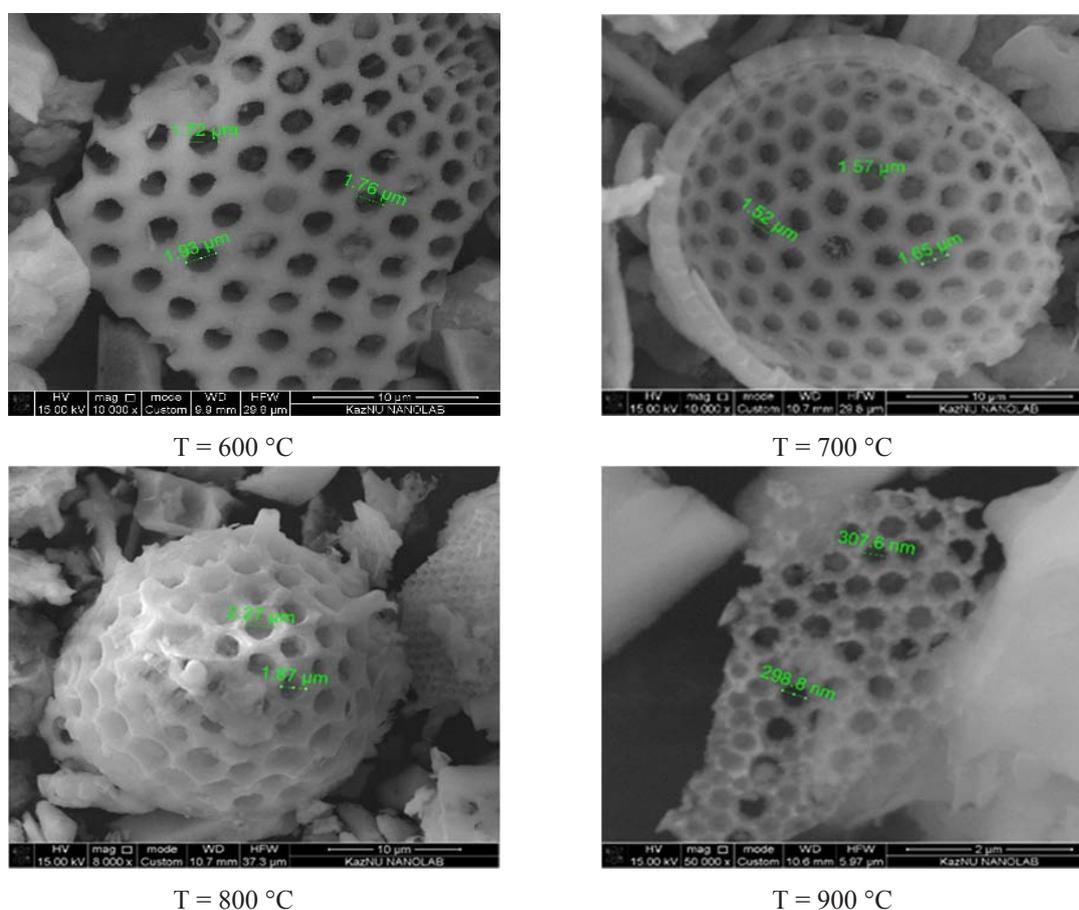


Fig. 4. SEM images of acid-treated diatomite (0.5 M HCl) and calcined at different final temperatures (600, 700, 800, 900 °C).

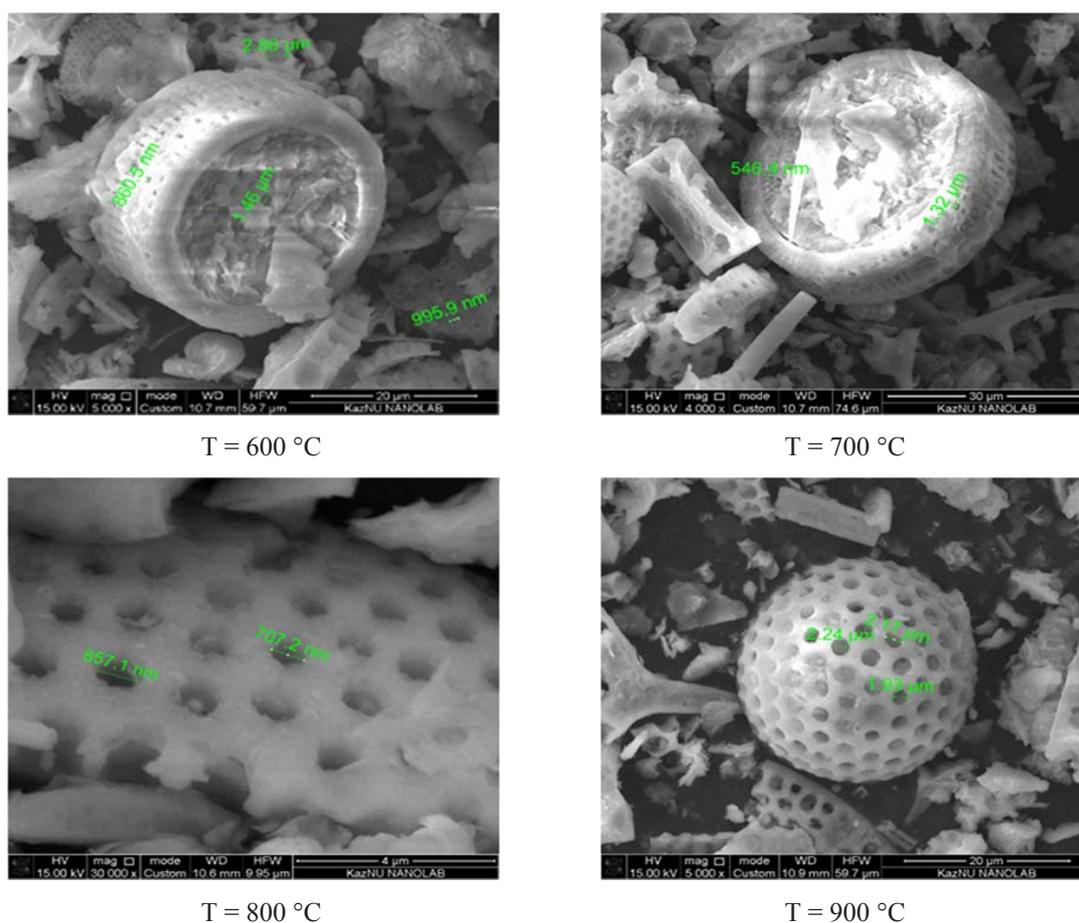


Fig. 5. SEM images of acid-treated diatomite (1 M HCl) and calcined at different temperatures (600, 700, 800, 900 °C).

The morphology of natural materials showed the dominant granulated species. The SEM micrographs of modified samples showed the original geometry of the pores to be preserved, but there is some sort of collapse in the skeleton structures.

All samples exhibited the presence of high pore after modification. The pore size of 0.5 M HCl treated diatomite has an average of 298 nm up to 2.27 μm , while 1.0 M HCl treated diatomite has an average of 546 nm up to 2.86 μm . The pore size of the natural diatomite was noticeably smaller than that of the modified diatomite (see Figs. 3–5). The BET principle was applied using a Sorbtometer M (Closed joint-stock company «Katakon», Russia) and ASAP 2400 V3.07 setups (Micromeritics Instrument Corporation, USA) devices for nitrogen adsorption/desorption measurements to establish the specific surface area.

BET analysis of treated and is reported in Table. Acid modification greatly altered surface properties by increasing surface area and porosity with a large number of reactive sites, resulting in the improved adsorption capacity.

From the trends reported in Table, it can be clearly observed that a porous structure with wider

macropores is obtained by increasing the calcination temperature (800 °C). This effect is more enhanced when a more concentrated HCl (1 M) is used.

To investigate structural features of diatomite samples before and after modification with HCl without calcination, samples were investigated by X-ray diffraction analysis. Figure 6 shows the result of X-ray diffraction analysis of selected diatomite samples.

In Fig. 6 it can be seen that the initial natural diatomite contains quartz (a polymorphic modification of silicon dioxide). On the X-ray pattern of the original diatomite, the most characteristic line of quartz with a distance of 3.35 Å is visible, and there are several lines, which characterize amorphous SiO_2 with interplanar distances of 2.49 and 4.26 Å, and lines with interplanar distances of 3.03; 3.28 and 3.39 Å, which indicate the presence of calcite in the sample.

The components of diatomite are also present: Illite-montmorillonite, $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ (kaolinite) are present in small quantities. SiO_2 (quartz) is present in a somewhat larger amount; in addition, a substantial amount of X-ray amorphous phase is present.

Table
BET analysis of acid modified samples

#	Name	T, °C	Specific pore volume, cm ³ /g	Specific surface area, BET, m ² /g
1	Modified sorbents based on diatomite – Sorbent 2 (S2) (0.5 M HCl, t = 3 h)	600	0.001	2.42
2	Modified sorbents based on diatomite – Sorbent 3 (S3) (0.5 M HCl, t = 3 h)	700	0.005	12.38
3	Modified sorbents based on diatomite – Sorbent 4 (S4) (0.5 M HCl, t = 3 h)	800	0.008	19.26
4	Modified sorbents based on diatomite – Sorbent 5 (S5) (0.5 M HCl, t = 3 h)	900	0.001	0.72
5	Modified sorbents based on diatomite – Sorbent 2 (S2) (1 M HCl, t = 3 h)	600	0.002	4.61
6	Modified sorbents based on diatomite – Sorbent 3 (S3) (1 M HCl, t = 3 h)	700	0.008	18.14
7	Modified sorbents based on diatomite – Sorbent 4 (S4) (1 M HCl, t = 3 h)	800	0.011	25.57
8	Modified sorbents based on diatomite – Sorbent 5 (S5) (1 M HCl, t = 3 h)	900	0.001	1.82

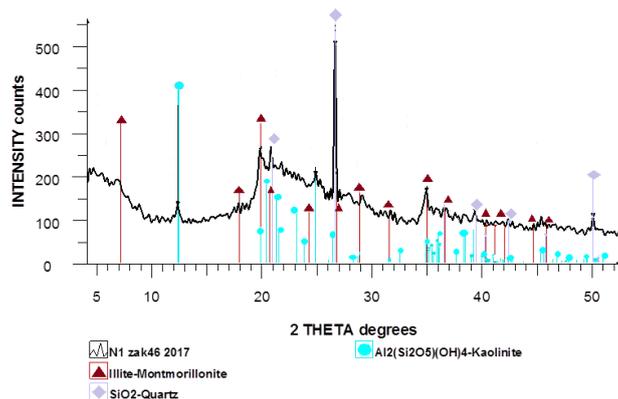


Fig. 6. X-ray diffraction pattern of natural diatomite. Triangle – Illite-montmorillonite, circle – $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ (kaolinite) and rhombus – quartz.

Figure 7 presents the X-ray pattern of diatomite samples treated with 0.5 M HCl without calcination.

Overall, the HCl-treated diatomite is qualitatively similar to initial natural diatomite indicating that the crystalline lattice is not destroyed.

$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ – kaolinite and MgFeSiO_4 are present in small amounts. A very low intensity line of 4.9676 Å appeared, it was not possible to identify it, since it may belong to the following compounds: $\text{Na}_6\text{Al}_2\text{S}_6$, AlSiCl_4 , $(\text{SiCl}_3)(\text{AlCl}_4)$, $\text{Ca}(\text{Al}_2\text{S}_4)\text{O}_{12}(\text{C}_{13})$. CaCl_2 is also present in a very small amount (diffraction peak of 3.0528 Å).

The adsorption capacity (A) and the degree of extraction (α) of the sorbent concerning Pb ions are

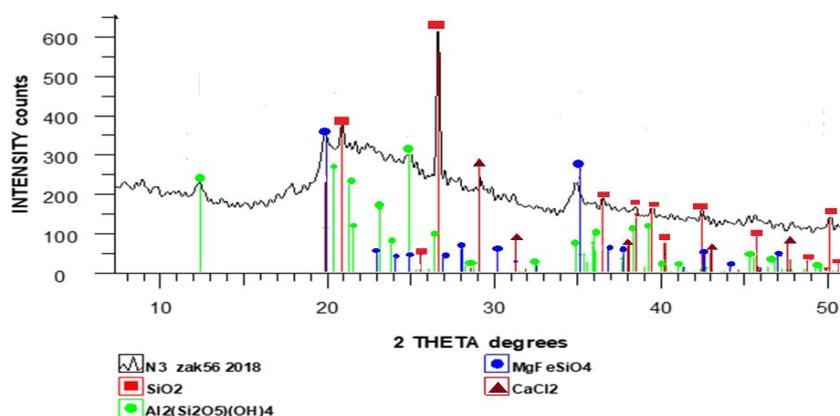


Fig. 7. X-ray diffraction pattern of HCl-treated diatomite (0.5 M HCl, t = 3 h). Triangle – CaCl_2 , green circle – $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ (kaolinite), blue circle – MgFeSiO_4 and square – SiO_2 quartz.

determined by the formula reported in [16].

$$A = (C_0 - C) V_{\text{sol}}/m_{\text{sorb}} \quad (1)$$

$$\alpha (\%) = (C_0 - C) \cdot 100/C_0 \quad (2)$$

where, C_0 , C – respectively, the initial and equilibrium concentration of metal ions, mg/l; V_{sol} – volume of the solution, l; m_{sorb} – mass of the sorbent, g; A – adsorption capacity, mg/g; α – degree of extraction, %.

Figures 8 and 9 show adsorption capacity of Pb ions (100 mg/L) from aqueous solutions by modified diatomite at different contact times (5, 30 and 120 min). All these tests were performed at controlled pH = 7 (neutral).

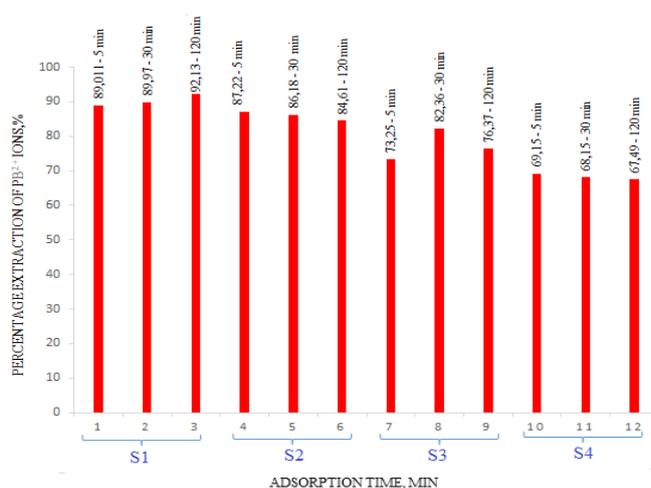


Fig. 8. The efficiency of Pb²⁺ ion extraction from 0.5 M HCl solution depending on the adsorption time: S1 – 600 °C; S2 – 700 °C; S3 – 800 °C; S4 – 900 °C.

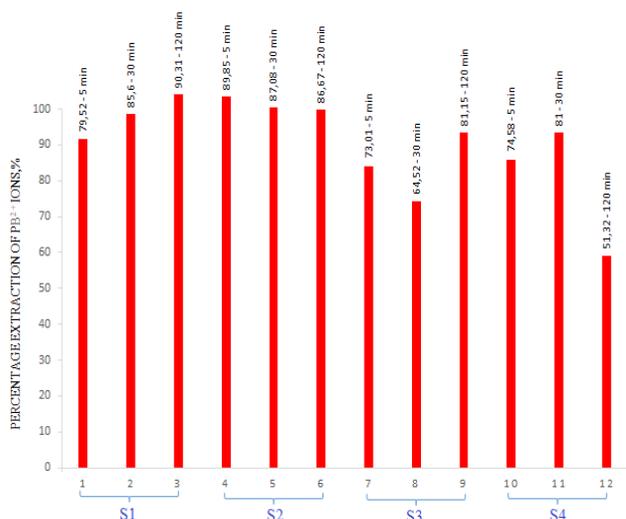


Fig. 9. The efficiency of Pb²⁺ ion extraction from 1.0 M HCl solution depending on the adsorption time: S1 – 600 °C; S2 – 700 °C; S3 – 800 °C; S4 – 900 °C.

The results indicate that the maximum Pb ions removal degree is achieved by acid modification of diatomite with 0.5 M HCl: 89.011%; 89.97%; 92.13% with mixing time of 5, 30, and 120 min, respectively. Considering heat treatment, higher calcination temperatures above 700 °C were found to be unsuitable as they could damage the surface of diatomite and cause a change in its unique properties.

As a result, it was established that diatomite treated with 0.5 and 1.0 M at 600 °C with mixing time 120 min shows better adsorption compared to 700, 800 and 900 °C due to the elimination of the organic impurities from the surface of diatomite.

4. Conclusion

Natural diatomite was activated using acid pre-treatment (HCl) and calcination. Different acid concentration (0.5, 1 M) and calcination temperature (600–900 °C) were studied. Modified diatomite were studied for water remediation from lead ions (Pb²⁺). It is found that the higher performance for removal of Pb²⁺ ions is achieved for the treated diatomite with 0.5, 1 M by 600 °C (92.13% and 90.31 % by mixing time of 120 min) in spite of its lower pore size, indicating that for this specific ion any significant improvement can be obtained upon the reported acid pre-treatment (with HCl)/thermal treatment.

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