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Effect of Acid Modification on Porous Structure and Adsorption Properties of Different Type Ukrainian Clays for Water Purification Technologies

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ABSTRACT

Clay minerals, as adsorbents, are widely available, have large specific surface area, and the ability for cation exchange, which makes them applicable in wastewater treatment from heavy metal ions. This study investigated the effect of acid modification on the porous structure and adsorption properties of montmorillonite (MMT) and palygorskite (PAL) clays of the Cherkasy deposit (Ukraine). Acid modification of clay samples was carried out with chloride acid after preliminary refining. Clay particles were analyzed using optical polarization microscopy with recording of digital images of the study. The area and perimeter of individual particles of clay samples were determined. The equivalent diameter and shape factor were calculated. The porosity characteristics of the samples were determined. Pore surface area was calculated by the Brunauer-Emmette-Teller (BET) method. Total volume, mean diameters, and pore size distribution were obtained using the Density Functional Theory (BFT) method. Acid modification improved the porous structure of clay samples. BET surface area of the pores of the initial sample of palygorskite clay is significantly higher compared to the montmorillonite type clay (140.66 and 83.61 m^2/g, respectively). Acid modification of the PAL sample contributes to an increase in the BET surface area by approximately 1.7 times. Acid modification increases the surface area and total pore volume by approximately 2.3 times for MMT samples and 1.76 times for PAL samples. Dimensional characteristics of the pores of the MMT sample were to shift after activation, while for the PAL sample, their average size increases sharply by approximately 3.2 times. This suggested the additional formation of pores in the interfibrillar regions of the PAL sample during its acid activation. The effect of acid modification on the sorption capacity was investigated by means of methylene blue exhaustion. Sorption efficiency increases by 6-14%, compared to unmodified samples and is determined by the contact time and the type of clay. Increasing the contact time from 24 to 72 hours leads to an increase in the sorption efficiency of activated MMT and PAL samples by 36 and 30%, respectively. Acid-activated clay minerals, in particular montmorillonite, can be used as part of sorption elements to increase the efficiency of wastewater treatment technologies from heavy metal ions.

Keywords: montmorillonite, palygorskite, acid modification, acid-activated clays, sorption capacity, water purification technologies, Brunauer-Emmette-Teller method, Density Functional Theory method.

INTRODUCTION

Clay minerals are one of the most common, environmentally tolerant, highly dispersed natural materials that are widely used in various industries [Bergaya and Lagaly, 2013]. They are effectively used as fillers in polymer compositions to improve their mechanical characteristics [Arbelaiz et al., 2021], increase resistance to elevated temperatures [Lima et al., 2021], and adjust the composition structure in situ [Budash et al., 2022]. Due to the specific layered structure, large surface area of particles, porosity, presence of active centers, high cation exchange capacity, clays are also actively used in water purification technologies as adsorbents for the removal of dangerous chemical products of organic and inorganic origin [Uddin, 2017; Kausar et al., 2018]. To improve the adsorption capacity, clays are usually modified (activated) by using various methods, depending on the specifics of a certain pollutant [Barakan and Aghazadeh, 2021].

The main methods for modifying clay minerals include mechanical, chemical (acidic, alkaline, salt), modification with organic compounds and thermal modification [Sarkar et al., 2019].

Organic modification of natural clays with surface-active substances allows reducing their hydrophilicity. Active surfaces of clay particles can be made hydrophobic by intercalation of organic cations into the interlayer space of clay minerals [Martín et al., 2018]. Replacing exchangeable inorganic cations in clay with organic cations (for example, cationic surfactants) increases the distance between layers and significantly improves the sorption of various organic pollutants [Ashiq et al., 2019; Zaghouane-Boudiaf et al., 2014; Anirudhan and Ramachandran, 2015].

Thermal modification is a complex process of structural transformations in clay minerals at certain temperatures, which significantly depends on the type and origin of clays, as well as on the processing conditions [Heller-Kallai, 2013]. Masindi et al. reported that South African bentonite heat-treated at 500 °C is an effective sorbent for removing chromium ions from aqueous solutions [Masindi and Ramakokovhu, 2021]. The heat treatment of Ethiopian bentonite in the temperature range of 300-500 °C [Tadesse, 2022] led to an increase in the surface area of the adsorbent from 147 to 310 m^2/g, which allowed its effective use for zinc removal from wastewater.

Acid modification of clay minerals consists in their treatment by inorganic acids (chloric, sulfate, nitrate, etc.) solutions [España et al., 2019]. This process reduces or removes most of the derived metals (calcium, magnesium) from the clay mineral, reduces the content of iron and aluminum, increases the specific surface area, porosity, and adsorption capacity of clay particles [Barakan and Aghazadeh, 2021; Sarkar et al., 2019; Komadel and Madejová, 2006]. The use of acid treatment (sulfuric acid, 60 °C) of the clays from South-Western Tunisia led to an increase in the surface area from 450 to 590 m^2/g [Chaari et al., 2021]. At the same time, the modified clay demonstrated 88% higher efficiency than the untreated clay in removing cubic dye from textile wastewater [Chaari et al., 2021].

Acid modification of clay minerals leads to significant structural changes [Amari et al., 2018]. At the same time, the surface area and the total volume of clay pores increased proportionally to the intensity of acid treatment. Zhu et al. demonstrated that acid treatment with HCl in a wide range of concentrations is a possible and effective method of optimizing the structure and surface of palygorskite (magnesium aluminum phyllosilicate) [Zhu et al., 2018]. That significantly increases the surface area (from 228 to 329 m^2/g) and porosity of palygorskite, which allows it to become a promising material for use as an adsorbent of volatile organic compounds [Zhu et al., 2018]. Acid-treated montmorillonite was used as a cheap adsorbent for the removal of several heavy metal ions from industrial wastewater [Akpomie and Dawodu, 2016]. Acid modification increased the surface area and total pore volume of montmorillonite from 55.76 to 96.48 m^2/g and from 0.069 to 0.101 cm^3/g, respectively. The intensity of removal of heavy metal ions was directly related to their concentration and occurred in the following order: Zn > Cu > Mn > Cd > Pb > Ni [Akpomie and Dawodu, 2016].

The effectiveness of acid treatment of clay minerals can be greatly increased by combining it with organic [Zaghouane-Boudiaf et al., 2014] or thermal [Akpomie and Dawodu, 2016; Toor and Jin, 2012] modification, as well as by combining clays with natural polymers [Pawar et al., 2020; Nguyen et al., 2020].

One of the problems with the commercial use of clay minerals is the wide variability and certain "authenticity" of their composition even for clays of the same type, which is determined by the specifics of the geographical location of the deposit. Therefore, it is necessary to study the properties of clay minerals of a specific deposit.

Ukraine has enough explored reserves of various clay minerals. The Cherkasy deposit is one of the largest studied and industrially exploited deposits of bentonite and palygorskite clays in Europe [Kadoshnikov et al., 2013; PJSC "Dashukivsky Bentonites"]. However, the processes of activation of such clays, their influence on porosity and adsorption properties have been paid insufficient attention until now.

The purpose of the work was to determine the effect of the acid modification process on the indicators of the porous structure and the sorption capacity of the montmorillonite and palygorskite types of clays of the Cherkasy deposit for application in water purification technologies.

MATERIALS AND METHODS

Clay powders of montmorillonite (MMT) and palygorskite (PAL) type produced by PJSC "Dashukivsky Bentonites" [PJSC "Dashukivsky Bentonites"] were used, the main characteristics of which are listed in Table 1.

Morphometric analysis of clay particles

The method of optical polarization microscopy (Amplival microscope, Carl Zeiss Jena, Germany) was used to analyze the sizes of clay particles with the recording of digital images of the research objects. The morphometric indicators of the particles were determined by using the method of image analysis via "ImageJ" [Pérez and Pascau, 2013]. The area (S_p) and perimeter (P_p) of individual particles of the samples were determined. The equivalent diameter (D_e) and shape factor (SF) of the particles were calculated using formulas 1 and 2:

$$D_e = \sqrt{\frac{4S_p}{\pi}} \quad (1)$$

$$SF = \frac{4\pi S_p}{P_p^2} \quad (2)$$

Refinement of clay minerals

The purified fraction of clay minerals was obtained by pre-sieving the original powdered sample through sieve No. 0071 to remove coarse impurities. Then, the clay was washed with distilled water in the ratio of solid and liquid phases of 1:100 with thorough mixing using a mechanical stirrer. After settling the resulting suspension for 24 hours, the highly dispersed fraction was decanted with a siphon into another container. The sample, cleaned of impurities, was centrifuged for 30 minutes and dried in ceramic cups at 80 °C in a drying oven to a constant mass. The obtained samples were ground in a porcelain mortar and sifted through a sieve No. 0071.

Acid modification of clay minerals

For acid modification of purified clay minerals, a 30% HCl solution was used with a ratio of solid to liquid phases of 1:1.5, on a water bath at a temperature of 95-100 °C during 1 hour with constant stirring. After that, the samples were repeatedly washed with distilled water until there was a negative reaction to Cl^- ions in the washing water (using $AgNO_3$ solution). The obtained samples were dried at 80 °C in a drying oven to a constant mass, ground in a porcelain mortar and sieved through sieve No. 0071.

Determination of clays porous structure indicators

Porosity characteristics were determined on a Quantachrome Nova 2200e porosimeter (Boynton Beach, FL). Before measurement, the samples were degassed at 150 °C in a vacuum for 3 hours. The adsorption/desorption isotherms were recorded at 0 °C using nitrogen as adsorbate. The pore surface area was calculated by the Brunauer-Emmette-Teller (BET) method [Brunauer et al., 1938] according to the adsorption branch of the isotherms, in the range of the adsorbate relative pressure P/P_0 = 0.2-0.4.

The method was developed for direct measurement of the surface area and pore sizes of powdered samples under high vacuum conditions. In a typical BET assay, the surface area is determined by the volume of N_2 adsorbed by the sample particles. It is assumed that the gas has access to the entire surface of the material. The measurement of the surface area is based on the adsorption of gas molecules in infinite layers without considering the interaction between the layers [Jamie, 2015]. The BET model assumes multilayer gas adsorption on the adsorbent surface [Jaroniec et al., 1998].

Table 1. Main characteristics of samples of montmorillonite (MMT) and palygorskite (PAL) type clays

Denotement	Industrial brand	Mass fraction of moisture, %	The balance on the sieve № 0071, %
MMT	C4T2K	8.7	2.1
PAL	PP-4	18.0	2.0

The total volume, average diameters, and pore size distribution were obtained using the Density Functional Theory (DFT) method [Ravikovitch et al., 1998]. The method is based on the description of the process of filling micro- and narrow mesopores at the molecular level. Owing to this, a more accurate approach to pore size analysis is provided in comparison with classical macroscopic theories and semi-empirical methods [Ravikovitch et al., 1998]. NovaWin v.11.04 software was used for calculations.

Determination of sorption properties of clays

The sorption properties of clay minerals were evaluated with a methylene blue (MB) aqueous solution. The adsorption process was performed under static conditions.

The sorption properties of modified clay minerals were studied according to the following scheme: first, the initial solution of MB with a concentration of 50 mg/l was prepared. Then, 0.1 g of clay was added to a beaker containing 50 ml of the initial MB solution and mixed. After 24 hours of exposure at a temperature of 20 °C, the first sample was taken, further samples were taken after 48 and 72 hours.

The concentration of the MB dye was measured using a photocolorimeter. The optical density of the prepared comparison solution was measured using a light filter with a wavelength of 670 nm in cuvettes with a light-absorbing layer thickness of 10 mm. Distilled water was used as a reference solution. The sorption efficiency (E_a) of modified and unmodified clays was evaluated by the degree of absorption of the MB, which was calculated according to formula 3:

$$E_a = \left(\frac{C_0 - C_e}{C_0}\right) \times 100\% \quad (3)$$

where: C_0 – initial concentration of the studied substance;
C_e – final concentration of the studied substance after a certain period of time.

Statistical processing of experimental data was performed with the help of software packages Statistica and Microsoft Excel.

RESULTS AND DISCUSSION

Dimensional characteristics of the clay particle types

The initial size and shape of particles and the nature of distribution according to these indicators are main physical characteristics of clay minerals [Bennett and Hulbert, 2012]. They determine both the technological features of their applications and the size of the active specific surface in the adsorption process.

Figure 1 illustrates micrographs of the clay particles of the MMT and PAL samples in polarized light with crossed polaroids. In both cases, the particles of the samples are characterized by an evident optical anisotropy and a wide distribution of their shape and size parameters.

Figure 2 demonstrates the results of quantitative analysis of the particles distribution for MMT and PAL samples by equivalent diameter (D_e).

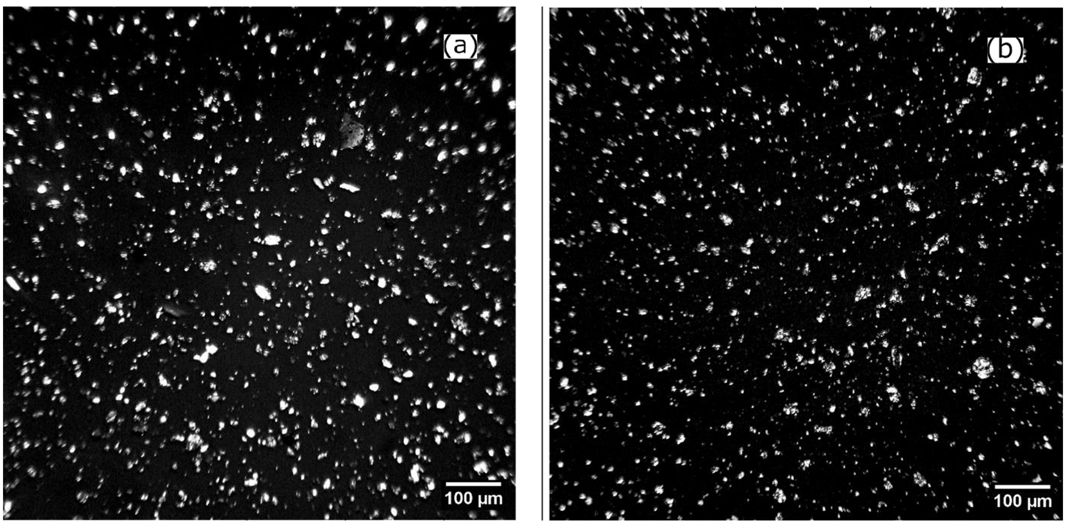

Figure 1. Micrographs in polarized light of clay particles of MMT (a) and PAL (b) samples

In both cases, there is a qualitatively similar, asymmetric distribution of particles by D_e, which is well approximated by a lognormal curve with a long right "shoulder". A similar type of distribution is typical for particles of other minerals in the process of their mechanical grinding [Basim and Khalili, 2015].

Histograms of the distribution of clay particles in MMT and PAL samples according to the shape factor (SF) are presented in Figure 3. This characteristic is directly related to the effective surface area of particles and their aggregates, and therefore determines their adsorption properties.

For both analyzed samples, a similar asymmetric nature of the distribution was observed, which is shifted towards higher SF values. To approximate the experimental values, the beta distribution can be used, the domain of which coincides with the range of SF values (0–1).

The largest number of particles belongs to the SF interval 0.7–0.8, which indicates a rounded shape of most of them. The number of particles with pronounced anisometricity (SF < 0.7) is significantly higher for the PAL sample. This may be related to the difference in the structural structure of montmorillonite and palygorskite, namely their layered and fibrillar structural organization at the individual nanoparticles level [Bennett and Hulbert, 2012].

Table 2 list the generalized results of the statistical analysis of the particles distribution by equivalent diameter and shape factor for MMT and PAL samples.

As shown in Table 2, the PAL clay is characterized by higher of the arithmetic mean (~7%) and median values of the equivalent diameter (D_e) of the particles, as well as the coefficient of variation of the distribution, in comparison with the MMT sample. At the same time, the average

Table 2. General statistical indicators of the distribution of MMT and PAL clay particles by equivalent diameter and shape factor

Index	Mean	Stand. Error	Conf. -95%	Conf. +95%	Median	Coef. var., %	Skewness	Kurtosis
Eq. diameter (MMT), μm	5.23	0.14	4.96	5.51	3.93	81.6	2.22	7.74
Eq. diameter (PAL), μm	5.64	0.15	5.35	5.94	4.05	87.5	2.22	7.67
Shape factor (MMT)	0.73	0.01	0.72	0.74	0.75	22.6	-0.62	-0.10
Shape factor (PAL)	0.66	0.01	0.65	0.67	0.67	28.2	-0.25	-0.61

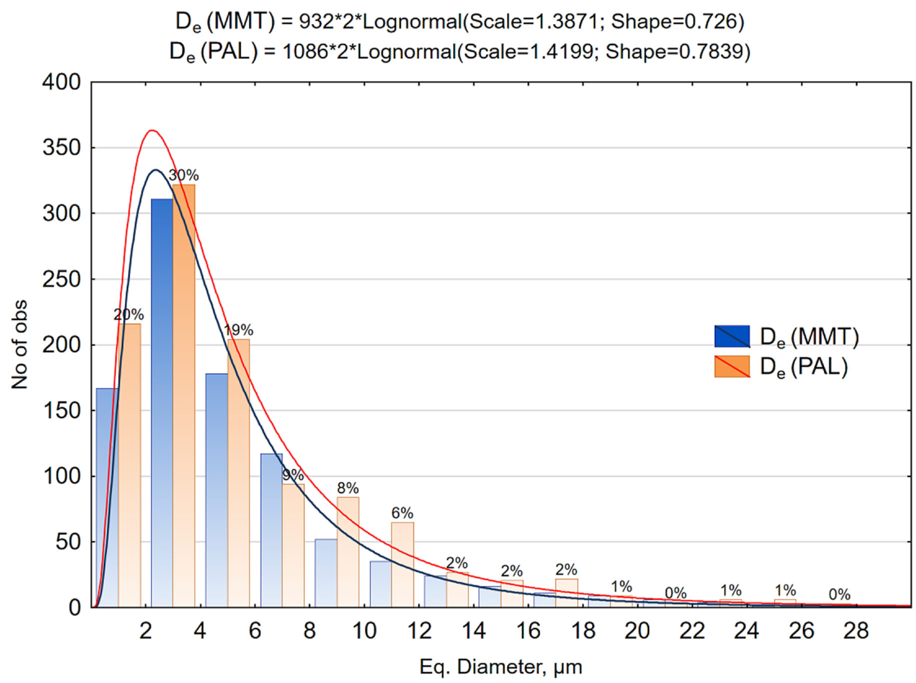

Figure 2. Distribution of MMT and PAL clay particles by equivalent diameter

values of the shape factor (SF) of the particles in the PAL sample are noticeably smaller (~10%) than those observed for the MMT clay.

Thus, with a qualitatively similar nature of the distribution, the investigated clay samples differ in terms of the quantitative indicators of the particles size and shape.

The effect of acid modification on the porous structure of MMT and PAL clays

Figure 4a shows nitrogen adsorption/desorption isotherms for the original and acid activated MMT sample. In both cases, type IV isotherms are realized. This characterizes mesoporous materials with a hysteresis loop of the H3 type, which is associated with the occurrence of pore condensation [Evans et al., 1986]. The initial part of the IV type isotherm can be attributed to monolayer-multilayer adsorption. According to the empirical IUPAC classification [Sing et al., 1985], hysteresis of type H3 does not show any marginal adsorption at high values of P/P_0 and is observed for aggregates of layered particles with slit-like pores.

As a result of acid modification, there is a significant increase in the volume of adsorbed nitrogen in the entire investigated range of relative pressure values and an increase around the hysteresis loop. Correlation analysis of the initial part of the isotherms in coordinates $1/(1 - W((P0/P) - 1)) = f(P/P0)$ in the range of relative adsorbate pressure P/P0 = 0.2–0.4 (Figures 4 b, c) shows an almost linear form of the dependences (determination coefficients $R^2 = 0.997$ (MMT) and $R^2 = 0.999$ (MMT H^+)). This allowed using the standard multipoint procedure of the BET method to calculate the main characteristics of the samples (Table 3).

Acid modification increased the BET surface area of montmorillonite pores by ~2.6 times (from 83.61 to 216.43 m^2/g). Such increase in surface area demonstrates the effectiveness of

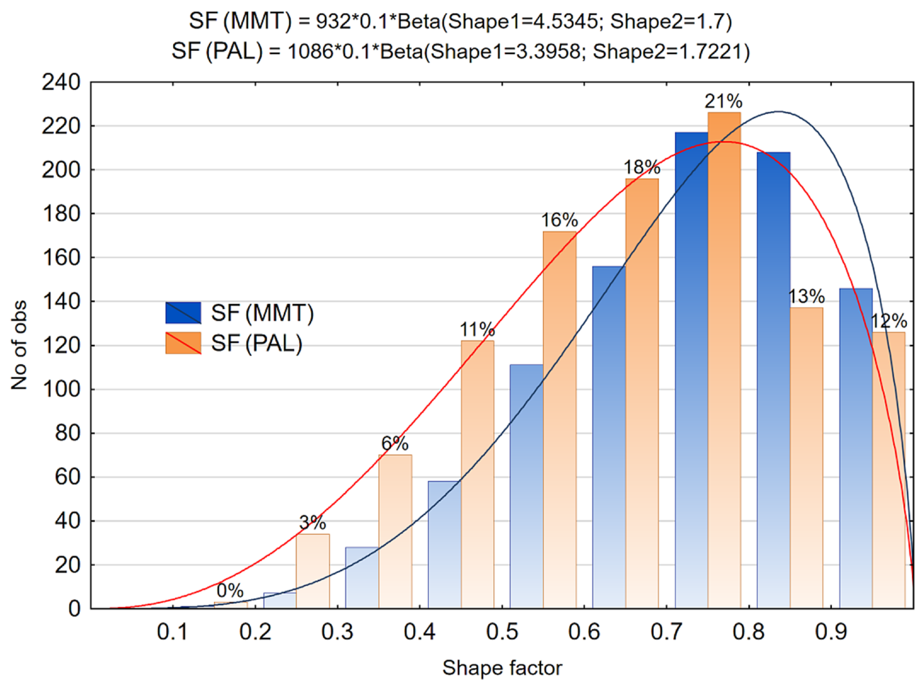

Figure 3. Distribution of MMT and PAL clay particles by shape factor

Table 3. Effect of acid activation on characteristics (BET method) of the clay adsorbent

Characteristic	Clay adsorbent			
	MMT	MMT H+	PAL	PAL H+
Slope	43.164	16.309	25.342	14.796
Intercept	-1.5150	-0.2180	-0.5830	-0.3530
C constant	-27.491	-73.812	-42.468	-40.915
Weight of a monolayer	0.0240	0.0621	0.0404	0.0692
BET surface area, m^2/g	83.61	216.43	140.66	241.13

this modification method for the MMT sample and is desirable for its further use as an adsorbent. Qualitatively similar results were obtained during acid modification of montmorillonites from other deposits [Chaari et al., 2021; Zhu et al., 2018; Akpomie and Dawodu, 2016].

The results of the adsorption/desorption study of the original and acid-activated PAL sample are shown in Figure 5a. As in the previous case, type IV isotherms with a hysteresis loop of type H3 are formed. Acid modification of the PAL sample leads to an increase in the volume of adsorbed nitrogen in the entire investigated range of relative pressure values. Correlation analysis of the initial part of the isotherms in coordinates $1/(1 - W((P_0/P) - 1)) = f(P/P_0)$ in the range of adsorbate relative pressure $P/P_0 = 0.2–0.4$ (Fig. 5b, Fig. 5c) demonstrates an almost linear form of the dependences.

The calculations in Table 3 show that the BET surface area of the pores of the initial sample of palygorskite clay is significantly higher compared to montmorillonite clay (140.66 and 83.61 m^2/g, respectively). The acid modification of the PAL sample contributes to an increase in the BET surface area by approximately 1.7 times (from 140.66 to 241.13 m^2/g). With larger absolute values of the BET area, the effectiveness of acid treatment of the palygorskite sample is lesser than in the case of montmorillonite. This can be explained both by the difference in their chemical composition and by the different structural organization of nanoparticles of montmorillonite (layered type) and palygorskite (fibrillar type).

In addition to surface area indicators, the analysis of adsorption/desorption processes using the DFT method allows one to effectively estimate the size distribution of pores and their volume [Chen et al., 2020; Fu et al., 2021]. The graph of the pores size distribution for the original MMT sample (Figure 6) shows one evident local maximum that belongs to the group of macropores with sizes of ~2 nm. The activation process increases and extends this maximum in both directions.

The initial PAL sample (Figure 7) is also characterized by a local maximum that corresponds to a group of macropores with sizes of ~2 nm,

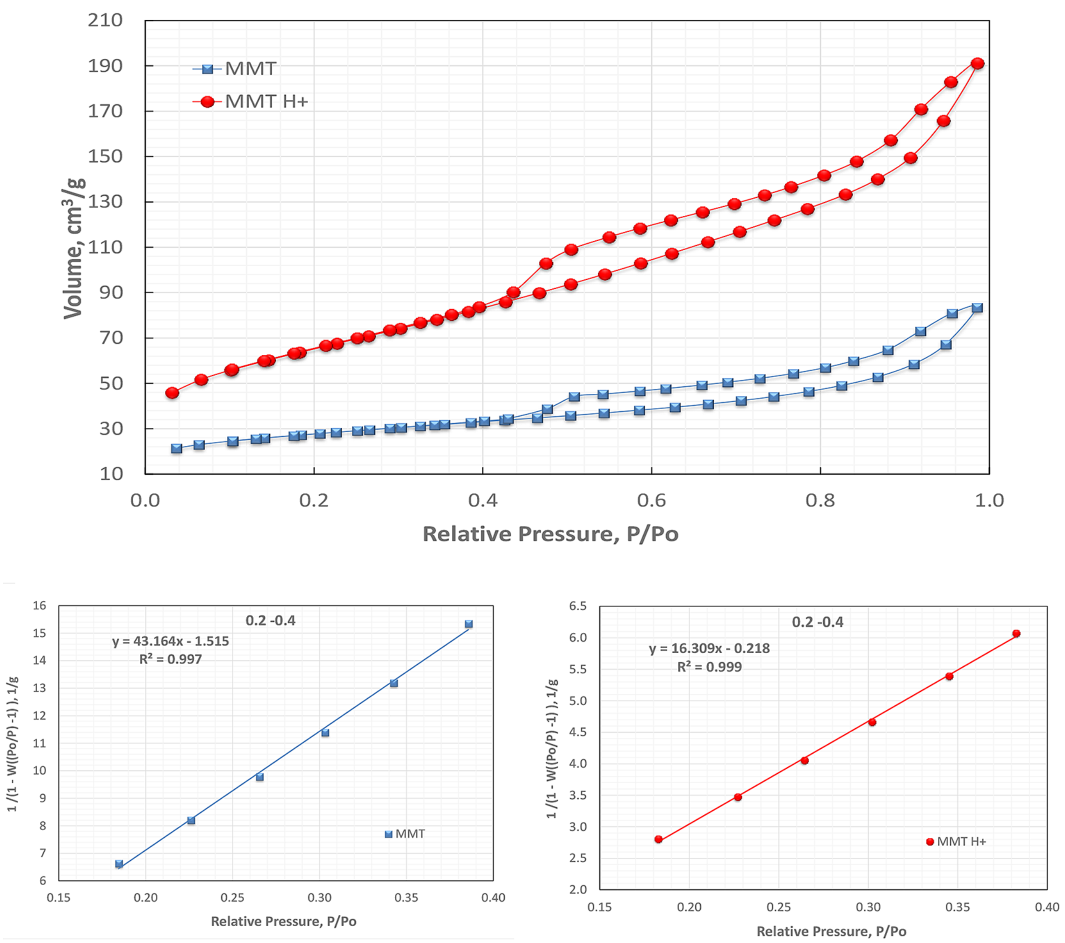

Figure 4. N_2 adsorption/desorption isotherms of pure and acid activated MMT (a) and linear fitting plots (b, c) of Multi-Point BET isotherm models

as well as less pronounced maxima in the region of larger values (~5.5 and 6.5 nm). The effect of acid modification on the nature of the pore size distribution is somewhat different from the previous case. There is a significant growth of the first maximum, its expansion and displacement to the

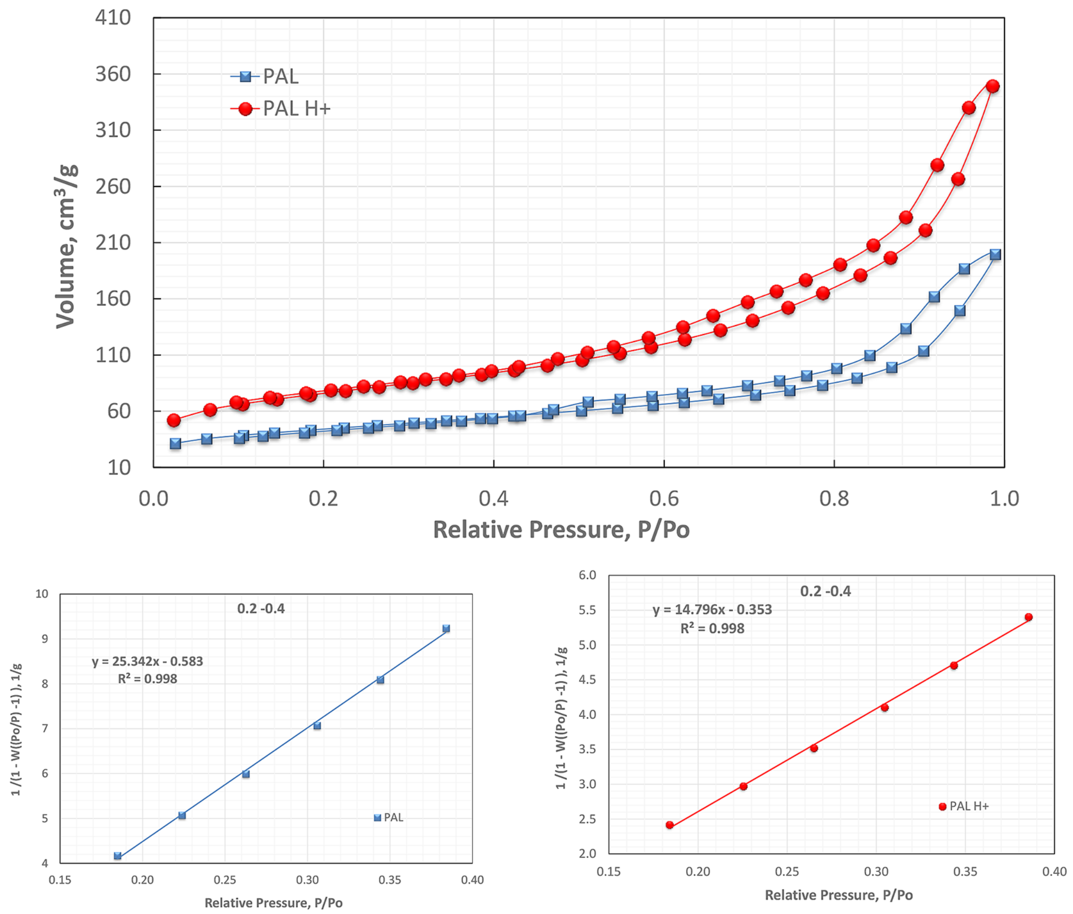

Figure 5. N_2, adsorption isotherms of pure and acid activated PAL (a) and linear fitting plots (c, d) of multi-point BET isotherm models

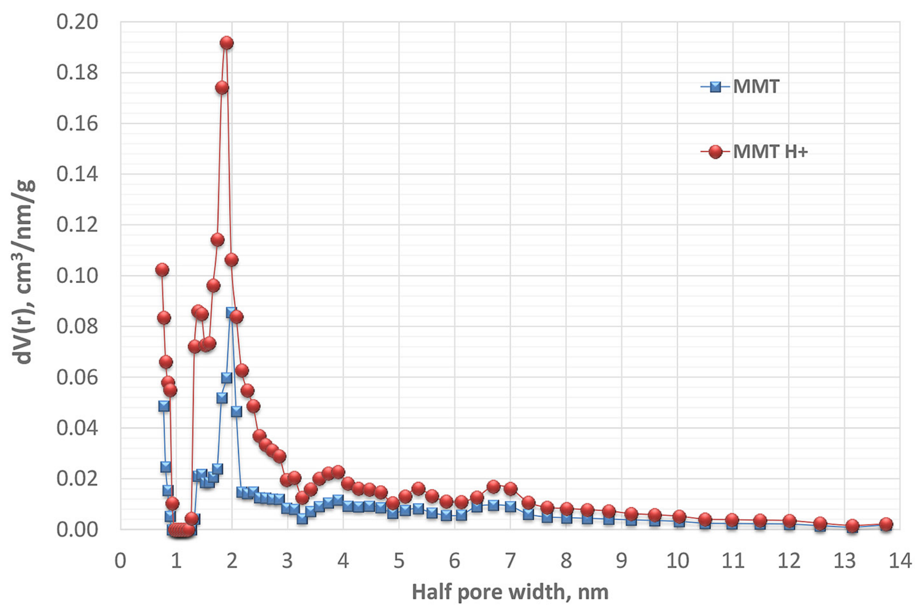

Figure 6. Pore size distributions in montmorillonite (DFT method) before (MMT) and after (MMT H^+) acid activation

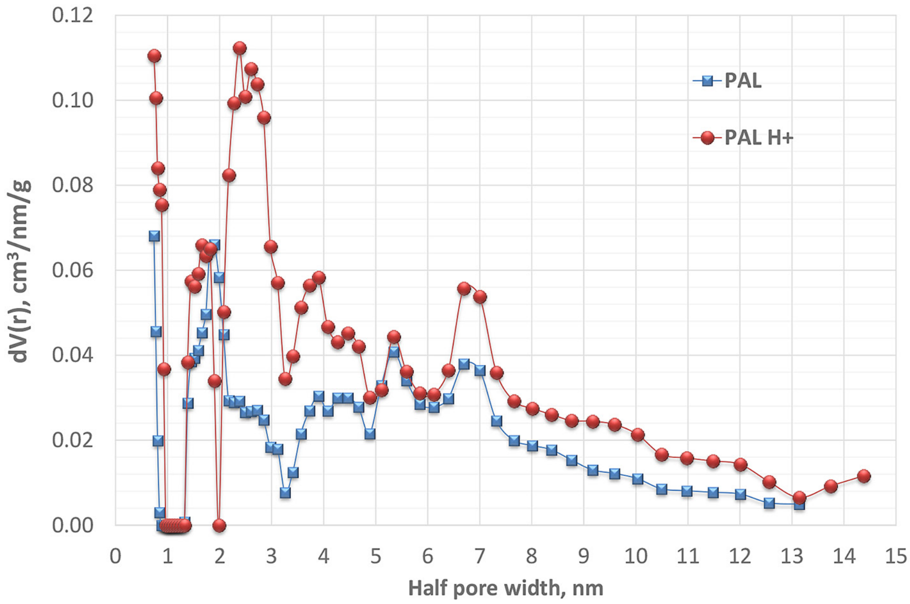

Figure 7. Pore size distributions in palygorskite (DFT method) before (PAL) and after (PAL H^+) acid activation

Table 4. Effect of acid activation on characteristics (DFT method) of the clay adsorbent

Characteristic	Clay adsorbent			
	MMT	MMT H^+	PAL	PAL H+
DFT surface area, m^2/g	77.148	176.320	119.413	210.199
Pore volume, cm^3/g	0.117	0.266	0.275	0.482
Half pore width (Mode), nm	1.984	1.897	0.737	2.376

region of 2–3 nm. The formation of a new, less pronounced maximum corresponding to a group of pores with sizes of ~3.5–4 nm is also observed. Such a difference may be related to the peculiarities of the structure of palygorskite and the possibility of additional pore formation in its interfibrillar region because of acid treatment.

Calculations of the characteristics of the investigated clay samples by the DFT method are presented in Table 4.

They show that acid modification increases the surface area and total pore volume for the studied samples by ~2.3 (MMT) and 1.76 (PAL) times. This is in good agreement with the results of determining the surface area of adsorbents by the BET method. It should be noted that because of activation, the dimensional characteristics of the pores of the MMT sample change slightly, while for the PAL sample there is a sharp increase in their average size (~ 3.2 times). As mentioned above, this may be due to the additional formation of pores in the interfibrillar regions of the PAL sample during its acid modification.

Thus, the research results demonstrate the effectiveness of acid modification in terms of improving the characteristics of the porous structure of the samples. Nevertheless, there is a certain difference in the changes of such characteristics for MMT and PAL samples, which can be due to both the difference in chemical composition and the peculiarities of their structural organization at the level of individual nanoparticles.

The effect of acid modification on the adsorption properties of MMT and PAL clays

The results of studying the effectiveness of adsorption of modified and unmodified clays of the montmorillonite and palygorskite type on the adsorption of methylene blue (MB) dye, depending on the duration of the interaction, are shown in Figure 8.

The sorption capacity of modified and unmodified clays, depending on the duration of the interaction and described by an almost linear dependence, both for montmorillonite and for palygorskite. Regardless of the contact time, both for the initial and modified samples, the efficiency of MB adsorption for MMT clays is significantly higher than for PAL clays.

The acid-activated clays have a higher sorption capacity to MB than the unmodified ones. After 24 hours of contact of the clays with MB, the degree of absorption is 32.5% for the MMT-activated sample and almost 28% for the PAL-activated sample, which is 8–14% higher than for the unmodified samples.

The adsorption properties of clay are determined by the contact time with the adsorbate and the amount of adsorbent. The results show that as the time of interaction between the adsorbent and the substance increases, the degree of MB absorption increases.

After 48 hours of contact of the clays with the MB solution, the degree of absorption is 52.4% for the MMT-activated sample and almost 40.3% for the PAL-activated sample, which is 8–9% higher than for the unmodified samples. Accordingly, after 72 hours of contact, the degree of absorption is 68.6% for the MMT-activated sample and almost 60% for the PAL-activated sample, which is 6–10% higher than for the unmodified clay samples. This may be explained by the improvement of the characteristics of the porous structure of the samples, which occurred because of acid activation.

Acid activation of clays significantly increases their sorption capacity due to an increase in the specific surface area of the sample, as well as due to the phenomenon of chemo adsorption on the cationic centers of clay minerals, as it was shown in [Anbia and Hariri, 2010]. The increase in the sorption capacity of samples during kinetic studies can be explained by the phenomenon of multilayer sorption of MB by particles of clay minerals. Similar results were observed by the authors [Anirudhan and Ramachandran, 2015] in the extraction of anionic dyes from aqueous solutions with modified bentonite clays.

CONCLUSIONS

This study investigated the effect of acid modification on the porous structure and adsorption properties of montmorillonite (MMT) and palygorskite (PAL) clays of the Cherkasy deposit (Ukraine). Clay minerals, as adsorbents, are widely available, have large specific surface area, and the ability for cation exchange, which makes applicable in wastewater treatment from heavy metal ions.

Particles of the MMT and PAL samples are characterized by a qualitatively similar asymmetric type of distribution both in terms of size characteristics and in the shape of the particles. At the same time, the values of the equivalent diameter are smaller by approximately 7% and the values of the shape factor are larger by approximately 10% for the MMT than for the PAL sample.

BET surface area of the pores of the initial sample of palygorskite clay is significantly higher compared to montmorillonite clay (140.66 and 83.61 m^2/g, respectively). Acid modification of the PAL sample contributes to an increase in the BET surface area by approximately 1.7 times (from 140.66 to 241.13 m^2/g). Thus, with larger absolute values of the BET area, the effectiveness of

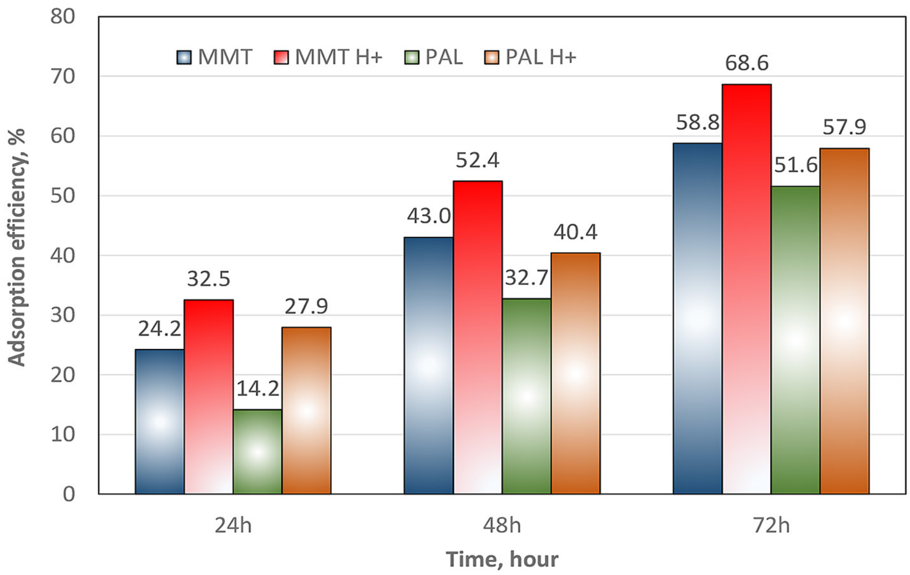

Figure 8. Adsorption efficiency of clays before (MMT, PAL) and after (MMT $H^{+,}$ PAL H^{+}) acid activation

acid treatment of the palygorskite sample on this indicator is lesser than that of montmorillonite.

It was found that acid activation improved the porous structure of clay samples. Surface area and total pore volume increase by approximately 2.3 (MMT) and 1.76 (PAL) times. At the same time, the dimensional characteristics of the pores of the MMT sample change slightly. Simultaneously, for the PAL sample, there is a sharp increase in the average pore size (approximately 3.2 times), which may be associated with additional pore formation in the interfibrillar regions.

The positive effect of acid activation on the sorption capacity of the investigated clay types according to methylene blue was established. Sorption efficiency increases by 6-14% compared to unmodified samples and is determined by the contact time and the type of clay. Increasing the contact time from 24 to 72 hours leads to an increase in the sorption efficiency of activated MMT and PAL samples by 36 and 30%, respectively.

Thus, clay minerals from the Cherkasy deposit (Ukraine), in particular montmorillonite, after acid activation can be used in the future as part of sorption elements to increase the efficiency of wastewater treatment technologies from heavy metal ions.

Acknowledgements

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REFERENCES

1. Akpomie, K.G., Dawodu, F.A. 2016. Acid-modified montmorillonite for sorption of heavy metals from automobile effluent. J Basic Appl Sci, 5(1), 1–12.
2. Amari, A., Gannouni, H., Khan, M.I., Almesfer, M.K., Elkhaleefa, A.M., Gannouni, A. 2018. Effect of structure and chemical activation on the adsorption properties of green clay minerals for the removal of cationic dye. Applied Sciences, 8(11), 2302.
3. Anbia, M., Hariri, S.A. 2010. Removal of methylene blue from aqueous solution using nanoporous SBA-3. Desalination, 261(1–2), 61–66.
4. Anirudhan, T.S., Ramachandran, M. 2015. Adsorptive removal of basic dyes from aqueous solutions by surfactant modified bentonite clay (organoclay): kinetic and competitive adsorption isotherm. Process Safety and Environmental Protection, 95, 215–225.
5. Anirudhan, T.S., Ramachandran, M. 2015. Adsorptive removal of basic dyes from aqueous solutions by surfactant modified bentonite clay (organoclay): kinetic and competitive adsorption isotherm. Process Safety and Environmental Protection, 95, 215–225. http://doi.org/10.1016/j.psep.2015.03.003
6. Arbelaiz, A., Fernández, G., Orue, A. 2021. The effect of montmorillonite modification and the use of coupling agent on mechanical properties of polypropylene–clay nanocomposites. Polymers and Polymer Composites, 29(6), 660–671.
7. Ashiq, A., Sarkar, B., Adassooriya, N., Walpita, J., Rajapaksha, A.U., Ok, Y.S., Vithanage, M. 2019. Sorption process of municipal solid waste biochar-montmorillonite composite for ciprofloxacin removal in aqueous media. Chemosphere, 236, 124384.
8. Barakan S., Aghazadeh V. 2021. The advantages of clay mineral modification methods for enhancing adsorption efficiency in wastewater treatment: a review. Environmental Science and Pollution Research, 28(3), 2572–2599.
9. Basim, G.B., Khalili, M. 2015. Particle size analysis on wide size distribution powders; effect of sampling and characterization technique. Advanced Powder Technology, 26(1), 200–207.
10. Bennett, R., Hulbert, M. 2012. Clay microstructure.
11. Bergaya, F., Lagaly, G. 2013. Handbook of clay science. 2nd edition. Elsevier, 1752.
12. Sarkar, B., Rusmin, R., Ugochukwu, U., Mukhopadhyay, R., Manjaiah, K.M. 2019. Modified clay minerals for environmental applications In book: Modified Clay and Zeolite Nanocomposite Materials, Publisher: Elsevier. DOI: 10.1016/B978-0-12-814617-0.00003-7
13. Brunauer, S., Emmett, P.H., Teller, E. 1938. Adsorption of gases in multimolecular layers. Journal of the American chemical society, 60(2), 309–319.
14. Budash, Y., Rezanova, N., Plavan, V., Rezanova, V. 2022. Thermally and organomodified montmorillonite as effective regulators of the structure formation process in polypropylene/polystyrene blends. Polymers and Polymer Composites, 2(30), 1–8.
15. Chaari, I., Medhioub, M., Jamoussi, F., Hamzaoui, A.H. 2021. Acid-treated clay materials (Southwestern Tunisia) for removing sodium leuco-vat dye: Characterization, adsorption study and activation mechanism. Journal of Molecular Structure, 1223, 128944.
16. Chen, F., Zheng, Q., Ding, X., Lu, S., Zhao, H. 2020. Pore size distributions contributed by OM, clay and other minerals in over-mature marine shale: A case study of the Longmaxi shale from Southeast Chongqing, China. Marine and Petroleum Geology, 122, 104679.
17. España, V.A., Sarkar, B., Biswas, B., Rusmin, R., Naidu, R. 2019. Environmental Applications of Thermally Modified and Acid Activated Clay Minerals: Current Status of the Art. Environ. Technol. Innov., 13, 383–397.

18. Evans, R., Marconi, U.M.B., Tarazona, P. 1986. Capillary condensation and adsorption in cylindrical and slit-like pores. Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics, 82(10), 1763–1787.
19. Fu, S., Fang, Q., Li, A., Li, Z., Han, J., Dang, X., Han, W. 2021. Accurate characterization of full pore size distribution of tight sandstones by low-temperature nitrogen gas adsorption and high-pressure mercury intrusion combination method. Energy Science & Engineering, 9(1), 80–100.
20. Heller-Kallai, L. 2013. Thermally modified clay minerals. Developments in Clay Science. Elsevier B.V., 411–433.
21. Jaroniec, M., Kruk, M., Sayari, A. 1998. Adsorption methods for characterization of surface and structural properties of mesoporous molecular sieves Studies in Surface Science and Catalysis, 117, 325–332. https://doi.org/10.1016/S0167-2991(98)81008-2]
22. Martín, J., del MarOrta, M., Medina-Carrasco, S., Santos, J.L., Aparicio, I., Alonso, E. 2018. Removal of priority and emerging pollutants from aqueous media by adsorption onto synthetic organo-funtionalized high-charge swelling micas Environmental Research, 164, 488–494. https://doi.org/10.1016/j.envres.2018.03.037
23. Kadoshnikov, V.M., Shekhunova, S.B., Zadvernyuk, H.P., Manichev, V.I. 2013. Authigenic minerals in the bentonite clay of Cherkassy deposit. Mineral. Journ. (Ukraine), 35(3), 54–60.
24. Kausar, A., Iqbal, M., Javed, A., Aftab, K., Bhatti, H.N., Nouren, S. 2018. Dyes adsorption using clay and modified clay: a review. Journal of Molecular Liquids, 256, 395–407.
25. Komadel, P., Madejová, J. 2006. Acid activation of clay minerals. Developments in clay science, 1, 263–287.
26. Lima, J.C., Costa, A.R.M., Sousa, J.C., Arruda, S.A., Almeida, Y.M. 2021. Thermal behavior of polyethylene terephthalate/organoclay nanocomposites: investigating copolymers as matrices. Polymer Composites, 42(2), 849–864.
27. Masindi, V., Ramakokovhu, M.M. 2021. The performance of thermally activated and vibratory ball milled South African bentonite clay for the removal of chromium ions from aqueous solution. Materials Today: Proceedings, 38, 964–974.
28. Nguyen, H., Chu, H., Hoang, T.L., Nguyen, D.V., Thuc, C.H. 2020. The starch modified montmorillonite for the removal of Pb (II), Cd (II) and Ni (II) ions from aqueous solutions. Arab J Chem, 13(9), 7212–7223.
29. Pawar, R.R., Ingole, P.G., Lee, S.M. 2020. Use of activated bentonite-alginate composite beads for efficient removal of toxic Cu^{2+} and Pb^{2+} ions from aquatic environment. International Journal of Biological Macromolecules, 164, 3145–3154.
30. Pérez, J.M.M., Pascau, J. 2013. Image processing with ImageJ. Packt Publishing Ltd. 140.
31. PJSC "Dashukivsky Bentonites" – a leading Ukrainian manufacturer of products from bentonite and paligorskite clays]. URL: http://dash-bent-pjsc.com/ [in Ukrainian].
32. Ravikovitch, P.I., Haller, G.L., Neimark, A.V. 1998. Density functional theory model for calculating pore size distributions: pore structure of nanoporous catalysts. Advances in colloid and interface science, 76, 203–226.
33. Sarkar, B., Rusmin, R., Ugochukwu, U.C., Mukhopadhyay, R., Manjaiah, K.M. 2019. Modified clay minerals for environmental applications. In Modified clay and zeolite nanocomposite materials. Elsevier, 113–127.
34. Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., Siemieniewska, T. 1985. International union of pure commission on colloid and surface chemistry including catalysis* reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, Pure Appl. Chem., 57(4C), 603–619.
35. Palchoudhury S., Baalousha M., Lead J.R. 2015. Chapter 5 – Methods for Measuring Concentration (Mass, Surface Area and Number) of Nanomaterials, Frontiers of Nanoscience, 8, 153–181. https://doi.org/10.1016/B978-0-08-099948-7.00005-1
36. Tadesse, S.H. 2022. Application of Ethiopian bentonite for water treatment containing zinc. Emerging Contaminants, 8, 113–122.
37. Toor, M., Jin, B. 2012. Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. Chemical Engineering Journal, 187, 79–88.
38. Uddin, M.K. 2017. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chemical Engineering Journal, 308, 438–462.
39. Zaghouane-Boudiaf, H., Boutahala, M., Sahnoun, S., Tiar, C., Gomri, F. 2014. Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing the 2, 4, 5-trichlorophenol. Applied clay science, 90, 81–87.
40. Zhu, J., Zhang, P., Wang, Y., Wen, K., Su, X., Zhu, R., Xi, Y. 2018. Effect of acid activation of palygorskite on their toluene adsorption behaviors. Applied Clay Science, 159, 60–67.