Acta Montanistica Slovaca
ISSN 1335-1788
actamont.tuke.sk
Acta Montanistica Slovaca

Statistical Analysis of Acid Treatment of Different Types of Clay Minerals

Tomáš BAKALÁR[1]***, *Henrieta PAVOLOVÁ*[1], *Zuzana HAJDUOVÁ*[2], *Maciej THOMAS*[3], *Lucia BEDNÁROVÁ*[1] *and Michal HROMJÁK*[1]

Authors' affiliations and addresses:
[1] Institute of Earth Resources, Faculty of Mining, Ecology, Process Control and Geotechnologies, Technical University of Košice, Letná 9, 042 00 Košice, Slovakia
e-mail: tomas.bakalar@tuke.sk;
e-mail: henrieta.pavolova@tuke.sk;
e-mail: michal.hromjak@student.tuke.sk;
e-mail: lucia.bednarova@tuke.sk

[2] Faculty of Business Management, University of Economics in Bratislava, Dolnozemská cesta 1/b, 852 35 Bratislava, Slovakia
e-mail: zuzana.hajduova@euba.sk

[3] Faculty of Environmental Engineering and Energy, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland
e-mail: maciej.thomas@pk.edu.pl

***Correspondence:**
Tomáš Bakalár, Institute of Earth Resources, Faculty of Mining, Ecology, Process Control and Geotechnologies, Technical University of Košice, Letná 9, 042 00 Košice, Slovakia
tel.: +421556022974
e-mail: tomas.bakalar@tuke.sk

Funding information:
Vedecká grantová agentúra MŠVVaM SR a SAV
Grant Number: VEGA 1/0328/25
Grant Number: VEGA 1/0109/24
Grant Number: VEGA 1/0554/24
Grant Number: APVV-24-0607

How to cite this article:
Bakalár, T., Pavolová, H., Hajduová, Z., Thomas, M., Bednárová, L. and Hromják, M., (2025). Statistical Analysis of Acid Treatment of Different Types of Clay Minerals, *Acta Montanistica Slovaca,* Volume 30 (3), 661-670

DOI:
https://doi.org/10.46544/AMS.v30i3.08

Abstract

Bentonite, which is composed of montmorillonite, is modified with acid to change its properties for use in agricultural and environmental applications and color. Hydrochloric acid and sulfuric acid were used for acid activation. Acid activation has been widely studied, but this study aims to find the correlations between the studied physical, chemical, and mineralogical properties via regression analysis, which is used to describe the relations among different variables via analysis of variance. Based on different colors, six types of bentonite were analyzed for loss on ignition, specific weight, specific surface, water absorption, chemical and mineralogical composition, and were modified with different concentrations of hydrochloric and sulfuric acids. All the samples, regardless of their original color, changed to a greyish white, with the highest whiteness observed for the sample treated with 35% hydrochloric acid. The correlations among the loss on ignition, specific weight, and specific surface area are significant. The surface area of modified bentonite increases with increasing acid concentration, which may imply that the acid-treated bentonite becomes more porous. Hydrochloric acid has a more significant effect on the mineralogical content than sulfuric acid. As the acid concentration increases, the contents of montmorillonite, illite, and kaolinite decrease, whereas the content of quartz increases. Sulfuric acid changes the contents of montmorillonite, illite, and quartz less significantly. The changes in the Si^{4+}, Fe^{2+}, and Na^{+} contents are insignificant with increasing acid concentrations. The changes in Al^{3+} and Ca^{2+} contents are more significant with increasing hydrochloric acid concentration.

Keywords

acid activation; analysis of variance; bentonite; montmorillonite; regression analysis; X-ray diffraction

Introduction

Bentonites are clays commonly used not only for industrial applications but also for agricultural and environmental applications, as well as for hobbies such as gardening and breeding domestic animals. Bentonite is usually a mixture of smectites classified according to the cations: montmorillonite, beidellite, nontronite, hectorite, and saponite (Yarmots and Yarmots, 2018; Tsakiri et al., 2022). The adsorptive and catalytic properties of smectites, along with their physical and chemical properties, affect their surface characteristics. Their nature and features can be treated and modified by physical and/or chemical activation (Bergaya et al., 2008; Hussin et al., 2011). The color and sorptive properties of bentonite (Bakalár et al., 2020; Bakalár, 2021a; Bakalár, 2021b; Essebaai et al., 2022) may also be important, especially for gardening and animal breeding (cat litter). Zeolites are also often applied in polymeric nanocomposites, packaging, nanodevice feedstock, antimicrobial and disinfectant applications, biomedical applications, coatings, etc. (Sukhadeorao Dongre 2020, Škvarlová et al. 2020).

There are several deposits of naturally white bentonite, including those in San Juan Province, Argentina (Allo and Murray, 2004); Kutahya Province, Turkey (Yildiz and Kuscu, 2004); and Orasu-Nou, Romania (Damian et al., 2021). However, most deposits are naturally brownish, blueish, or greyish bentonites. Although the color is not important for industrial applications, it may be decisive for agricultural and environmental applications (Yildiz et al., 2004; Önal and Sarıkaya, 2007). The contact of bentonite with mineral acids, called acid activation, involves not only color changes but also some physical, chemical, and mineralogical properties of bentonite, especially the chemical composition, crystallinity, water absorption capacity, loss on ignition (LOI), specific weight, and specific surface area (Vuković et al., 2006; Sharma and Sarasan, 2017; Elhechi et al., 2023). Acid activation has been widely studied (Kashani Motlagh et al., 2011; Madejová et al., 2012; Bieseki et al., 2013; Akpomie and Dawodu, 2016); however, all studies focused on each parameter separately, and the correlations among them were not considered.

In this study, bentonite was modified with HCl and H_2SO_4. These acids were selected on the basis of a literature survey as acids suitable for the modification of clays (Yildiz et al., 2004; Önal and Sarıkaya, 2007; Vuković et al., 2006; Sharma and Sarasan, 2017; Elhechi et al., 2023; Kashani Motlagh et al., 2011; Madejová et al., 2012; Bieseki et al., 2013; Akpomie and Dawodu, 2016). This study aims to determine changes in bentonite properties (physical, chemical, and mineralogical) resulting from acid activation and to examine the correlations among the studied parameters. The color change of bentonite is also considered because animal breeding is important. In agricultural and environmental applications, other parameters may have a significant influence. Water absorption capacity is also important for mitigating water evaporation in agriculture and for use as clumping cat litter. The mineralogical and chemical composition may also affect the use in agriculture as a fertilizer or additive for various applications.

The main objective of this study is to relate the mineralogical and chemical composition of bentonite to its response to acid activation. Various parameters were analyzed, as mentioned above, to evaluate the behavior and properties of different types of bentonites, including their composition and color, when activated by hydrochloric or sulfuric acid. This analysis provides a deeper insight into the interaction between acids and bentonites, which may have important implications for their future use in agriculture and other industries.

Materials and Methods

Bentonite containing montmorillonite was obtained directly from a quarry. The composition of natural clay and its properties may change even within the same deposit as mining progresses. A precise characterization of the samples in terms of physical, chemical, and mineralogical properties and compositions is crucial for determining the impact of acids; thus, the results are comparable based on clay properties, not deposits.

The samples were sorted into six types based on color. As the samples were taken from a bentonite quarry, they were assigned as bentonite samples regardless of the montmorillonite content. The sorted samples were analyzed for their LOI, specific weight, specific surface area, water absorption, and chemical and mineralogical composition.

LOI tests were performed on samples of each type. The LOI ($\%_w$) test was performed at 900°C and was calculated via:

$$\boldsymbol{LOI = \frac{S - L}{S} \cdot 100} \tag{1}$$

where S [kg] is the weight of the sample and L [kg] is the weight of the sample after ignition.

The specific weight was measured with a pycnometer. The specific surface area was measured by N_2 gas adsorption (BET) using a Micromeritics® Tristar II (USA). Water absorption was estimated for pellets from compressed bentonite particles at pressures of 30 and 60 kN at pH = 6.0 and 25°C.

For each chemical analysis, 0.2g of dried sample was placed in a platinum crucible, mixed with 2.0g of Na_2O_2 (ITES Vranov, a.s., Vranov, Slovakia), heated to 750°C for 10 min, and cooled to room temperature. The crucible was placed into a beaker with 15% HCl to dissolve the precipitate. The cooled solution was diluted to 200 ml. The metal content was analyzed by Flame Atomic Adsorption Spectrometry (iCE 3300 – ThermoFisher Scientific, Grand Island, NY, USA). The results are presented as the mass% % of the metal oxides.

The mineralogical composition was determined by X-ray diffraction (XRD) performed by a Perkin Elmer XRD 4343 CT 2D detector with a pixel size of 150 × 150 μm^2 (USA). The phase identification of the studied samples was carried out using a SEIFERT 3003/PTS (Germany) under the conditions in Tab. 1.

Tab. 1. XRD measurement conditions.

Parameter	Valie
Generator	35 kV, 40 mA
X-ray radiation	Co-line focus
Filter	Fe
Scan step	0.02 Θ
Range of measuring	10 - 120° 2Θ
Input slits	3 mm, 2 mm
PSD Detector	Meteor1D

Bentonite was modified by adding 10 g of bentonite clay to 100 mL of HCl or H_2SO_4 (ITES Vranov, a.s., Vranov, Slovakia) solution (15%, 25%, and 35%). Each sample was suspended in a round-bottom flask and heated at 90°C for 16h under magnetic stirring, with a reflux condenser. Each leached sample was centrifuged. The obtained samples were washed with distilled water until a neutral pH was reached. After drying at 105°C for 4h, the samples were stored in closed glass bottles and analyzed for the same properties as raw bentonites. The chemicals used were of analytical purity (p.a.).

The results are presented as the average value of triplicate experiments.

Regression analysis is a statistical method used to describe the relationships among different variables (Cipra, 2013) and is used in different applications involving rocks, especially clays (Bang et al., 2020; Yoon et al., 2021). A simplified model with specified parameters and variables is a model whose parameters are not exactly known. However, such a model does not account for the effects of various changes, deviations, and randomness.

Let us assume a general linear regression model as defined by:

$$\boldsymbol{y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_k x_k + u} \tag{2}$$

where y represents the dependent (explained) variable; x_1, x_2, x_3, …, x_k represent independent (explaining) variables; and u is a random component (Tebeje et al. 2022; Akbay, 2023). Since there is often more than one observation, i.e., there are n observations, where n is a natural number, i = 1, 2, 3, ..., n applies as:

$$\boldsymbol{y = \beta_0 + \beta_1 x_{i,1} + \beta_2 x_{i,2} + \cdots + \beta_k x_{i,k} + u} \tag{3}$$

In the context of the presented data, the characteristics of location and data processing variability were used. The hypotheses, set employing tests on mean values and tests of comparisons of two middle values, were verified. To determine the impact of qualitative variables on quantitative variables, the analysis of variance (ANOVA) was used (Montgomery, 2019; Castro-Castro et al., 2020). The basic principle of this method is that the distribution of the total dispersion of the obtained values into random variances is realized, and the dispersion, which is caused by the influence of the qualitative quantity, is determined. The aim was to identify the differences in average values for different variations of the qualitative variable, which were defined as a factor. Hypothesis H_0 represents an argument that presents the equality of average values of the dependent variable. H_1 is an alternative to H_0. In the processed data, normality, independence, and homoscedasticity, which are prerequisites for using the ANOVA method, were verified (Datta et al., 2020; Akomah et al., 2021).

The hypotheses are as follows:

H_0: average values do not depend on factor levels ($\mu_1 = \mu_2 = ... = \mu_\Delta$),
H_1: average values depend on factor levels,

where the number of baselines is compared (number of factor levels).

The model of one-way analysis is defined by:

$$\boldsymbol{Y_{ij} = \mu + \tau_i + \varepsilon_{ij}, i = 1, 2, \dots, A, j = 1, 2, \dots, N_i} \tag{4}$$

where μ is the overall average, τ_i is the effect of both the level and the factor A, and ε_{IJ} is an additional random component (error) that is stochastically independent of the division of $N(0, \sigma^2_\varepsilon)$.

To measure variability in ANOVA models, the sum of squares SST = SSM + SSE, where the SST is the total of the squares of deviations, SSM is the sum of squares explained by the model, and SSE is the sum of squares not explained by the model, was used (Gelman, 2008). The sums of squares must be converted into average amounts, which express what variability–explained or unexplained–falls per unit. Test statistics for ANOVA compare the model's explained unit variability with the unexplained unit variability, as measured by the so-called F statistics. If the factor has the final number of tiers and all its levels are considered when calculating the model, it is a model with fixed levels of factors. In two-factor analysis of variance, two factors influence resonance, and their interaction is also possible. There are interactions between two factors if the difference between the levels of one factor depends on the levels of another factor. The factors between which there are no interactions are called additives. Interaction is a special influence resulting from the joint operation of one condition and the other. The interaction between two factors occurs when at least one combination of levels of both factors is not additive. Given the nature of the research and the data being cross-cut, a linear regression model shape was also used, as defined by Gelman (2008).

$$\boldsymbol{y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_k x_k + \varepsilon_k} \tag{5}$$

where β_0, β_1, β_2, ..., β_k are the parameters of the model, and the functions of one or more explanatory variables are known.

Results and Discussion

The original sample of bentonite from the quarry was sorted into six color groups: yellow, grey, white-red, red, brown, and blue. Qualitatively, all six samples contain the same phases, but quantitatively, they differ. The color may be affected by the atoms incorporated into the structure. Quartz (SiO_2) has several modifications, which are differently colored based on interstitial elements, such as amethyst (purple) and citrine (yellow) (Rossman, 1994; Henn and Schultz-Güttler, 2012) (Tab. 2-4).

Tab. 2. Basic characterization of the original samples.

Sample No.	Color	LOI [$\%_w$]	Specific weight [$kg.m^{-3}$]	Specific surface [10^3 $m^2.kg^{-1}$]	Water absorption [%]
1	yellow	15.72	2693	22.495	394
2	grey	14.49	2638	22.505	389
3	white-red	7.61	2534	20.409	221
4	red	17.55	2671	22.395	498
5	brown	17.83	2685	20.123	512
6	blue	18.04	2704	21.887	526

Tab. 3. Mineralogical compositions of the original samples.

Sample No.	Montmorillonite $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$	Quartz SiO_2	Illite $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	Kaolinite $Al_2Si_2O_5(OH)_4$
1	15.9	17.5	44.4	22.2
2	13.8	7.7	51.3	27.2
3	1.2	56.3	15.1	27.4
4	20.5	9.8	42.2	27.5
5	50.4	8.2	15.9	25.5
6	53.8	7.0	12.4	26.8

Tab. 4. Chemical composition of the samples.

Sample No.	SiO_2 [%$_w$]	Al_2O_3 [%$_w$]	CaO [%$_w$]	Fe_2O_3 [%$_w$]	FeO [%$_w$]	Na_2O [%$_w$]
1	61.71	9.67	2.13	0.30	0.10	0.10
2	40.49	12.21	2.18	1.32	0.08	0.46
3	71.32	9.01	1.65	0.20	0.10	0.00
4	48.81	11.56	2.86	1.00	0.09	0.80
5	41.27	10.54	1.97	1.5	0.10	0.83
6	44.78	11.66	2.53	2.08	0.10	0.39

The results for acid-modified samples 1–6 are presented in Tables 5–10, respectively. Based on the analyses, it can be concluded that there are significant differences in some parameters that may affect the color of bentonite. The whiteness was the highest for samples modified with 35% HCl, regardless of the original color. The highest whiteness of all the samples was reached for the yellow bentonite treated with 35% HCl. The whiteness of the samples from highest to lowest was as follows: 35% HCl, 25% HCl, 35% H_2SO_4, 25% H_2SO_4, 15% HCl, and 15% H_2SO_4. The color and whiteness may be significantly affected by the mineral content and structural decomposition, which depend strongly on the acid concentration (Yildiz and Kuscu, 2004).

Changes in other parameters, as well as in the mineralogical and chemical compositions, were also observed. With increasing acid concentration, the LOI and specific weight decreased, but the specific surface area increased. In some cases, the water absorption capacity decreased significantly. This may negatively impact the usability of modified bentonite in some agricultural and environmental applications, especially gardening and animal breeding, where water-sorption capacity is important. Regarding the mineralogical composition, montmorillonite content decreased significantly, while quartz content increased. The contents of illite and kaolinite also decreased, while a significant increase was recorded between 15% and 25%. Nevertheless, the SiO2 content did not change significantly and even increased, whereas the Al_2O_3 content slightly decreased. The contents of CaO and Fe_2O_3 did not change significantly. The impact of HCl on the FeO and Na_2O content was more significant than the impact of H_2SO_4.

Tab. 5. Characterization of the yellow sample (sample 1) after acid treatment.

Acid	Acid [%]	LOI [%$_w$]	SpW	SpS	WA	M	Q	I	K	SiO_2 [%$_w$]	Al_2O_3 [%$_w$]	CaO [%$_w$]	Fe_2O_3 [%$_w$]	FeO [%$_w$]	Na_2O [%$_w$]
HCl	15	8.92	2050	56	300	11.9	27.8	42.4	17.9	63.2	8.29	0.29	0.20	0.10	0.10
	25	7.8	2004	126	198	8.8	54.9	23.5	12.8	65.9	7.36	0.26	0.13	0.08	0.07
	35	5.8	1986	101	121	2.5	65.9	22.2	9.4	69.7	6.52	0.25	0.11	<LQ	<LQ
H_2SO_4	15	7.99	2051	46	190	14.8	20.8	42.4	22.0	62.3	9.01	2.03	0.31	0.10	0.10
	25	7.86	2020	156	87	12.3	32.9	33.1	21.7	64.0	8.39	1.57	0.27	0.10	0.09
	35	7.65	1992	222	55	10.8	43.7	23.5	22.0	65.0	7.89	1.56	0.25	0.09	0.09

*key: SpW [kg.m^{-3}]= specific weight; SpS [10^{3}m^{2}kg^{-1}]= specific surface; WA [%] = water absorption; M [%$_w$] = montmorillonite; Q [%$_w$] = quartz; I [%$_w$] = illite; K [%$_w$] = kaolinite; <LQ = below limit of quantification.

Tab. 6. Characterization of the grey sample (sample 2) after acid treatment.

Acid	Acid [%]	LOI [%$_w$]	SpW	SpS	WA	M	Q	I	K	SiO_2 [%$_w$]	Al_2O_3 [%$_w$]	CaO [%$_w$]	Fe_2O_3 [%$_w$]	FeO [%$_w$]	Na_2O [%$_w$]
HCl	15	9.02	2060	55	294	12.1	23.8	47.0	17.1	51.7	11.0	0.33	0.98	0.08	0.32
	25	8.31	2003	119	208	8.4	55.4	21.1	15.1	62.8	7.6	0.28	0.18	0.08	0.10
	35	6.00	1982	100	142	3.4	64.8	22.3	9.5	70.5	6.7	0.26	0.10	<LQ	<LQ
H_2SO_4	15	8.01	2047	49	183	12.2	10.8	50.9	26.1	44.9	11.8	2.05	1.28	0.08	0.40
	25	7.93	2030	150	89	11.1	28.0	35.1	25.8	45.7	9.7	1.54	1.27	0.08	0.33
	35	7.96	1990	247	52	9.9	48.0	20.2	21.9	52.9	8.00	1.55	1.25	0.08	0.23

*key: SpW [kg.m^{-3}]= specific weight; SpS [10^{3}m^{2}kg^{-1}]= specific surface; WA [%] = water absorption; M [%$_w$] = montmorillonite; Q [%$_w$] = quartz; I [%$_w$] = illite; K [%$_w$] = kaolinite; <LQ = below limit of quantification.

Tab. 7. Characterization of the white-red sample (sample 3) after acid treatment.

Acid	Acid [%]	LOI [%$_w$]	SpW	SpS	WA	M	Q	I	K	SiO_2 [%$_w$]	Al_2O_3 [%$_w$]	CaO [%$_w$]	Fe_2O_3 [%$_w$]	FeO [%$_w$]	Na_2O [%$_w$]
HCl	15	3.33	2049	51	202	1.0	59.8	20.5	18.7	72.1	8.09	0.30	0.12	0.09	<LQ
	25	3.00	1999	136	167	1.0	62.8	21.9	14.3	73.0	7.49	0.22	0.10	0.10	<LQ
	35	2.60	1992	81	133	1.0	67.2	22.5	9.3	73.8	6.60	0.20	0.09	<LQ	<LQ
H_2SO_4	15	3.11	2044	40	193	1.0	68.0	3.9	27.1	71.5	9.34	1.64	0.19	0.10	<LQ
	25	3.01	2027	104	88	1.1	67.4	4.5	27.0	71.7	8.41	1.59	0.19	0.10	<LQ
	35	2.96	1995	201	48	1.1	68.9	7.2	22.8	72.0	7.87	1.54	0.17	0.08	<LQ

*key: SpW [kg.m^{-3}]= specific weight; SpS [10^3m^{2}kg^{-1}]= specific surface; WA [%] = water absorption; M [%$_w$] = montmorillonite; Q [%$_w$] = quartz; I [%$_w$] = illite; K [%$_w$] = kaolinite; <LQ = below limit of quantification.

Tab. 8. Characterization of the red sample (sample 4) after acid treatment.

Acid	Acid [%]	LOI [%$_w$]	SpW	SpS	WA	M	Q	I	K	SiO_2 [%$_w$]	Al_2O_3 [%$_w$]	CaO [%$_w$]	Fe_2O_3 [%$_w$]	FeO [%$_w$]	Na_2O [%$_w$]
HCl	15	8.94	2056	56	305	12.7	30.1	40.2	17.0	52.7	10.9	0.34	0.40	0.08	0.42
	25	8.33	2019	129	220	7.9	53.1	27.0	12.0	63.0	7.6	0.29	0.20	0.08	0.11
	35	6.32	1899	102	132	2.9	66.6	20.7	9.8	72.0	6.6	0.27	0.12	<LQ	<LQ
H_2SO_4	15	8.18	2048	49	199	18.6	12.8	42.1	26.5	44.0	11.0	2.80	0.98	0.09	0.70
	25	8.11	2031	170	89	15.6	31.4	25.9	27.1	47.7	9.8	1.59	0.90	0.08	0.43
	35	8.00	1994	251	53	11.0	45.5	21.7	21.8	51.9	7.9	1.55	0.83	0.08	0.34

*key: SpW [kg.m^{-3}]= specific weight; SpS [10^3m^{2}kg^{-1}]= specific surface; WA [%] = water absorption; M [%$_w$] = montmorillonite; Q [%$_w$] = quartz; I [%$_w$] = illite; K [%$_w$] = kaolinite; <LQ = below limit of quantification.

Tab. 9. Characterization of the brown sample (sample 5) after acid treatment.

Acid	Acid [%]	LOI [%$_w$]	SpW	SpS	WA	M	Q	I	K	SiO_2 [%$_w$]	Al_2O_3 [%$_w$]	CaO [%$_w$]	Fe_2O_3 [%$_w$]	FeO [%$_w$]	Na_2O [%$_w$]
HCl	15	9.09	2066	50	301	15.8	32.8	31.6	19.8	50.8	10.9	0.26	1.1	0.09	0.43
	25	8.91	1989	106	216	10.8	53	23.2	12.9	63.0	7.5	0.25	0.21	0.09	0.1
	35	6.39	1945	175	148	3.8	65.9	20.4	9.9	70.0	6.1	0.25	0.12	<LQ	<LQ
H_2SO_4	15	8.03	2050	50	200	50.1	9	15.9	25	44.8	10.0	1.91	1.49	0.10	0.74
	25	7.92	2022	156	90	49.3	20.5	5.1	25.1	46.3	9.7	1.61	1.41	0.08	0.44
	35	7.89	1995	259	55	22.1	32.9	23	22	50.3	8.0	1.57	1.31	0.09	0.32

*key: SpW [kg.m^{-3}]= specific weight; SpS [10^3m^{2}kg^{-1}]= specific surface; WA [%] = water absorption; M [%$_w$] = montmorillonite; Q [%$_w$] = quartz; I [%$_w$] = illite; K [%$_w$] = kaolinite; <LQ = below limit of quantification.

Tab. 10. Characterization of the blue sample (sample 6) after acid treatment.

Acid	Acid [%]	LOI [%$_w$]	SpW	SpS	WA	M	Q	I	K	SiO_2 [%$_w$]	Al_2O_3 [%$_w$]	CaO [%$_w$]	Fe_2O_3 [%$_w$]	FeO [%$_w$]	Na_2O [%$_w$]
HCl	15	8.92	2020	52	310	16	33	31.1	19.9	51.9	11.0	0.25	1.73	0.1	0.21
	25	7.99	2000	108	228	11	53.8	20.3	14.9	62.8	7.4	0.23	0.19	0.08	0.1
	35	5.93	1934	186	150	3.7	67.9	18.5	9.9	71.3	6.6	0.23	0.12	<LQ	<LQ
H_2SO_4	15	8.15	2048	49	198	52.8	8.9	12.4	25.9	45.5	10.8	2.5	2	0.1	0.31
	25	8.12	2025	160	92	48.7	19.1	5.1	26.9	47.9	9.5	1.59	1.98	0.09	0.2
	35	8.03	2000	267	57	25.6	30.8	20.9	22.7	49.5	7.9	1.55	1.89	0.09	0.14

*key: SpW [kg.m^{-3}]= specific weight; SpS [10^3m^{2}kg^{-1}]= specific surface; WA [%] = water absorption; M [%$_w$] = montmorillonite; Q [%$_w$] = quartz; I [%$_w$] = illite; K [%$_w$] = kaolinite; <LQ = below limit of quantification.

The results of the ANOVA are presented in Fig. 1. Compared to other samples, the LOI, specific weight, specific surface area, and water adsorption of the unmodified samples were significantly lower for white-red bentonite. A low specific surface area was also recorded for brown bentonite. The content of montmorillonite varies from 1.2% to 53.8%. The content of quartz varies from 7% to 17.5%, except for white-red bentonite with 56.3%. The illite content varies widely from 12.4% to 51.3%, whereas the kaolinite content varies only within a narrow range from 22.2% to 27.5%. Statistically, the contents of SiO_2, Al_2O_3, CaO, Fe_2O_3, FeO, and Na_2O do not significantly deviate from the mineralogical composition. This fact may also be caused by the chemical composition of the minerals. The results of the analysis of bentonites modified with different concentrations of HCl and H_2SO_4 are similar to those shown above, but with different ranges, as discussed below.

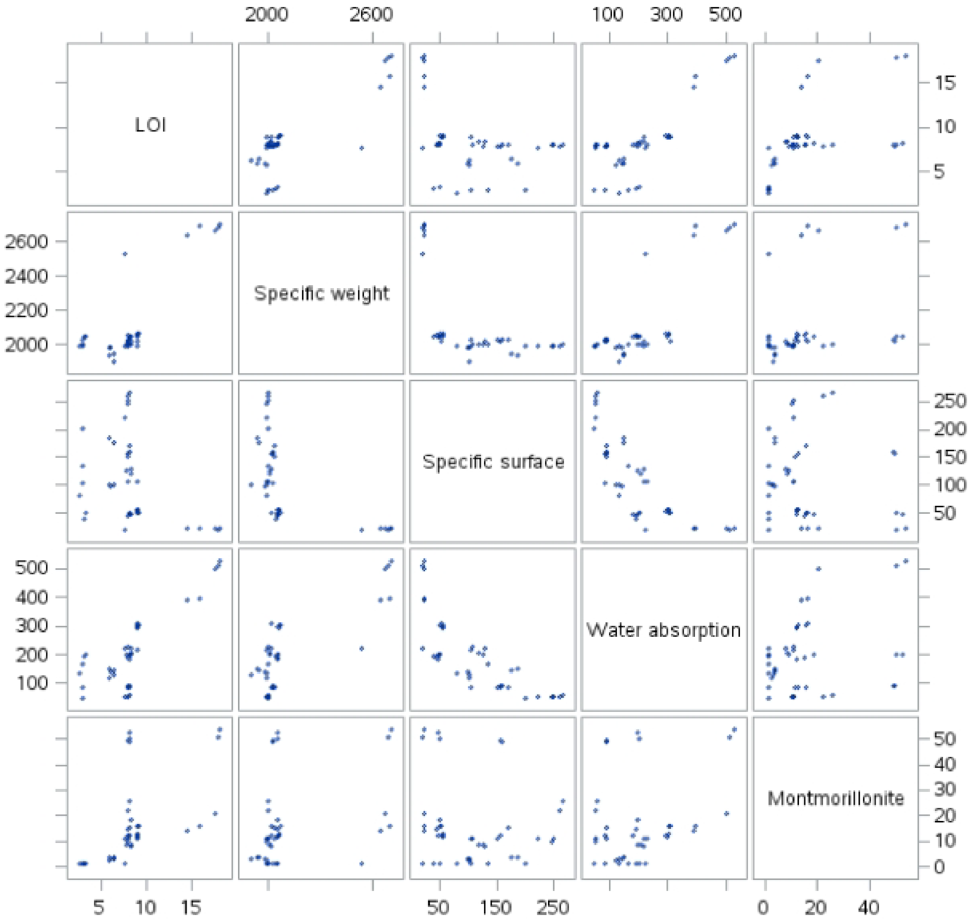

Fig. 1. Scatter plot matrix of correlation analysis.

The LOI, specific weight, and specific surface area strongly correlate (Tab. 11). The values of the LOI, specific weight, and specific surface area are proportional to the acid concentration. Water absorption is another important parameter for use in agricultural and environmental applications. This parameter is also correlated with the LOI, specific weight, and specific surface area. All values for the treated samples are lower than those for the untreated samples. The higher the acid concentration, the lower the water absorption capacity; however, while the effect of H_2SO_4 is more significant (the values of water absorption are lower) than the effect of HCl is, the effect of HCl is more significant than the effect of H_2SO_4 on the LOI, specific weight, and specific surface area. The surface area increases with increasing acid concentration and treatment time; thus, the treated bentonite becomes more porous (Sharma and Sarasan, 2017; Alamery and Ahmed, 2021).

Tab. 11. One-way analysis of the variance-dependent variable LOI.

Source	DF	Sum of Squares	Mean Square	F Value	PR > F
Model	6	361.624	60.271	10.47	<0.0001
Error	35	201.467	5.756		
Corrected Total	41	563.091			
R-Square	**Coeff. Var.**	**Root MSE**	**LOI Mean**		
0.642	29.144	2.399	8.232		
Source	**DF**	**Anova SS**	**Mean Square**	**F Value**	**PR > F**
Acid	6	361.624	60.271	10.47	<0.0001

HCl has a significant effect on montmorillonite content: in all studied samples, the distribution of montmorillonite content is narrow, irrespective of the montmorillonite content in the raw samples (Tab. 12). The montmorillonite content decreased significantly with the addition of HCl. The impact of H_2SO_4 is also negative but not very significant, and the distribution of the values is not as narrow.

Tab. 12. One-way analysis of the variance-dependent variable montmorillonite.

Source	DF	Sum of Squares	Mean Square	F Value	PR > F
Model	6	2935.033	489.172	2.34	<0.0527
Error	35	7318.223	209.092		
Corrected Total	41	10253.256			

R-Square	Coeff. Var.	Root MSE	LOI Mean
6	2935.033	489.172	2.340

Source	DF	Anova SS	Mean Square	F Value	PR > F
Acid	6	2935.033	489.172	2.34	<0.0001

The content of quartz significantly increased with increasing concentrations of both acids (Tab. 13). In most samples, the impact of HCl is more significant, as the higher the HCl concentration, the higher the quartz content. This occurs because the resistance of quartz to acid dissolution has been confirmed by different authors for HCl-activated (Temuujin et al., 2004; Kiani et al., 2022) and H_2SO_4-activated clays (Amari et al., 2018).

Tab. 13. One-way analysis of the variance-dependent variable quartz.

Source	DF	Sum of Squares	Mean Square	F Value	PR > F
Model	6	11166.336	1861.056	8.23	<0.0001
Error	35	7913.588	226.103		
Corrected Total	41	19079.924			

R-Square	Coeff. Var.	Root MSE	LOI Mean
0.585	38.403	15.037	39.155

Source	DF	Anova SS	Mean Square	F Value	PR > F
Acid	6	11166.336	1861.056	8.23	<0.0001

The illite content decreases significantly with increasing HCl and H_2SO_4 concentrations, as confirmed by other studies (Yener et al., 2020). The content of kaolinite is also significantly decreased, but only by HCl. The impact of H_2SO_4 is insignificant (Tab. 14).

Tab. 14. One-way analysis of the variance-dependent variable kaolinite.

Source	DF	Sum of Squares	Mean Square	F Value	PR > F
Model	6	1517.505	252.917	115.77	<0.0001
Error	35	76.460	2.185		
Corrected Total	41	1593.965			

R-Square	Coeff. Var.	Root MSE	LOI Mean
0.952	7.336	1.478	20.148

Source	DF	Anova SS	Mean Square	F Value	PR > F
Acid	6	1517.505	252.917	115.77	<0.0001

However, the content of Si^{4+} does not change significantly. This fact may be caused by the content of Si not only in quartz but also in montmorillonite, illite, and kaolinite, which are discussed above, and the fact that the Si^{4+} ions at tetrahedral sites are not dissolved by acid activation (Önal and Sarıkaya, 2007; Li et al., 2016). Silica is also decomposed by acid activation (Yildiz et al., 2004). The contents of Al^{3+} and Ca^{2+} decrease with increasing acid concentration. The impact of HCl is more significant. A sharp decrease in Ca^{2+} content was also confirmed by another study (Vuković et al., 2006). The contents of Fe^{2+} and Na^+ also do not change significantly. As reported by another study, the contents increase in the order of Ca^{2+}, Na^+, Mg^{2+}, $Fe^{2+,3+}$, Al^{3+}, K^+, Si^{4+}, and Ti^{4+} in bentonite with increasing H_2SO_4 (Önal and Sarıkaya, 2007). It was also observed that the relative SiO_2 content increased with increasing acid concentration, whereas those of the other cations decreased (Vuković et al., 2006). At low acid concentrations, there is little difference between the activated and raw samples; thus, there are minimal changes in the concentrations of Al_2O_3, Fe_2O_3, Na_2O, and CaO. However, as the acid concentration increases, the chemical structure changes due to the release of ions from bentonite layers. An increase in the concentration of acids causes a collapse in the chemical structure almost fully (Yildiz et al., 2004).

Conclusions

The data presented in the results and discussion sections, which study the change in montmorillonite by acid activation using HCl and H_2SO_4, suggest the following:

1. The physical appearance (color) of clay is strongly affected by acid activation, causing a change in color from yellow/red/brown/gray to grayish-white.
2. There is a strong correlation between the LOI, specific weight, and specific surface area.
3. The acid-treated bentonite becomes more porous as the surface area increases with increasing acid concentration.
4. Hydrochloric acid has a significant effect on the mineralogical content. The contents of montmorillonite, illite, and kaolinite decrease, and the content of quartz increases.
5. Sulfuric acid decreases the contents of montmorillonite and illite and increases the content of quartz but less significantly.
6. The changes in the Si^{4+}, Fe^{2+}, and Na^{+} contents are insignificant with the addition of acids.
7. The changes in the Al^{3+} and Ca^{2+} contents are more significant with increasing HCl concentration than with increasing H_2SO_4 concentration.

Future studies may focus on the use of other acids, such as nitric and aqua regia (a mixture of concentrated nitric and hydrochloric acids), which are considered strong inorganic acids, as well as acetic and/or citric acids, which are considered weak organic acids.

References

Akbay D (2023) Investigating the Accuracy of Specimen Shape for Point Load Index Test in Predicting the Uniaxial Compressive Strength for Rocks Using Regression Analysis and Machine Learning. Min Metallurgy Explor 40:2107–2115. https://doi.org/10.1007/s42461-023-00865-4

Akomah U; Nwaogazie IL, Akaranta O, David AO (2021) Comparative analysis of Activated Corn Cob and Bentonite Clay for the Removal of Lead and Nickel from Raw Water. Slovak J Civ Eng 29:30–38. http://doi.org/10.2478/sjce-2021-0011

Akpomie KG, Dawodu FA (2016) Acid-modified montmorillonite for sorption of heavy metals from automobile effluent. Beni-Suef Univ J Basic Appl Sci 5:1–12. https://doi.org/10.1016/j.bjbas.2016.01.003

Alamery HRD, Ahmed SA (2021) Purification and activation of the Iraqi bentonite for edible oil Production. IOP Conf Ser: Mater Sci Eng 1090:012039. https://doi.org/10.1088/1757-899X/1090/1/012039

Allo WA, Murray HH (2004) Mineralogy, chemistry and potential applications of a white bentonite in San Juan province, Argentina. Appl Clay Sci 25:237–243. https://doi.org/10.1016/j.clay.2003.10.003

Amari A, Gannouni H, Khan MI, Almesfer MK, Elkhaleefa AM, Gannouni A (2018) Effect of structure and chemical activation on the adsorption properties of green clay minerals for the removal of cationic dye. Appl Sci 8:2302. https://doi.org/10.3390/app8112302

Bakalár T. (2021a) Competitive adsorption of Cr(VI), K(I) and NH4(I) ions onto natural zeolites and bentonites. Arch Tech Sci 24:73–81. https://doi.org/10.7251/afts.2021.1324.073B

Bakalár T. (2021b) Effect of pH on adsorption of Cr(VI), K(I) and NH4(I) ions onto natural zeolites and bentonites. Desalin Water Treat 232:244–255. https://doi.org/10.5004/dwt.2021.27349

Bakalár T, Kaňuchová M, Girová A, Pavolová H, Hromada R, Hajduová Z (2020) Characterization of Fe(III) adsorption onto zeolite and bentonite. Int J Environ Res Public Health 17: 5718. https://doi.org/10.3390/ijerph17165718

Bang H, Yoon S, Jeon H (2020) Application of machine learning methods to predict a thermal conductivity model for compacted bentonite. Annals Nucl Energy 142: 107395. https://doi.org/10.1016/j.anucene.2020.107395

Bergaya F, Theng BKG, Lagaly G (2006) Handbook of Clay Science. Elsevier, Amsterdam.

Bieseki L, Bertella F, Treichel H, Penhad FG, Pergher SBC (2013) Acid Treatments of Montmorillonite-rich Clay for Fe Removal Using a Factorial Design Method. Mater Res 16: 1122–1127. https://doi.org/10.1590/S1516-14392013005000114

Castro-Castro JD, Sanabria-González NR, Giraldo-Gómez GI (2020) Experimental data of adsorption of Cr(III) from aqueous solution using a bentonite: Optimization by response surface methodology. Data Brief 28: 105022. https://doi.org/10.1016/j.dib.2019.105022

Cipra T (2013) Finanční ekonometrie. Ekopress, Praha.

Damian G, Damian F, Szakács Z, Iepure G, Aştefanei D (2021) Mineralogical and Physico-Chemical Characterization of the Oraşu-Nou (Romania) Bentonite Resources. Minerals 11:938. https://doi.org/10.3390/min11090938

Datta R, Holatko J, Latal O, Hammerschmiedt T, Elbl J, Pecina V, Kintl A, Balakova L, Radziemska M, Baltazar T, Skarpa P, Danish S, Zafar-ul-Hye M, Vyhnanek T., Brtnicky M. (2020) Bentonite-Based Organic

Amendment Enriches Microbial Activity in Agricultural Soils. Land 9:258. https://doi.org/10.3390/land9080258

Elhechi A, Amor OB, Zargouni F, Srasra E (2023) Effect of clay mineralogical composition on the structural and textural properties after hydrochloric acid treatment. Episodes. https://doi.org/10.18814/epiiugs/2022/022021.

Essebaai H, Lgaz H,·Alrashdi AA, Habsaoui A,· Lebkiri A, Marzak S, Rifi EH (2022) Green and eco-friendly montmorillonite clay for the removal of Cr(III) metal ion from aqueous environment. Int J Environ Sci Technol 19:2443–2454. https://doi.org/10.1007/s13762-021-03303-4

Gelman, A. (2008). Variance, Analysis Of. In: The New Palgrave Dictionary of Economics. Palgrave Macmillan, London. https://doi.org/10.1057/978-1-349-95121-5_2402-1

Henn U, Schultz-Güttler R. (2012) Review of some current coloured quartz varieties. J Gemmology 33:29–43.

Hussin F, Aroua MK, Daud WMAW (2011) Textural characteristics, surface chemistry and activation of bleaching earth: A review. Chem Eng J 170:90–106. https://doi.org/10.1016/j.cej.2011.03.065

Kashani Motlagh MM, Youzbashi AA, Amiri Rigi Z (2011) Effect of acid activation on structural and bleaching properties of bentonite. Iran J Mater Sci Eng 8(4):50–56.

Kiani F, Mazloom G, Ghani M, Banisharif F (2022) Acid-modified mineral bentonite as catalyst for efficient furfural formation from glucose. Biomass Conv Bioref. https://doi.org/10.1007/s13399-022-03243-0

Li WB, Liu Z, Meng ZF, Ren S, Xu E, Zhang Y, Wang MY (2016) Composite modification mechanism of cationic modifier to amphoteric modified kaolin and its effects on surface characteristics. Int J Environ Sci Technol 13:2639–2648. https://doi.org/10.1007/s13762-016-1091-3

Madejová J, Pálková H, Jankovič Ľ (2012) Degradation of surfactant-modified montmorillonites in HCl. Mater Chem Phys 134:768–776. https://doi.org/10.1016/j.matchemphys.2012.03.067

Montgomery DC (2019) Design and Analysis of Experiments. Wiley, New York.

Önal M, Sarıkaya Y (2007) Preparation and characterization of acid-activated bentonite powders. Powder Technol 172:14–18. https://doi.org/10.1016/j.powtec.2006.10.034

Rossman GR (1994) Colored varieties of the silica minerals. In: Peter J. Heaney, Charles T. Prewitt Gibbs GV (eds) Silica: Physical Behavior, Geochemistry, and Materials Applications, De Gruyter, Berlin, Boston, pp 433-468. https://doi.org/10.1515/9781501509698-018

Sharma S, Sarasan G (2017) Influence of Acid Activation on Natural Calcium Montmorillonite Clay. IOSR J Appl Chem 10:71–77. https://doi.org/10.9790/5736-1006027177

Sukhadeorao Dongre R (2020) Reinforce Fabricated Nanocomposite Matrixes for Modernization of S & T in New Millennium. Composite and Nanocomposite Materials - From Knowledge to Industrial Applications. IntechOpen. http://dx.doi.org/10.5772/intechopen.91305.

Škvarlová A, Kaňuchová M, Kozáková Ľ, Bakalár T, Oravcová A, Škvarla J. (2020) XPS (X-ray photoelectron spectroscopy) study of removing iron ions from water by zeolite and bentonite. Inżynieria Mineralna 2:201–204. http://doi.org/10.29227/IM-2020-01-67

Tebeje A, Worku Z, Nkambule TTI, Fito J (2022) Adsorption of chemical oxygen demand from textile industrial wastewater through locally prepared bentonite adsorbent. Int J Environ Sci Technol 19: 1893–1906. https://doi.org/10.1007/s13762-021-03230-4

Temuujin J, Jadambaa T, Burmaa G, Erdenechimeg S, Amarsanaa J, MacKenzie K (2004) Characterisation of acid activated montmorillonite clay from Tuulant (Mongolia). Ceram Int 30:251–255. https://doi.org/10.1016/S0272-8842(03)00096-8

Tsakiri D, Douni, Taxiarchou M (2022) Structural and Surface Modification of Oxalic-Acid-Activated Bentonites in Various Acid Concentrations for Bleaching Earth Synthesis—A Comparative Study. Minerals 12:764. https://doi.org/10.3390/min12060764

Vuković Z, Milutović A, Rožić L, Rosić A, Nedić Z, Jovanović D (2006) The influence of acid treatment on the composition of bentonite. Clays Clay Miner 54:697–702. https://doi.org/10.1346/CCMN.2006.0540605

Yarmots GA, Yarmots LP (2018) Natural Sorbents in Agriculture. Adv Eng Res 151:795–801. https://doi.org/10.2991/agrosmart-18.2018.149

Yener N, Biçer C, Pekdemir AD, Sarıkaya Y, Önal M (2020) Preparation and characterization of nanoporous powders from bentonite by hydrochloric acid leaching and using as bleaching earth. SN Appl Sci 2:717. https://doi.org/10.1007/s42452-020-2545-2

Yildiz A, Kuscu M (2004) Origin of the Basoren (Kutahya, W Turkey) bentonite deposits. Clay Miner 39:219–231. https://doi.org/10.1180/0009855043920132

Yildiz N, Aktas Z, Calimli A (2004) Sulphuric Acid Activation of a Calcium Bentonite. Part. Sci. Technol. 22:21–33. https://doi.org/10.1080/02726350490422392

Yoon S, Kim M, Park S, Kim G (2021) Thermal conductivity prediction model for compacted bentonites considering temperature variations. Nucl Eng Technol 53:3359–3366. https://doi.org/10.1016/j.net.2021.05.001