DOI: 10.7251/JEPMEN1507037M
UDK: 552.527
Scientific paper

ACID ACTIVATION OF PRRENJAS CLAY MINERAL

Altin Mele[1], Krenaida Taraj[2], Arjan Korpa[1]
altin.mele@fshn.edu.al

[1]*University of Tirana, Faculty of Natural Sciences, 1016 Tirana, Albania*
[2]*Albanian University, Rruga "Kajo Karafili", Faculty of Medicine, 1016 Tirana, Albania*

Abstract

Prrenjas clay mineral is found in southeast Albania and has a high content on bentonite. The influence of the sulphuric acid activation on the composition, structure and surface properties of Prrenjas clay mineral is investigated in this study by means of elemental chemical analysis, X-Ray Diffractometry, IR Spectroscopy and gas adsorption-desorption measurement. H_2SO_4 *concentrations of 0.143 M, 0.232 M, 0.371 M, 0.537 M, 0.734 M, 0.927 M and 1.456 M were used in the treatment of samples. The treatment by increasing the acid concentration brings the leaching of* Al^{3+}, Fe^{2+}, Mg^{2+} *from the clay structure. The specific surface area and the pore volume of the clay samples increases respectively from 83* m^2/g *and 0.069* cm^3/g *for the untreated clay to 420* m^2/g *and 0.384* cm^3/g *for the clay mineral treated with 1.456 M* H_2SO_4 *solution. New mesopores were created during the acid activation mainly in the range of 2 – 8 nm. For the samples treated with 0.927 M and 1.456 M solutions the increase in specific surface area and pore volume is very high. The cationic exchange capacity decreases steadily with the concentration of* H_2SO_4 *used for the treatment.*

Keywords: *clay mineral, acid activation, surface properties*

1. INTRODUCTION

Clay minerals are natural products of a wide range of applications. Their surface properties as specific surface area (SBET) and pore volume (V) and the cation exchange capacity (CEC) are the main parameters promoting their broad application in many industries. Clay minerals are use as catalysts [1 -3], catalyst carriers [4 – 6] and also in the beverage technology [7].

Nanotechnology, environment protection and water purification are promising future application fields of clay minerals. Bentonites are use in their natural or modified form (after acid, alkali, organic or thermal treatment). The acid modification, known as acid activation, has been investigated by several authors using hydrochloric acid [8-11] or sulfuric acid [12-15], to change the surface properties and smectite structure of the bentonites influencing their adsorption and catalytic properties [8,12].

This study was focused on the optimization of the sulfuric acid activation process in order to improve the surface properties of the Prrenjas clay mineral by preserving the CEC.

2. EXPERIMENTAL PART

2.1. Materials and methods

Clay mineral from Prrenjas region in southeast Albania (bentonite) were treated with sulfuric acid (96%, Fluka) solutions of different molar concentrations of 0.143 M, 0.371 M, 0.734 M, 0.927 M and 1.456 M. The impurities were separated by decantation.

Typically, 10 g of bentonite were dispersed in 1 L of distilled water and left to precipitate for 24 h. A fraction was separated, which corresponds to 2/3 of the height of the upper limit and left to dry in air. Such prepared bentonites were labeled P/M, P denote Prrenjas bentonite whereas M is the molarity of H_2SO_4, respectively (P/0.143, P/0.371, P/0.734, P/0.927 and P/1.456).

2.2. Acid activation

For the H_2SO_4 acid treatment, 5 g of previously purified Prrenjas bentonite was dispersed in 50 mL of 0.143 M, 0.371 M, 0.734 M, 0.927 M and 1.456M H_2SO_4. The dispersion was heated for 3 hours at 90ºC under stirring as shown in the figure 1 and flushed with distilled water to a negative reaction to the sulfate ion, which was checked by $BaCl_2$. The bentonites were dried at room temperature.

2.3. Characterization

Chemical analyses were performed second the ASTM C114 standard [16], where the procedures for the determination of the oxides SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, SO_3 are described. Cation exchange capacity (CEC) was determined by the methylene blue (MB) adsorption method. For that 100 cm^3 of distilled water and 0.5 g dried clay mineral are mixed under stirring in an Erlenmeyer flask. The dispersion is titrated with a MB 12.5 mM solution and MB cation is exchanged for the other cations in between of the clay layers. The equilibrium is controlled through the color of solution in contact with the clay as described in detail in [17].

The bentonite mineral composition was checked by X-ray powder diffraction (XRD) employing the SIEMENS D5000 automated system. The diffractograms were recorded using Cu Kα = 1.5406 Å radiation, setting the current of 20 mA and voltage of 35 kV (Ni filter). X-ray powder diagrams were collected in the 2θ range from 3 to 80º.

FT-IR spectra were recorded on a Thermo Scientific Nicolet 6700 (ATR) in the 4000–400 cm^{-1} region.

Specific surface area tests were undertaken by determining the adsorption and desorption nitrogen isotherms at liquid nitrogen temperature (−196ºC). Before measurement, the sample was degassed at 120ºC and vacuumed over 24 hours. The achieved vacuum was measured with a Pirani vacuum gauge (measurement range 0.001 − 1 mbar). The analysis entailed determination of the sample specific surface area using the BET equation. Pore volume was determined based on the Gurwitsch's rule, from the volume of liquid nitrogen adsorbed at the equilibrium pressure p = 920 mbar in the adsorption isotherm.

3. RESULTS AND DISCUSSION

3.1. Variation of chemical composition with the H_2SO_4 activation

Table 1 shows the chemical composition and CEC of untreated and treated bentonites with 0.143 M, 0.371 M, 0.734 M, 0.927 M and 1.456 M H_2SO_4 solutions. By increasing the sulfuric acid concentration there was an increase in SiO_2 content. The bentonite activation caused an increase of the SiO_2 content due to remobilization of octahedral cations [18]. Octahedral cations shifted into the solution while the silicon, owning to its insolubility, remained and increased its content with the H_2SO_4 concentration. The SiO_2 to the sum of the other metal oxides ratio ($SiO_2/\Sigma M_xO_y$) increases from 1.239 to 4.073. One can observe from these analyses that the increase of sulfuric acid molarity provoked flushing of the interlayer cations Ca^{2+} and Mg^{2+} whose positions are occupied by the H^+ ions. With the raise of sulfuric acid concentration the clay mineral shows a gradual decrease of the cation exchange capacity (CEC) from 82.5 to 45.5 mmol(eq)/100 g.

Impact of acid on structural characteristics XRD of the Prrenjas clay mineral is shown in Figure 2. The clay mineral displays peaks belonging to the mineral montmorillonite and non-clay mineral quartz (Figure 2). Is shown that the sulfuric acid activation of bentonite caused evident structural changes. The intensity of the indexed peaks (001), (003) and (006) was reduced with the increase of H_2SO_4 concentration treatment with 6 M acid.

The XRD showed gradual dissolving of the octahedral sheets by treatment with 0927 M and 1.456 M of H_2SO_4. The disappearance of the M (001) peak shows the exfoliation of the mineral.

The structural changes that evolve the Prrenjas clay mineral samples are monitored by FTIR spectroscopy (Figure 3). The spectra show changes in the 4000–400 cm^{-1} region as described in previous papers [1, 15, 19, 20]. Namely, the most intensive band at 977 $cm^{-}1$ is attributed to Si–O stretching vibrations of the tetrahedral sheets, have not been affected by acid treatment.

The band Si-O-Al (500 – 520 cm^{-1}) is the most sensitive one indicating the remaining Al^{3+} in the octahedral sheets. It decreases steadily with the increase of acid concentrations showing the leaching of Al^{3+}. The bands of the region 600 – 700 cm^{-1} shows vertical vibrations of cations (R-O-Si) in the octahedral sheets with (R = Al, Mg, Fe) and also disappears after treatment with high acid concentration. In 1632 cm^{-1} and its overtone in 3264 cm^{-1} (overlapped by adsorptions of other vibrations which forms a broad band 3700 – 3200 cm^{-1}) there are vibrations of the water molecules of mineral. They becomes smaller with the increase of acid concentration because the mineral loses its hydrophilic cations. The adsorption in 3660cm^{-1} is explained by vibrations of OH groups coordinated cations of Fe^{2+}, Al^{3+} and Mg^{2+}, and almost disappears with the increasing acid concentration.

3.2. Impact of acid on the surface properties of Prrenjas clay mineral

The adsorption isotherms given as a share of the adsorbed nitrogen in the function of the relative pressure (at −196ºC) are shown in Figure 4. The specific surface area of Prrenjas clay mineral rises with the increase of molarity of the H_2SO_4. Based on the presented adsorption isotherms, the specific surface area of untreated and treated clay samples was calculated using the BET equation. The obtained values are shown in Table 2. In Prrenjas clay mineral there is a considerable change in the specific surface area and porosity specially after the treatment with 0.927 M and 1.456 M H_2SO_4. Differences occur due to the change in the montmorillonite structure and the same changes were observed in the XRD and IR analyses.

4. CONCLUSION

According to structural and textural characteristics, the Prrenjas clay mineral untreated or treated with H_2SO_4 acid, due to its large surface area, can be used as good adsorbents and catalysts in many industries. Acid activation increased the surface area of the clay samples examined up to 420 m^2/g. With the change of the chemical composition, structural and textural characteristics of sheets, a high specific surface area was created and a low cation exchange capacity was observed. Acid processing caused a quick loss of exchangeable Ca^{2+} and Mg^{2+} from the solid phase.

Using higher concentration of acid than 0.734 M, the removal of further Mg^{2+} and Al^{3+} and Fe^{2+} from octahedral sites leads to an increase of amorphous Si. It was concluded that reducing the layer charge occurred with decreasing cation exchange capacity and follows an increase in specific surface area and pore volume with increasing acid concentration.

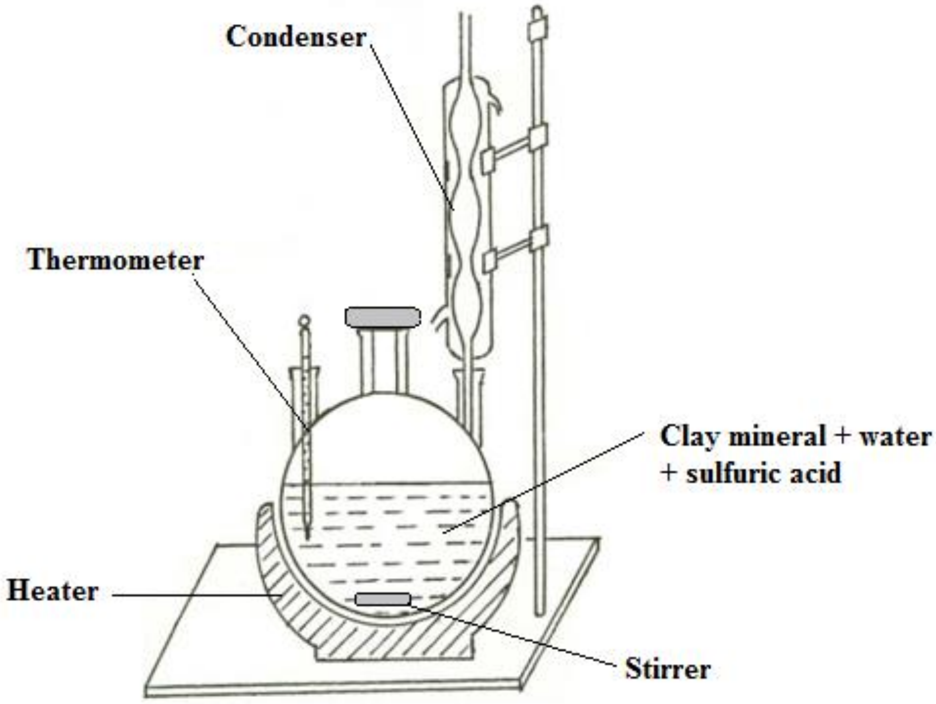

Figure 1. Schematic design of the acid activation appratus.

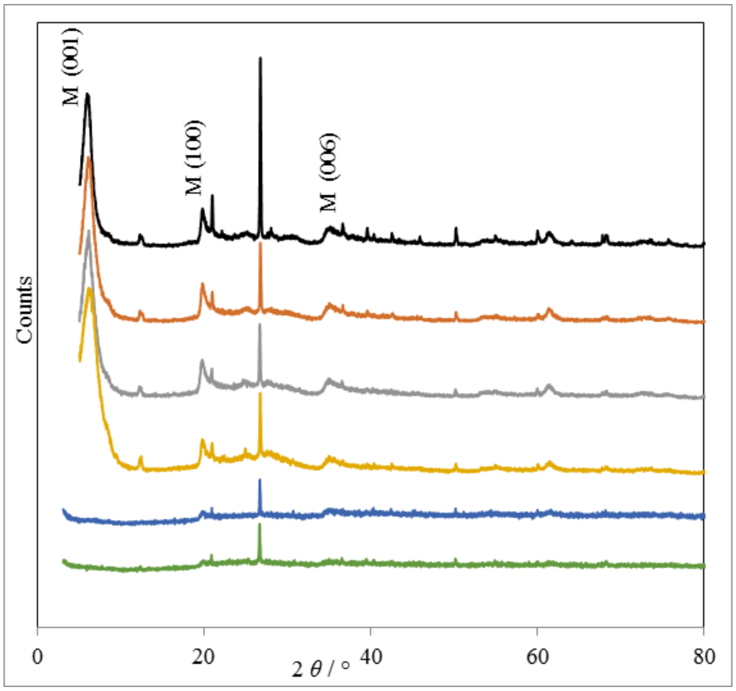

Figure 2. XRD diagrams of untreated Prrenjas clay mineral (top) and P/0.143, P/0.371, P/0.734, P/0.927 and P/1.456 M respectively in the top-down order. The letter M is for identifying the montomillonite peaks, the peak at 2θ=26° belongs to quartz impurities.

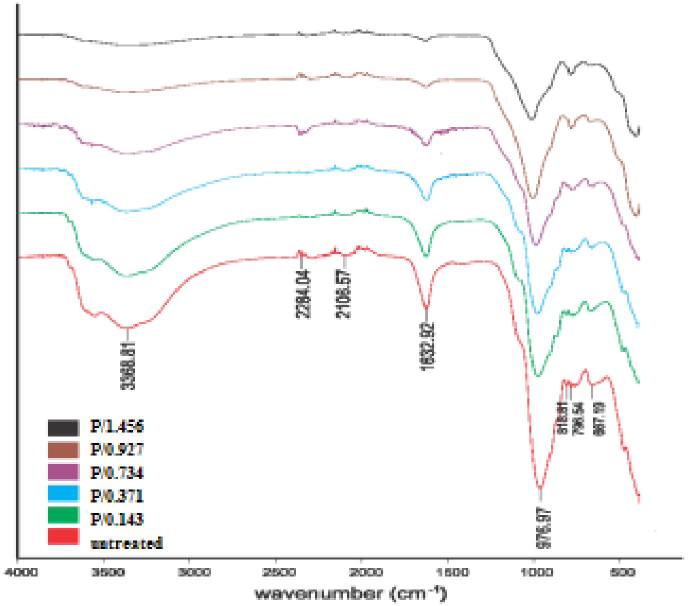

Figure 3. FT-IR spectra of the untreated (down) and H_2SO_4 treated Prrenjas clay mineral P/0.143, P/0.371, P/0.734, P/0.927, P/1.456 M respectively in the down-top order.

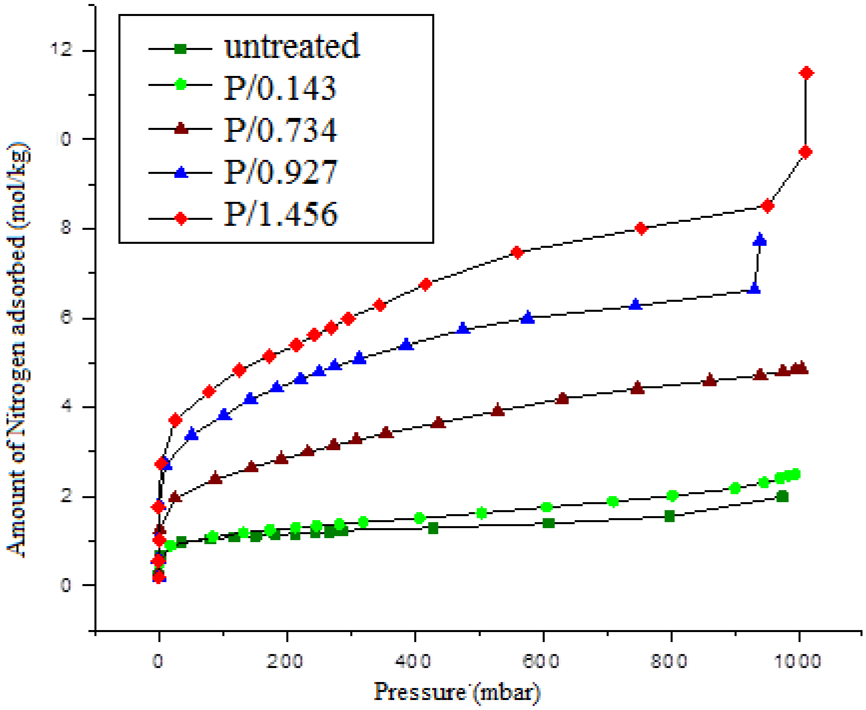

Figure 4. adsorption isotherms of nitrogen at T=77 K on untreated and H_2SO_4 activated Prrenjas clay mineral samples.

Table 1. Chemical composition (wt. %), ratio SiO_2 to the sum of other metal oxides content and CEC (mmol(eq)/100 g) of untreated and H_2SO_4 treated Prrenjas clay mineral

Clay mineral	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	SiO_2 / ΣM_xO_y	CEC
untreated	47.05	13.4	14.97	2.7	9.58	0.11	1.239	82.5
P/0.143	47.49	12.52	15.53	0.85	7.83	0.15	1.323	74.25
P/0.371	49.15	9.55	16.04	0.96	7.12	0.23	1.502	68.75
P/0.734	51.74	9.31	14.16	0.89	6.10	1.15	1.901	65.25
P/0.927	59.26	6.95	10.11	0.55	4.97	0.12	2.429	57
P/1.456	65.54	6.82	5.32	1.10	3.95	0.35	4.073	45.5

Table 2. Specific surface area and pore volume for untreated and H_2SO_4 treated Prrenjas clay mineral samples

Prrenjas clay mineral samples	*Specific surface area (m^2/g)*	*Pore volume (cm^3/kg)*
untreated	*83.75*	*69.27*
P/0.143	*110.4*	*86.2*
P/0.371	*200*	*128*
P/0.734	*265*	*200*
P/0.927	*380*	*325*
P/1.456	*420*	*384*

REFERENCES

[1] Steudel, L.F. Batenburg, H.R. Fischer, P.G. Weidler, K. Emmerich, Appl. Clay Sci. 44, 2009, 105–115.

[2] J.M. Adams, Appl. Clay Sci. 2, 1987, 309–342.

[3] A. Vaccari, Appl. Clay Sci. 14, 1999, 161–198.

[4] W. Teng-You, P. Yuan-Feng, L. Guo-Qing, T. Zhang-Fa, X. Hui-Ning, Environ. Eng. Sci. 27, 2010, 531–535.

[5] C.N. Rhodes, M. Franks, G.M.B. Parkes, D.R. Brown, J. Chem. Soc. Chem. Comm. 12, 1991, 804–807.

[6] C.N. Rhodes, D.R. Brown, J. Chem. Soc. Faraday Trans. 88, 1992, 2269–2274.

[7] G.E. Christidis, P.W. Scott, A.C. Dunham, Appl. Clay Sci. 12, 1997, 329–347.

[8] J. Ravichandran, B. Sivasankar, Clays Clay Miner. 45, 1997, 854–858.

[9] P. Komadel, D. Schmidt, J. Madejova, B. Čičel, Appl. Clay Sci. 5, 1990, 113–122.

[10] J. Madejova, J. Budjak, M. Janek, P. Komadel, Spectrochim. Acta A 54, 1998, 1397–1406.

[11] H. Palkova, J. Madejova, D. Righi, Clays Clay Miner. 51, 2003, 133–142.

[12] P. Komadel, M. Janek, J. Madejova, A. Weekes, C. Breen, J. Chem. Soc. Faraday Trans. 93, 1997, 4207–4210.

[13] C. Breen, J. Madejova, P. Komadel, J. Mater. Chem. 5, 1995, 469–474.

[14] H.N.M. Onal, Y. Sarikaya, Food Chem. 105, 2007, 156–163.

[15] B. Tyagi, C.D. Chudasama, R.V. Jasra, Spectrochim. Acta A 64, 2006, 273–278.

[16] ASTM Standard C114. http://www.astm.org/Standards/C114.htm

[17] Kahr, G. and F.T. Madsen. Applied Clay Sci., 9, 1995, 327-336.

[18] J.L. Venaruzzo, C. Volzone, M.L. Rueda, J. Ortiga, Micropor. Mesopor. Mater. 56, 2002, 73–80.

[19] V.C. Farmer (Ed.), The Infrared Spectra of Minerals, Mineralogical Society, London,1974, pp. 331–358.

[20] K. Emmerich, F.T. Madsen, G. Kahr, Clays Clay Miner. 47 (1999) 591–604.