MODIFICATION OF SMECTITE STRUCTURE BY SULFURIC ACID AND CHARACTERISTICS OF THE MODIFIED SMECTITE

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Abstract: Bentonite samples from Petrovac and Aleksinac were treated with sulfuric acid of different molarities. Differences in structure and texture of the initial and modified bentonite were determined by chemical analysis and X-raypowder diffraction (XRPD), infra-red spectroscopy (FTIR), scanning electron microscopy (SEM) and physisorption nitrogen at $-196°C$. Sulfuric acid caused an exchange of Al^{3+}, Fe^{3+} and Mg^{2+} with H^+ ions which led to a modification of the smectite crystalline structure. The Mg and Fe substitution in the octahedral sheet promoted the dispersion of those layers and forming of amorphous silicon. The sequence according to which the cations left the octahedral sheets was as follows: $Mg^{2+}>Fe^{3+}>Al^{3+}$. The sulfuric acid activated bentonites exhibiting a lower cation exchange capacity (CEC) and a change of specific surface area (S_{BET}) from 6 to 387 for bentonite from Petrovac and from 44 to 1784 m^2 g^{-1} for bentonite from Aleksinac, positioning them as an excellent absorber in wine technology and in the protection of soil and environment.

Key words: bentonite, acid activation, smectite, cation exchange capacity, specific surface area.

Introduction

Bentonite clay has various applications in the protection of soil and environment. It is used to protect land from erosion, stabilization and reclamation of infertile land and landfill, soil protection from pollution, detoxification of drinking water, purification of waste water and wine technology, etc. (Bergaya et al., 1996).

Two types of octahedral sheets occur in smectites: the dioctahedral type, where two-thirds of the octahedral sites are occupied mainly by trivalent cations, e.g. Al (III) or Fe (III), and the trioctahedral type, with most of the sites occupied by divalent cations, e.g. Mg (II). The negative charge of the layers is balanced by hydrated exchangeable cations in the interlayers (mostly Ca^{2+}, Mg^{2+}, Na^+). The variable chemical composition influences the layer charge, CEC, S_{BET} and pore volume (V), which is why the clay minerals have such a broad application (Christidis et al., 1997).

Acid modified natural bentonites are the subject of many studies and papers (Bergaya and Lagaly, 2001; Carrado and Komadel, 2009; Madejová et al., 2009; Amari et al., 2010). The first step in modifying the clay mineral structure with acid is a separation of exchangeable cations from protons. The second step is flushing Al, Mg and Fe from octahedral and tetrahedral sheets, in the way that SiO_4 groups of tetrahedral sheets remain mostly intact. Increasing of the specific surface area is an important physical change (Kheok and Lim, 1982; Morgan et al., 1985; Taylor et al., 1989; Rhodes and Brown, 1992; Christidis et al., 1997; Komadel, 2003) which is a function of the structure and removal of octahedral sheets (Madejová et al., 1998; Komadel and Madejová, 2006, Tyagi et al., 2006). The focus of this study was the modification of bentonite with sulfuric acid while keeping the layered structure and developing a large specific surface area as well as retaining CEC.

Materials and Methods

Two dioctahedral smectites, extracted from bentonite from Petrovac and Aleksinac, were treated with sulfuric acid of different molarities. Bentonite particles not exceeding 2μm were separated by the decantation method. Typically, 10 g of bentonite were dispersed in 1l of distilled water and left to precipitate for 24hrs. A fraction which corresponds to 2/3 of the height of the upper limit was separated, centrifuged for 5 minutes at 5000 revolutions/minute and left to dry in air.

Such prepared bentonites were labeled MP and MA where M is the molarity of H_2SO_4 (1.5MP, 3MP, 4.5MP, 6MP and 1.5MA, 3MA, 4.5MA, 6MA). The untreated bentonites were labeled P (bentonite from Petrovac) and A (bentonite from Aleksinac). For the H_2SO_4 acid treatment 5g of previously purified P and A bentonite was separated and dispersed in 50 ml of 1.5M, 3M, 4.5M and 6M H_2SO_4 (98% Zorka Šabac). The solid/liquid phase ratio was 1:10. The dispersion was heated for 2hrs at 85°C, centrifuged and flushed with distilled water to a negative reaction to the sulfate ion, which was checked using $BaCl_2$

The bentonite mineral composition was determined using an X-ray powder diffractometer which is a part of the SIEMENS D500 automated system. The diffractograms were obtained with Cu Kα = 1.54184 Å radiation, with a current of 20 mA and voltage of 35 kV, with a Ni filter.

FT-IR spectra were recorded on a Perkin Elmer model 597 in the 4000-400 cm^{-1} region using the KBr pellet method (2 mg of sample dispersed in 200 mg KBr). Chemical analyses were done using the atomic absorption spectrophotometry method (AASF), by a flame technique, on an AAS 4000 Perkin Elmer and the CEC was determined by ammonium acetate method, pH 7.0. Changes in particle morphology were observed with scanning electron microscope using a JEOL JSM-6610LV connected with an INCA350 energy-dispersion X-ray (EDX).

The specific surface area was determined using the adsorption and desorption nitrogen isotherms, at liquid nitrogen temperature ($-196°C$). Before measurement, the sample was degassed at 120°C and vacuumed for more than 24 hrs. Analysis of results involved the determination of specific surface area of the sample using the BET equation.

Results and Discussion

Chemical characteristics of bentonite

The CEC and chemical analyses of untreated and treated (P and A) bentonites with 1.5, 3, 4.5 and 6M H_2SO_4 are shown in Table 1. With the increase of concentration of sulfuric acid both bentonites showed a gradual decrease of the CEC until dissolving with 4.5M acid. In treatment with 6M H_2SO_4 acid, as the SiO_2 content decreased, an increase of CEC was observed in comparison with the CEC of samples treated with 4.5M.

Table 1. Chemical analysis (wt. %), CEC (mmoleq 100 g^{-1}) and the specific surface area (m^2 g^{-1}) of untreated and treated bentonite from Petrovac (P) and Aleksinac (A).

S*	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	Si/(Al + Fe + Mg)	CEC	S$_{BET}$
P	68.6	12.44	1.26	2.16	1.16	1.99	1.07	4.32	60	6
1.5P	82.3	7.36	0.84	1.58	1.09	1.15	0.77	8.41	52	84
3P	87.9	3.87	0.73	0.91	0.74	0.85	0.22	15.95	28	120
4.5P	92.9	3.12	0.69	0.42	0.31	0.81	0.78	21.96	15	341
6P	92.6	3.30	0.70	0.50	0.42	0.86	0.83	20.57	18	387
A	60.5	16.72	1.21	4.17	2.72	0.36	0.14	2.73	89	44
1.5A	78.2	7.84	0.43	1.59	1.54	0.12	0.06	7.93	72	116
3A	91.5	1.98	0.29	0.32	1.25	0.05	0.02	35.27	14	1784
4.5A	96.5	0.45	0.14	0.13	1.26	0.05	0.02	134.02	8	1223
6A	96.2	0.94	0.14	0.15	1.27	0.08	0.04	78.21	15	799

*Sample; CEC-cation exchange capacity; S$_{BET}$-specific surface area.

By increasing the sulfuric acid concentration from 1 to 4.5M in both bentonites, there was an increase in SiO_2 content and at a concentration of 6M it

slightly decreased. The same behavior is observed in the ratio of Si/(Al + Fe + Mg) which increased in both bentonites until treatment with 4.5M, and with 6M it decreased. Bentonite activation with sulfuric acid caused an increase of the SiO_2 content due to remobilization of octahedral cations (Venaruzzo et al., 2002; Carrado and Komadel, 2009; Amari et al., 2010). Octahedral cations shifted into the solution while the silicon, owning to its insolubility, remained and its content increased with the increase of H_2SO_4 concentration.

After the treatment with 6M, the Al_2O_3 content decreased by 73.17%, Fe_2O_3 content by 44.44% and MgO content by 95.68% for P bentonite. For A bentonite greater dissolving occurred so the Al_2O_3 content decreased by 94.55%, Fe_2O_3 by 88.42% and MgO by 96.4%. One can observe from these analyses that with the increase of molarity the interlayer cations Ca^{2+}, Na^+ and K^+ are also flushed and their places are left to H^+ ions.

Structural characteristics of bentonite

XRPD analysis showed that P bentonite contains montmorillonite, cristobalite, quartz and traces of muscovite and feldspar, bentonite, while A contains montmorillonite, impurities of quartz, and traces of muscovite, feldspar and kaolinite. Untreated bentonites were recorded as an air dry sample (AD), saturated with ethylene glycol (EG) and samples heated at 550°C as shown in Figure 1.

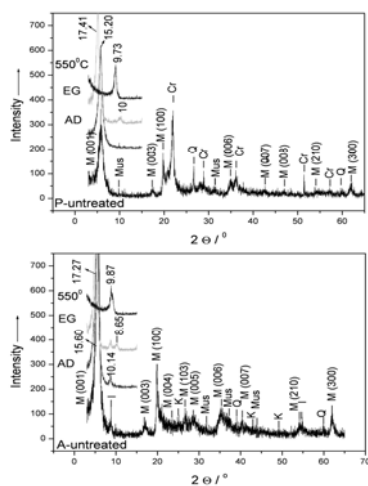
Figure 1. X-ray powder diffraction of untreated bentonite from Petrovac (P) and Aleksinac (A). The detected minerals are as follows: M-montomillonite, Mus-muscovite, Cr-cristobalite, Fl-feldspar, Q-quartz, I-illite, K-kaolinite. The peak arising from (001) planes (Å) of P and A treated bentonites (AD-air dry; EG-saturated ethylene glycol, 550°C-heated to 550°C).

The most intense peak of P bentonite $d_{(001)}$ was registered at 5.821° (2Θ), which corresponds to the interlamellar distance of 15.20 Å, while the main corresponding reflection in A bentonite diagram corresponds to interlamellar distance of 15.60 Å. After the saturation with ethylene glycol both reflections $d_{(001)}$ (P-EG and A-EG) showed an increase in the interlamellar distance to 17.41 Å and 17.27 Å in P and A bentonite, respectively. By heating at 550°C, the position of $d_{(001)}$ peak resulted in collapse of the interlamellar distance to 9.73 Å for P and 9.87 Å for A bentonite that corresponds to smectites i.e. montmorillonite with two layers of water in the interlayer space (Christidis et al., 1997; Calarge et al., 2003; Komadel, 2003).
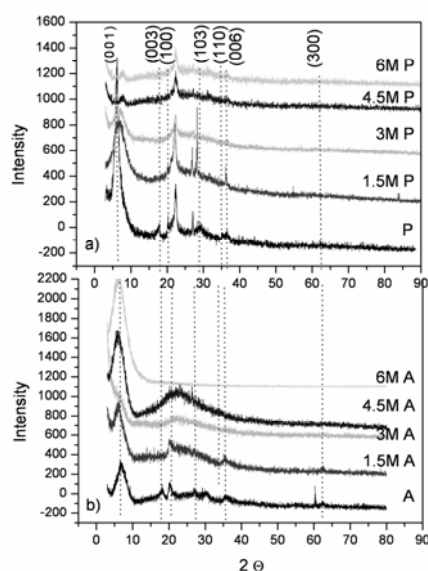

Figure 2. X-ray powder diffraction of the untreated and treated bentonites from Petrovac (a) and Aleksinac (b) with different H_2SO_4 acid molarities.

The intensity of the reflections (001), (003) and (300) in P bentonite was reduced with the increase of H_2SO_4 concentration, whereas the intensity of the peaks termed (100) and (006) increased (Figure 2). The intensity of the reflection indexed as (001), (003) and (300) in P bentonite decreases with increasing concentration of H_2SO_4, while the intensity of the peaks (100) and (006) increases. Also, the background increased due to an increasing amount of amorphous SiO_2 between 17 and 30° released by dissolving the octahedral sheet. Tetrahedral sheets in the montmorillonite structure of P bentonite remained unchanged after the treatment with 6M acid.

The X-ray of A bentonite showed gradual dissolving of the octahedral sheets by treatment with 1.5 to 3M H_2SO_4. The intensity of the reflections (001), (003), (100) and (300) decreases with increasing molarity of H_2SO_4. Surprisingly, the sample treated with 4.5MA acid, promotes a sudden increase of intensity and crystallinity of the main $d_{(001)}$ peak and $d_{(110)}$ maximum. The appearance of the new peaks shows the formation of an enlarged phase and interlamellar expansion (Erena and Afsin, 2009).

FTIR spectra also show changes in the structure of bentonite P and A (Figure 3). The spectra show sharp band vibrations in the region between 1400 and 400 cm^{-1} as described in earlier papers (Farmer, 1974; Emmerich et al., 1999; Steudel et al., 2009). Positions and assignment of the vibrational bands of the dioctahedral smectites are shown in Table 2. Namely, the most intensive band at 1036 cm^{-1} and 1037 in cm^{-1} in the spectra of P and A bentonite, respectively, were attributed to Si-O stretching vibrations of the tetrahedral sheets, whereas the bands around 520 and 467 cm^{-1} are ascribed to Si-O-Al (where Al is the octahedral cation) and Si-O-Si bending vibrations, respectively (Madejová et al., 1998).

Table 2. Wavenumbers and assignment of the bands in the IR spectra of the untreated dioctahedral smectites from Petrovac (P) and Aleksinac (A).

Maxima (cm^{-1})		Assignment
P	A	
3623	3620	OH stretching
3442	3431	OH stretching from H_2O
1641	1637	OH bending from H_2O
1088	/	Si–O stretching vibration (out-of-plane)
1036	1037	Si–O stretching vibration (in-plane)
915	916	Al–Al–OH bending
874	/	Al–Fe–OH bending
841	843	Al–Mg–OH bending
794	793	Cristobalite
692	695	Quartz
623	625	R–O–Si with R = Al, Mg, Fe (Li)
519	521	Si–O–Al vibration (Al octahedral cation)
467	467	Si–O–Si bending vibration

In treated P bentonite samples this absorption band R-O-Si (622.9 cm^{-1}) remains after treatment with 6M sulfuric acid (Figure 3). In bentonite 4.5M A band with 624.8 cm^{-1} changes to bending but remains after the treatment with 6M H_2SO_4 acid. This reflects the very high, but still incomplete dissolving of the montmorillonite structure in this bentonite (Madejová et al., 1998; Tyagi et al., 2006).

The intensity of Al-Mg-OH bands (near 840 cm^{-1}) very quickly decreases with the increase of the acid concentration. In A bentonite the intensity of this band is considerably smaller in comparison with P bentonite during the acid treatment. The intensity of Al-Al-OH bands (915 cm^{-1}) gradually decreases with the increase of the acid concentration and remains constant in both bentonites after treatment with 6M (Figure 3). The Al-Fe-OH band, during the treatment, is considerably weaker compared to Al-Al-OH and Al-Mg-OH counterparts.
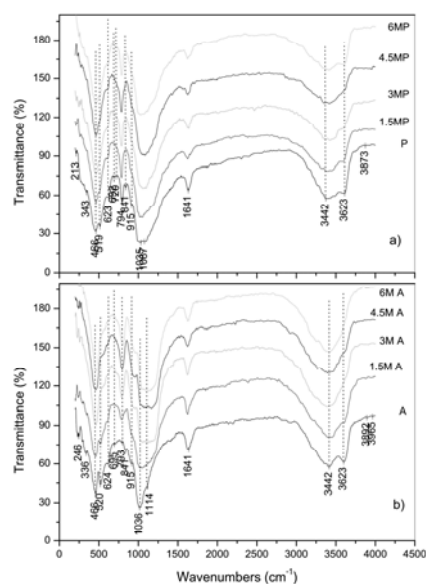

Figure 3. Infra-red spectra of the untreated and treated bentonites from Petrovac (a) and Aleksinac (b) with different H_2SO_4 acid molarities.

Such changes of bands intensity indicate the leaching of substituted Mg and Fe cations in the octahedral sheets with increasing concentration of acid. The Al-Mg-OH band intensity quickly decreases in comparison with the intensity of Al-Fe-OH bands. The reduction of intensities points out quicker flushing of Mg^{2+} compared to Fe^{2+} cations from tetrahedral sheets.

Textural characteristics of bentonite

The adsorption-desorption isotherms given as a share of the adsorbed nitrogen in the function of the relative pressure (at −196°C) are shown in Figure 4. The specific surface area of P bentonite increases with the increase of molarity of the H_2SO_4, whereas for A bentonite somewhat different changes occur. The isotherms

have a shape which, according to the IUPAC classification (Kaneko et al., 1992), belongs to type IV. Clear hysteresis loops are noticeable on the isotherms which indicate that the adsorption and desorption processes do not occur in the same manner (Sing et al., 1985; Amari et al., 2010).
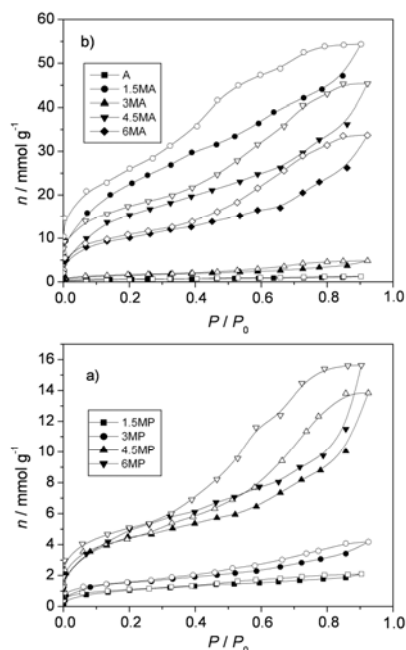

Figure 4. The adsorption isotherms of nitrogen on the untreated and treated bentonites from Petrovac (a) and Aleksinac (b) (solid symbols-adsorption, empty symbols-desorption).

Based on the presented adsorption isotherms, the specific surface area of untreated and treated bentonites (P and A) was calculated, using the BET equation. The obtained values are shown in Table 1. The specific surface area decreases with acid molarity in the following manner for P bentonite: 1.5M>3M>4.5M>6M and for A bentonite: 1.5M>6M>4.5M>3M.

Amari et al. (2010), in the line with the previous results reported by Morgan et al. (1985) and Kheok and Lim (1982), state that the surface increases with the increase of acid concentration to the highest value, while in high acid concentrations the surface decreases. During bentonite activation, the edges of the sheets are opened and separated, even though the sheets remain firmly in the center as evidenced by SEM (Figure 5).
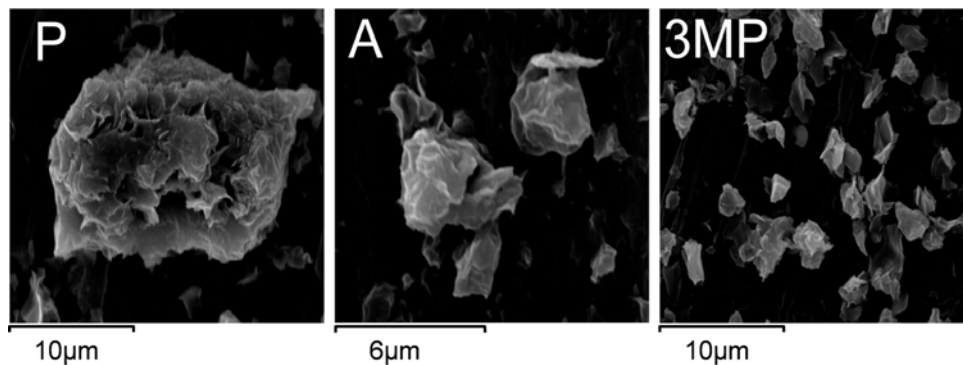
Figure 5. Scanning electron microscopy of untreated Petrovac and Aleksinac bentonite (a and b) and treated with 3M H_2SO_4 from Petrovac bentonite (c).

Conclusion

With the change of the chemical composition, structural and textural characteristics of sheets and high specific surface area were created and a low cation exchange capacity was observed. According to structural and textural characteristics, the montmorillonite from Petrovac and Aleksinac treated with H_2SO_4 acid can be used as good adsorbents in wine production and in the protection of soil and environment. It was found that montmorillonite exhibit different behavior in treatment with H_2SO_4 which depends on the content of Mg, Fe and Al in the octahedral sheets. Octahedral positions in P bentonites were abandoned according to the sequence Mg>Fe>Al. Acid processing caused a quick loss of Na, K and Ca from the solid phase. Using higher concentration of acid than 3.5 M, the removal of Al^{3+} and Mg^{2+} ions from octahedral sites led to an increase of amorphous Si. Treatment with higher acid concentration (6 M) tends to destroy the structure of the clay. Moreover, it was shown that the treatment of bentonite with higher concentrations of acid may cause the remaining Al to connect with oxygen and further connect with the H+ions, which provoke a sudden increase in the intensity of d (001) reflection. It can be concluded that the reduction of the layer charge occurred with a reduction of the CEC and was followed by an increase of the S_{BET}.

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MODIFIKACIJA STRUKTURE SMEKTITA SUMPORNOM KISELINOM I
KARAKTERISTIKE MODIFIKOVANIH SMEKTITA

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R e z i m e

Uzorci bentonita iz Petrovca i Aleksinca tretirani su različitim molaritetima sumporne kiseline. Promene u strukturi i teksturi polaznih i modifikovanih bentonita utvrđene su hemijskom i analizom rendgenske difrakcije praha X-zraka (XRPD), infra crvenom spektroskopijom (FTIR), skening elektronskom mikroskopijom (SEM) i fizisorpcijom azota na −196°C. Dejstvo H_2SO_4 kiseline izazvalo je zamenu Al^{3+}, Fe^{3+} i Mg^{2+} sa H^+ jonima što je dovelo do modifikacije kristalne strukture smektita. Supstitucija Mg i Fe u oktaedarskom listu smektita promovisala je raspuštanje tih slojeva i formiranje silikatne faze. Redosled kojim su ovi katjoni napuštali oktaedarske listove bio je sledeći: $Mg^{2+}>Fe^{3+}>Al^{3+}$. Sumpornom kiselinom aktivirani bentoniti pokazali su niži kapacitet katjonske izmene (CEC) i promenu specifične površine (S_{BET}), od 6 na 387 kod bentonita Petrovca i od 44 na 1784 m^2 g^{-1} kod bentonita Aleksinca, što ih svrstava u odlične absorbente u tehnologiji vina, zaštiti zemljišta i životne sredine.

Ključne reči: bentonit, aktiviranje kiselinom, smektit, kapacitet katjonske izmene, specifična površina.

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