

Physico-chemical variation in bentonite by sulfuric acid activation

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Abstract—The physico-chemical behavior of Iranian typical bentonite was characterized during the activation process by sulfuric acid. The main variations were studied by evaluating specific surface area, chemical and mineralogical composition, thermal gravimetric curves, Fourier transform infrared spectrometry pattern, and morphology of starting and activated samples. The effects of acid concentration, particle size distribution, activation temperature and time on specific surface area were discussed. It was found that the above parameters have significant role in the activation process. The optimum condition was also obtained for the activation of typical bentonite.

Key words: Bentonite, Specific Surface Area, Activation Temperature and Time, Montmorillonite, Illite

INTRODUCTION

Bentonite is the best known member of clay groups that contains montmorillonite crystals. The montmorillonite structure is classified as dioctahedral, having two thirds of octahedral sites occupied by trivalent cations. Dioctahedral montmorillonite has its structural charge originating from the substitution of Mg^{2+} for Al^{3+} in the octahedral sheet. The idealized structural formula for montmorillonite is $M_nH_2O(Al_{2/3}Mg_{1/3})Si_4O_{10}$ where M is a cation. The negative charge is balanced by cations intercalated between structural units. These cations may be alkali earth ions such as Ca^{2+} and Mg^{2+} or the alkaline metals such as Na^+ [1]. When Ca^{2+} cations are exclusively exchanged in montmorillonite surface, the clay is known as Ca-montmorillonite. Illite also is the second important mineral that can be found in bentonite composition having K^+ ions [2].

The application range of bentonites depends on the kinds and amounts of its montmorillonite type, other clay minerals and non-clay crystals [3]. The application of bentonites in production of selective adsorbents, bleaching earth, catalyst beds, carbonless copy paper and medication depends on the pore structures of montmorillonite [4]. If the pore diameters are smaller than 2 nm, these are called microspores. If their sizes are between 2 nm and 50 nm, these are called mesopores, and macropores if their sizes are larger than 50 nm. The adsorption capacity of the macropores is at a negligible level compared to that of the microspores and mesopores [5].

Acid-activated bentonites are usually used as adsorbent in the above applications [6]. Activation is the chemical or physical treatment applied to certain types of clay to develop their capacity to absorb coloring matters and other impurities in oils. The term of activity denotes chemical and physico-chemical reactivity whose increase is usually traceable to an increase in surface area of solids [7]. Activation of bentonite by acid is an important step for adsorption of some impurities by active clay. This is so-called "activation process." The activation of bentonite is carried out in a continuous stirred tank reactor at low temperatures between 70 and 120 °C in

the presence of activation agents, mostly sulfuric acid. During the reaction, the surface area of bentonite increases due to decomposition of smectite structure. The most significant mechanism in the activation of natural bentonite is cation exchange by H^+ ions. During the activation process, a considerable amount of cations are substituted by hydrogen cations, which increases the specific surface area. These transformations in montmorillonite and illite layers give rise to significant changes in cation exchange capacity (CEC), chemical and mineralogical characteristics of bentonite [8]. These transformations in montmorillonite layers give rise to significant changes in cation exchange capacity, chemical and mineralogical characteristics of bentonite [9]. The following parameters affected the activation process of bentonite: acid concentration, particle size distribution, activation temperature and time, chemical-mineralogical properties of natural bentonite and type of applied acid [8,10].

The aim of the present investigation was to study the variations in physico-chemical properties such as specific surface area, chemical, mineralogical and morphology changes of bentonite during the activation process by sulfuric acid. For this purpose, typical Iranian natural clay was used and the variations of above parameters were evaluated.

EXPERIMENTAL PROCEEDURE

Natural white calcium bentonite from the Zanjan region of Iran was used in the experiments. For the study of the activation process, three particle size distributions of bentonite, fine-sized (–200 mesh), middle-sized (–100 to +200 mesh) and coarse-sized (+100 mesh) were prepared by laboratory dry milling equipment. The obtained powders were dried in a laboratory oven at 105 °C. Also, sulfuric acid with different concentration from 2 to 8 M was used as activation medium. Bentonite was weighted and mixed in laboratory 2-neck flask equipped by heater and condenser. The activation process was performed at different acid concentration, activation temperatures and times.

After the activation process, the specific surface area was measured by methylene blue adsorption method. Methylene blue dye has been used to determine the surface area of clay minerals for

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several decades. Its chemical formula is $C_{16}H_{18}ClN_3S$ with a corresponding molecular weight of $319.86 \text{ g} \cdot \text{mol}^{-1}$. Methylene blue in aqueous solution is a cationic dye, $C_{16}H_{18}N_3S^+$ which is a large polar organic cation and is absorbed on the negatively charged surfaces of clay minerals. Hence, the specific surface area of particles can be determined by the amount of absorbed methylene blue. The surface area covered by one methylene blue molecule is typically assumed to be 130 \AA^2 [11,12]. The methylene blue stain test makes it possible to quantify the ionic absorption capacity of clay by measuring the quantity of needed methylene blue to cover the total external and internal surface of the clay particles contained in the clay. This testing technique was carried out based on the chemical reactions between excess negative electric charges in the clay particles and methylene blue cations released by methylene blue during its decomposition in water. The particles having the largest specific surface area and the greatest negative charge can be most rapidly exchanged. Furthermore, the absorption capacity of clay is a function of the minerals found in clay. The absorption capacity increases as a function of clay particle specific surface area and charge. The relationship between specific surface area and used methylene blue amount can be presented as follows [12]:

$$S = \frac{1}{319.87200} \frac{1}{(0.5N)A_V A_{MB}} \quad (1)$$

where S is specific surface area, N is the number of methylene blue increments added to the clay suspension solution to form a halo around soil, A_V is Avogadro's number ($6.02 \times 10^{23} \text{ molecule/mol}$), and A_{MB} is the area covered by one methylene blue molecule typically assumed to be 130 \AA^2 . The entire experimental procedure was found to give satisfactory reproducible results.

The activated samples were filtered under vacuum and the precipitates were washed with distilled water until they were free of SO_4^{2-} ions and were dried at 60°C in electrical laboratory oven. The X-ray analyses (XRF: Model S4 Explorer, XRD Model Siemens 500D) were carried out to understand chemical and mineralogical changes in bentonite. The TG curves of all the samples were obtained by thermogravimetric instrument (Model Perkin Elmer SII) at heating rate of 10°C/min and α -alumina was used as an inert material. An FTIR analysis (Model Unicam, Mattson1000) was performed to identify the chemical band variations. The morphologies of natural and activated bentonite were also analyzed by scanning electron microscopy (Model EOL. 4401).

RESULTS AND DISCUSSION

The variations of specific surface area versus acid concentration were plotted at different particle size distributions in Fig. 1. As the acid concentration rises, the value of specific surface area increases up to a maximum value, then decreases again to reach a constant value. It may be due to electrical layer around particles [13]. As the sulfuric acid concentration increases from zero to 3 M, the exchangeable cations between the montmorillonite and illite layers leave and are replaced by the hydrogen ions. Since only a small quantity of Na^+ , K^+ and Ca^{2+} of the crystals leave the layers, the increment rate of specific surface area values is slow. As the concentration of acid increases from 3 to 5 M, the K^+ , Mg^{2+} , Fe^{2+} and Al^{3+} cations dissolve easily from the montmorillonite and illite layers. Furthermore,

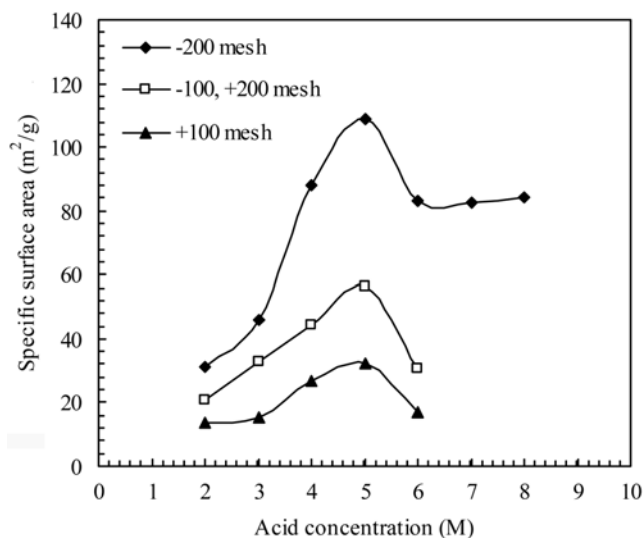


Fig. 1. The specific surface area variations with sulfuric acid concentration at different particle size distributions.

Table 1. The specific surface area of natural bentonite at different particle size distributions

Particle size distribution	-200 mesh	-100 to +200 mesh	+100 mesh
Specific surface area (m²/g)	5.2	4.8	4.3

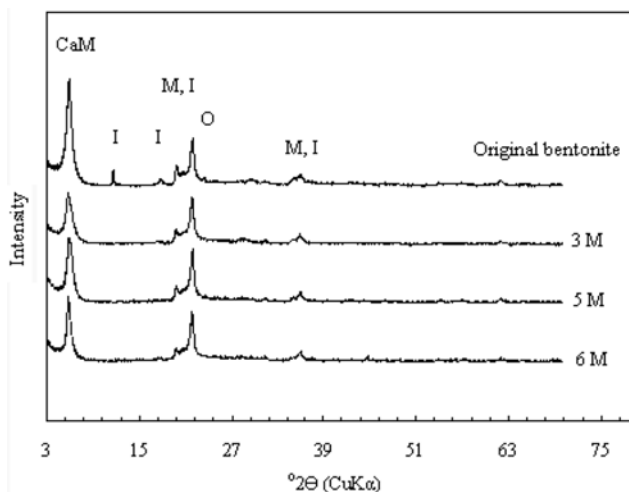


Fig. 2. The XRD pattern of natural and activated bentonites (O: Opal-CT, M: Montmorillonite, CaM: Calcium Montmorillonite, I: Illite).

acid attacks the structure of smectite, so the increase in specific surface area is great. As the concentration of acid increases more than 5 M, the specific surface area drops to a constant value. This phenomenon shows that the concentration of acid is a very important parameter in the activation process in order to reach a maximum specific surface area. The identical behavior in the nature of the plots can be observed at different particle size distributions, but the interesting point is the variation in specific surface area as the particle

Table 2. The chemical analyses of natural and activated bentonites

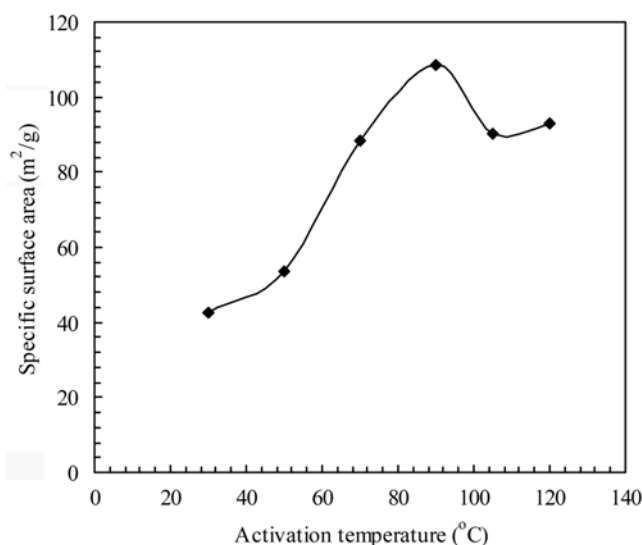
L.O.I	SO ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	K ₂ O	Na ₂ O	Al ₂ O ₃	SiO ₂	Acid concentration (mol/lit)
9.34	0.80	0.10	0.57	2.13	1.48	0.27	0.28	12.17	72.75	0
11.00	0.09	0.11	0.40	1.30	0.09	0.07	0.03	9.28	77.48	5

sizes are shifted to fine dimensions. The specific surface areas are presented in Table 1 for different particle size distributions of the starting raw material. This returns to the fact that the surface area increases mainly in edge area of crystals as particle size decreases with rising milling time. Therefore, the contact region of acid and clay rises. This factor is the main cause entailing a considerable increase in specific surface area when the particle size decreases [9].

The XRD patterns of original and activated samples which are activated using different concentrations of acid at 90 °C during 120 min are shown in Fig. 2. The Ca-montmorillonite peak intensity gradually decreases. This decrement is considerable when the activation process is carried out in the presence of 5 M acid concentration. The intensity of illite peaks decreases as the concentration of acid rises. The illite peaks disappear when the concentration of acid reaches to 5 M. The intensity of Opal-CT approximately is constant for all samples due to its insoluble sulfuric acid solutions.

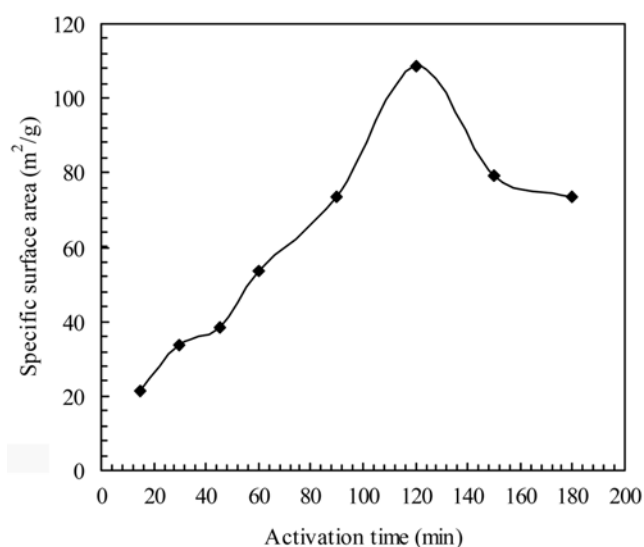
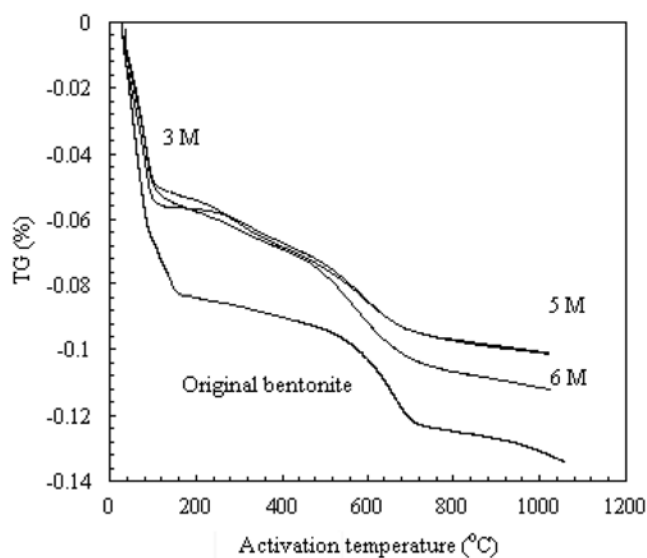
The chemical analyses of starting and activated bentonite using 5 M sulfuric acid are presented in Table 2. The decrease in the $R_xO_y\%$ (R is one of the Na⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺, Fe³⁺ cations) is obvious, which shows the mentioned cations left the montmorillonite and illite crystal layers after activation process. As the sulfuric acid increased from zero to 5 M, the exchangeable cations between crystal layers left first and were replaced by H⁺ ions. K⁺, Mg²⁺, Fe²⁺ and Al³⁺ cations also dissolved easily from the smectite structure. Since a large quantity of cations leave the crystal layers, the change in $R_xO_y\%$ is great. The decrease in CaO and MgO percent confirmed this. This phenomenon is accompanied with transforming microspores into mesopores [14].

The variations of specific surface area versus activation temperature is shown in Fig. 3, referring to fine particle size of bentonite

**Fig. 3. The effect of activation temperature on bentonite specific surface area in presence of 5 M sulfuric acid.**

(–200 mesh). The activation process was performed in the presence 5 M acid and 120 minutes. It is obvious that the specific surface area increases with the activation temperature, reaching to a maximum value at 90 °C and then decreases to a constant. The activation rate is enhanced when the samples are activated between 50 to 90 °C. It is interesting to note that the activation temperature has negligible effect on specific surface area in high temperature ranging 100 to 120 °C.

The influence of activation time is presented in Fig. 4 when the

**Fig. 4. The effect of activation time on bentonite specific surface area in presence of 5 M sulfuric acid.****Fig. 5. TG curves of natural and activated bentonites by 3, 5 and 6 M of sulfuric acid solutions.**

activation process was performed in the presence of 5 M sulfuric acid at 90 °C. It is observed that the specific surface area increases progressively with activation time until a maximum value and then drops considerably, which indicates that the crystal structure of the clay decomposes after an optimum activation time. However, as the activation time rises, the number of mesopore increases continuously, which influences the specific surface area, reaching a maximum value at about 120 min. After this time, the crystal structure of clay may be assumed to be decomposed.

The TG curves corresponding to different acid concentrations are presented in Fig. 5. The weight loss of the samples decreases as the acid concentration reaches 5 M. It is observed that weight loss of activated samples is lower than for original bentonite, because of cation exchange during the activation process.

To obtain complementary evidence for the intercalation of H^+ ions into the bentonite minerals, FTIR spectra were performed in the region of 400–4,000 cm^{-1} . Fig. 6 shows the FTIR curve of na-

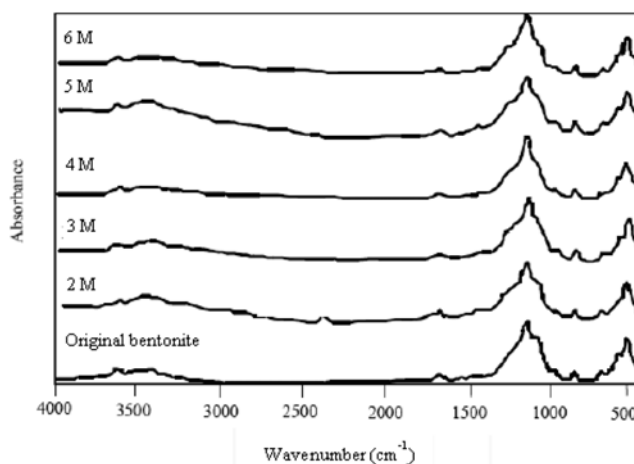


Fig. 6. FTIR spectra curves of natural and activated bentonites by 2, 3, 4, 5 and 6 M of sulfuric acid solutions.

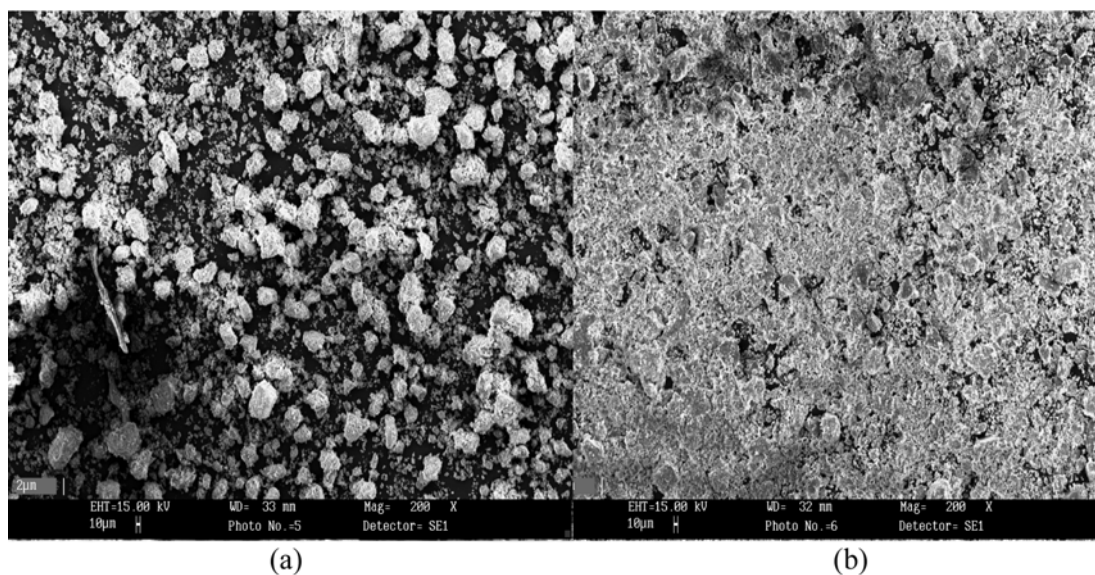


Fig. 7. SEM microphotographs of (a) natural and (b) activated bentonite in presence of 5 M sulfuric acid.

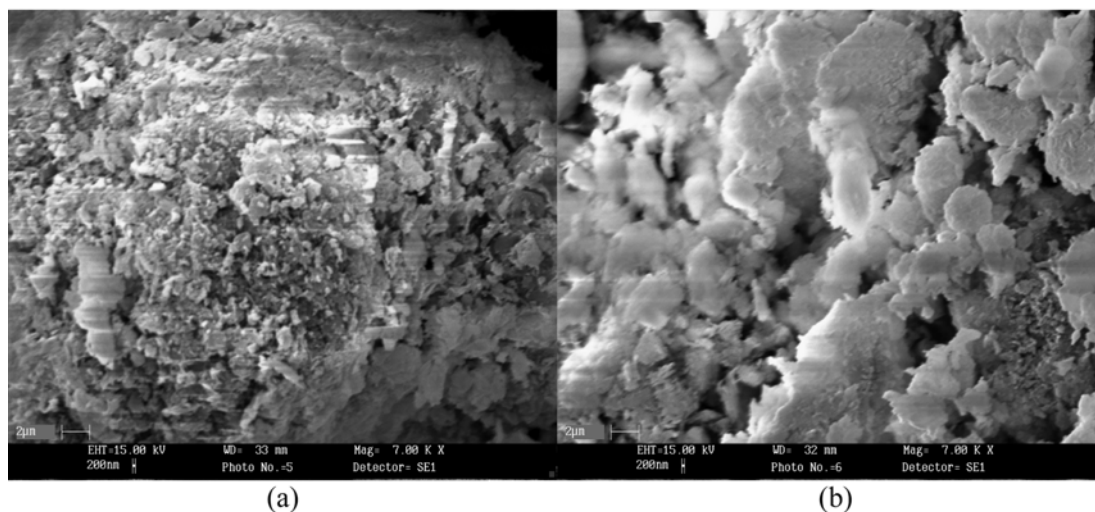


Fig. 8. The laminated structure of (a) natural and (b) activated bentonite in presence of 5 M sulfuric acid.

tural and activated bentonite by different concentrations of sulfuric acid at 90 °C during 120 min. All the samples show a group of absorption peaks between 3,450 and 3,650 cm^{-1} which is due to stretching bands of the OH groups, and the band at 1,640 cm^{-1} also corresponds to OH deformation of water to observe natural bentonite and activated samples at different concentrations of acid [15]. A significant difference is not observed between the FTIR curves.

Fig. 7 shows the morphology of samples corresponding to starting and activated bentonite using 5 M acid concentration at 90 °C during 120 min. It is obvious that the dimension of the particles decreases markedly due to activation and cation exchange process. The separation of clay minerals and laminated structure (Fig. 8) shows that cation exchange was performed in montmorillonite and illite layers. These findings confirmed the studding of specific surface area changes as activation process progresses.

CONCLUSIONS

The interpretation of the reaction between natural bentonite and sulfuric acid used in this study, leading to activated bentonite formation, can be summarized as follows:

1. The maximum specific surface area was obtained in the presence of 5 M sulfuric acid, and the results show that a greater increase in acid concentration has a negligible role in the activation process.
2. The particle size distribution of starting bentonite influences the maximum specific surface area value considerably. The optimum acid concentration for reaching maximum specific surface area remains constant in each particle size distribution.
3. The particle size distribution of original bentonite strongly favors the activation process, allowing us to achieve active bentonite with a specific surface area of about 110 m^2/g when fine-sized (–200 mesh) of raw material was used.
4. The optimum activation temperature for obtaining maximum specific surface area was determined. The experimental data showed that 90 °C is the best temperature for activation of natural bentonite. A greater increase in activation temperature decomposes the

crystal structure.

5. These findings were confirmed via studying the original and activated samples with chemical and mineralogical analysis, thermal gravimetric curves and scanning electron microscope analyses.

NOMENCLATURE

- A_{MB} : surface area covered by one methylene blue molecule [\AA^2]
 A_v : Avogadro's number [mol^{-1}]
 N : number of methylene blue increments
 S : specific surface area [$\text{m}^2 \cdot \text{g}^{-1}$]

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