

Experimental Study of Adsorption Properties of Acid and Thermal Treated Bentonite from Tehran (Iran)

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Abstract—The Iranian bentonite was first characterized by Scanning Electron Microscopy (SEM), Inductively Coupled Plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF), X-ray Diffraction (XRD) and BET. The bentonite was then treated thermally between 150°C-250°C at 15min, 45min and 90min and also was activated chemically with different concentration of sulphuric acid (3N, 5N and 10N). Although the results of thermal activated-bentonite didn't show any considerable changes in specific surface area and Cation Exchange Capacity (CEC), but the results of chemical treated bentonite demonstrated that such properties have been improved by acid activation process.

Keywords—Acid activation, Bentonite, CEC, Thermal activation.

I. INTRODUCTION

BENTONITE is a soft rock with structure based on aluminum silicate layers in various colors. Smectites are major clay minerals in bentonite with 2:1 layer structure (i.e. two silica tetrahedral sheets sandwich an aluminum octahedral sheet) [1]. Replacement of some trivalent ions such as Al^{3+} , by some divalent ions like Fe^{2+} and Mg^{2+} in octahedral layer, or substitution of Si^{4+} with Al^{3+} in tetrahedral layer causes a negative electric charge arises in the whole layers. This negative charge is balanced by Ca^{2+} and Na^{+} cations [1]-[4].

Bentonites, by virtue of Montmorillonite, are able to take some certain cations from solutions and exchange them with their own molecules and hence they have high capacity of absorption. Montmorillonites are clay minerals widely in industrial processes [1], [5], [6]. In presence of water, cations

of bentonite (Ca^{2+} and Na^{+}) are hydrated and then swelling of bentonite occurred, owing to its lamellar structure. In other words, hydration of bentonite allows water to migrate to the interlayer where the cations become more hydrated which begins to force the layers apart. As more water is added, the cations become more hydrated causing causing the interlayers to widen and to swell [3]. Based on major exchangeable ion, bentonites are divided into sodium (Na) or calcium (Ca) types, which are called Na-bentonite and Ca-bentonite, respectively. It should be noted that Ca-bentonite doesn't expand as much as the one with mainly Na^{+} due to the size of the ions and the hydration shells around them and also the power between the 2+ charge and the negative surface is greater than that of a 1+ charge that makes the layers be connected more tightly [2].

Although the first or maybe the only use of clays returned to 5000 B.C., when people used clays as a cleaning material for animals and later in America as soap for washing and cleaning cloths, but today clays, particularly bentonites, are used in various field and several applications [7] such as drilling mud, ceramic, sealant, bleaching clay, adhesive, carrier, catalyst and catalyst support, clarification of beer and wine, animal feed additives, emulsion stabilizer, cosmetic, purification, paint, decolorization, civil engineering, food technology [7]-[11].

Bentonite quality and properties (i.e. the amount of clay minerals, surface area, cation exchange capacity (CEC), surface acidity, porosity, selectivity and etc.) are very important in industrial applications and could be modified by activation methods. In other words, before bentonite becomes a suitable material to be used in the industrial applications, some of its properties should be improved by some activation or treatment procedures. Since, the structure, composition, and physical properties of clays (bentonite) deeply influence their utilizations, examining the qualitative properties and determining the physicochemical properties and the mineral compositions which define their behavior, is of great importance [2], [12].

Cation Exchange Capacity is a measure of the soils capacity to exchange ions. The clays and organic matters of the soils have the negative charges attract any element with a positive charge. Cations have the ability to be exchanged for other positively charged ion from the surface of clay minerals and organic matters [13].

Specific surface area of bentonite which is defined by the total surface area of one gram bentonite significantly affects

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most of its industrial utilization like adsorbent, bleaching earth and etc. Altering the cations located in the bentonite interlayers with larger organic cations could be used to enhance its specific surface area. [14]

Adsorption capacity of bentonites could be improved by activation process through increasing the surface area, porosity or pore volume. There are four methods for activation of bentonite, the two simple and conventional ones included in: thermal and chemical activation which in former crystalline structure or chemical composition of bentonite altered by heating at a proper temperature, and in latter using an inorganic acid not only leaches out cations from octahedral and tetrahedral sheets but also soluble impurities like calcite, or other cations are exchanged with hydrogen ions. Acid dissolution of clays provides useful information on the reactivity of the mineral involved, e.g. kinetic parameters or characteristic of reactants and reaction products. The other two are physical method and pillaring technique. The surface area of bentonite in physical activation increases mechanically by milling or crushing. Pillaring method deals with setting some metal hydroxyl cluster cations, followed by calcinations, between the bentonite's layers as pillars to create more spaces that encourage adsorption property of the clay [15].

The preferred changes in the physicochemical properties of a bentonite considerably depend on the condition of activation procedure (for acid activation system especially) such as the acid concentration and the duration and the temperature of the activation process [16], [17]

Naturally occurring bentonites may show very little efficiency in industrial applications. It is for this reason that activation methods are usually applied in order to promote the adsorptive capacity of the clays. Therefore, this work is aimed at evaluating the effects of acid and thermal activation on the adsorptive properties, such as specific surface area and cation exchange capacity (CEC) of a bentonite from Tehran (Iran).

II. MATERIALS AND METHOD

A. Materials

The Bentonite used in this experiment was provided from Tehran (Iran). The bentonite was further characterized by Scanning Electron Microscopy (SEM) (Fig. 1), Inductively Coupled Plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF) (Table I). Analytical pure sulfuric acid (98%) was also supplied by Merck chemical company.

The X-ray Diffraction (study) analysis, based on a frequently specified method for determining monmorillonite content and other minerals through identification of scattered beam angle, was performed using a powder diffractometer. The XRD operated at 40kV and 100mA in a step scan mode and showed that the components of the bentonite were Montmorillonite, Quartz, Cristobalite, Dolomite, Feldspar.

Adsorption properties of the bentonite were conducted by ASAP method (ASTM 4567) included in: surface area of $45\text{m}^2.\text{g}^{-1}$, mean pore diameter of 7.7nm and total pore volume at $0.0898\text{cm}^3.\text{g}^{-1}$. The Cation Exchange Capacity (CEC) of the bentonite was measured by Methylene Blue Method (VDG P

69) at 58meq/100g.

The Methylene Blue method measures the cation exchange capacity of a bentonite. Methylene Blue molecules which positively charged attach to interlayer space which negatively charged within monmorillonite. The quantity of adsorbed Methylene Blue by bentonite sample regarded as an indication of the exchange capacity and usually expressed in milliequivalents per 100g.

The swelling index of bentonite, used to determine the general swelling characteristics of sodium bentonite clay, was measured at 15ml/2g (according to ASTM D5890). To perform these tests, a 2g sample of dried and finely ground bentonite clay is dispersed into a 100ml graduated cylinder in 0.1g increments. A minimum of 10 minutes must pass between additions to allow for full hydration and settlement of the clay to the bottom of the cylinder.

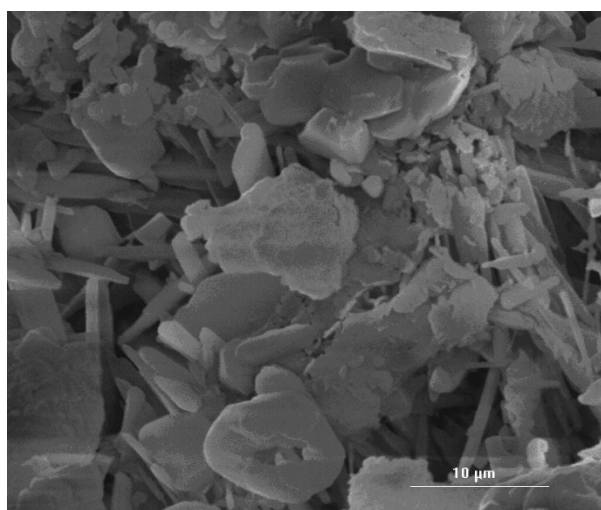


Fig. 1 Scanning Electron Microscopy (SEM) of raw bentonite

III. RESULTS AND DISCUSSIONS

A. Thermal Activation

The received bentonite contained dissimilar particles in terms of size and shape, so was passed through different sieves to have a uniform sample with the size of about 250 microns. Then samples of 50g were separated and prepared for heating in a furnace at different times and temperatures. The prepared samples (9 samples) were heated for 15min, 45min and 90 min at 150°C, 200°C and 250°C. Table II shows the results of Specific surface area and cation exchange capacity of the thermal activated bentonite.

It can be seen from table II that heating the raw bentonite in three different temperatures 150°C, 200°C and 250°C for three different times (15min, 45min and 90min) didn't affect the specific surface area, in other words, significant changes were not observed during thermal activation. It could also be realized from this table as the temperature increased the CEC value partially decreased.

B. Acid Activation

The bentonite samples were activated with three different solutions of sulfuric acid (3N, 5N and 10N). The activation procedure was performed in a water bath at 95°C to 98°C on a magnetically stirred hot plate for 2h. At the end of the experimental duration, the resulting slurry content of the container was immediately filtered and then were washed several times with deionized water till neutral pH 7 obtained, afterward dried to a constant weight.

Actually, when the bentonite samples are acid activated as a result of treatment with hot mineral solutions, hydrogen ions attack the aluminosilicate layers through the interlayer regions. This attack changes the structure, chemical composition and physical properties while increasing the adsorption capacity.

TABLE I
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) AND
XRF RESULTS FOR THE IRANIAN BENTONITE

ICP-MS analysis			
Element	Concentration (ppm)	Element	Concentration (ppm)
Ag	<0.01	Li	0.04
Al	270	Mg	22.8
As	0	Mn	1.4
B	99	Mo	0.1
Ba	9	Na	94
Be	<0.01	Ni	0.3
Ca	68	Pb	0.3
Cd	<0.01	Sb	0.0
Co	0.03	Sc	0.0
Cr	0.17	Se	<0.02
Cu	0.06	Sr	0.7
Fe	125	Ti	11.0
K	32	V	0.2
La	0.04	Zn	0.3
XRF ANALYSIS (WT. %)			
L.O.I	8.37	K ₂ O	0.94
Na ₂ O	3.17	MgO	0.95
CaO	2.38	TiO ₂	0.46
Al ₂ O ₃	12.75	Fe ₂ O ₃	4.46
SiO ₂	64.13	K ₂ O	

TABLE II
SPECIFIC SURFACE AREA AND CATION EXCHANGE CAPACITY OF THE
THERMAL ACTIVATED BENTONITE

SAMPLE	SURFACE AREA (BET) m ² /g	CEC (meq/100g)
BASE SAMPLE	45	59
150°C-15 MIN	46	58
150°C-45 MIN	48	59
150°C-90 MIN	47	59
200°C- 15 MIN	45	57
200°C- 45 MIN	47	57
200°C- 90 MIN	42	55
250°C-15 MIN	46	54
250°C-45 MIN	44	55
250°C-90 MIN	45	55

TABLE III
SURFACE AREA DATA OBTAINED USING BET TECHNIQUE FOR BENTONITE
SAMPLES ACTIVATED BY DIFFERENT CONCENTRATION OF SULFURIC ACID

Sample	Surface area (m ² /g)	CEC (meq/100g)
Base Sample	45	59
3N	62	71
5N	68	82
10N	66	79

In fact, Bentonite activation was performed with three different concentration of sulfuric acid in order to investigate the influence of acid concentration on the surface area. The results of the samples are presented in Table III. As can be seen from this table, the base sample had 45m²/g that has been changed to 68m²/g. So, the sample activated with 5N-sulfuric acid solution had the largest surface area.

It should also be noted that increasing the acid concentration from 3N to 5N had a partial impact on the surface area but further increasing in concentration brought about solving some parts of bentonite structure and then leading to collapse of layers and consequently, a reduction in the specific surface area was observed.

IV. CONCLUSION

In this study, modification of the bentonite properties was investigated through thermal and chemical activation. Thermal activation of bentonite, in different temperatures 150°C, 200 °C, 250°C and different times (15min, 45min and 90 min), not only didn't show significant changes in the specific surface area and CEC but also with increasing temperature the CEC value was partially decreased. Besides, acid activated bentonite displayed considerable changes in specific surface area and CEC value. It is worth mentioning that increasing the acid concentration from 3N to 5N had a partial impact on the surface area but further increasing in concentration brought about solving some parts of bentonite structure and then leading to collapse of layers.

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