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Investigation of the effects of hydrochloric acid modification on the structural of Algerian-bentonite clay

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Abstract : The objective of this work is to determine changes of surface properties of a bentonite after acid activation, using hydrochloric acid solutions (HCl) at room temperature. XRD, FX, FTIR, MEB, and BET analyses of the samples have been carried out to examine the structure of bentonite before and after acid activation. It is found that the raw bentonite is composed of dioctahedra Imontmorillonite with predominant quantity and certain amounts of quartz, orthodase, albiteandillite, *etc.*. It also has a CEC of 74.32 meq/g which allow it to be characterized as typical sodium bentonite. Changes at low acid concentrations have resulted from cations exchange (exchangeable cations

with H⁺ ions). Differences of surface area at high acid concentrations (0.25 - 0.4M) have been caused by structural changes and partial decomposition of the samples. Surface area measurements have showed that with the increase of concentration of HCl solution the surface area has increased. the maximum value (837.11m²/g) has been reached by the sample activated with 0.4M HCl. Activation with higher concentration (0.6 M) has caused a decrease in the surface area.

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Keywords : Bentonite; Sodic-Montmorillonite; Acid activation; Cation exchange capacity; Surface area.

INTRODUCTION

Bentonite refers to naturally occurring material which consists primarily of fine-grained mineral, is which generally plastic with in appropriate water contents and hardens when it is dried or fired^[1]. Major clay minerals in bentonites are smectites, such as montmorillonite, beidellite, saponite, nontronite, and hectorite^[1-3]. Two types of octahedral sheets occur in smectites: the dioctahedraltype, 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 (Ca²⁺, Mg²⁺, Na⁺)^[4-7]. The variable chemical composition influences the layer charge, CEC, S_{BET} and pore volume that is why the clay minerals have such a broad application^[8]. Bentonite clay has various applications in the protection of soil and environment. It is used to protect

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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.^[3,9].

Industrial uses of bentonite powders depend on quality and quantity of their smectites and other minerals, valence and the amount of exchangeable cations. Bentonites may be used both naturally and after some physicochemical treatments, such as acid activation, ion exchange, and heating according to the application areas^[10,11]. Acid-activated bentonite powders have been used in diverse applications, such as adsorbent, catalyst and bleaching earth, and also in the preparations of carbonless copy paper, electrode, pillared clay, organoclay, and nanocomposites^[12-14].

Some physicochemical properties of bentonite change considerably with acid activation. The change in the properties appear on crystallinity of its smectite, CEC, swelling, pore structure, surface area, surface acidity, decolorizing power, catalytic activity, strength, plasticity, cohesion, and compressibility as well as the chemical and mineralogical compositions^[15-20].

In this work, Algerian Na-bentonite has been activated with hydrochloride acid at room temperature for 24 hours and the resulting materials which have been obtained with different acid concentrations have been analyzed with regard to changes in their structural and textural properties. The focus of this study is the modification of bentonite with hydrochloric acid while keeping its layered structure and developing a large specific surface area as well as retaining CEC.

MATERIALS AND METHODS

Materials

Natural bentonite clay which used in this investigation has purchased from National Company for Geological and Mining and it has been collected from Hammam Boughrara deposit which is located on the west of Algeria. The sample have been purified in laboratory to remove carbonates, calcites, iron hydroxide and organic metals. It has been dispersed in distilled water and the clay fraction (= 0.74mm) has been recovered by centrifugation, dried at 105 °C for 24 hours, and stored in tightly closed plastic bottles for use in the

experiments.

The hydrochloric acid (HCl) (98%, $d=1.98\text{ g/cm}^3$) and other used chemicals are of analytical grade. They have been supplied by Merck Chemical Company.

Acid activation

The bentonite has been prepared for activation by air-drying and grinding to a particle size of 0.075 mm. Twenty (20) g of the prepared sample has been weighed into flask (1000 ml capacity) and 400 ml of hydrochloric acid solution has been added. The resulting suspension has been stirred at room temperature for 24 h. At the end of the experimental duration, the resulting slurry has been poured into a Buchner funnel to separate the acid and bentonite. The residual bentonite has been washed several times with distilled water until it has been released from Cl^- against 5% AgNO_3 solution. After drying them at 105 °C for 4 h, the activated samples have been stored in tightly closed plastic bottles. The activation process repeated with varying acid concentrations of 0.05 – 0.6 M of HCl.

Instrumentation

The elemental analysis of samples has been conducted by X-ray fluorescence (XRF) on PHILIPS PW 1480 spectrometer that has used a dispersive technical wave length. The X-ray diffraction (XRD) data of natural and acid activated samples have been obtained by a SIEMENS D 5000 diffractometer equipped with graphic mono-chromator $\text{CuK}\alpha$ radiation and a fixed power source (40 KW, 40 mA) has been used. The scan rate was $0.5^\circ (2\theta) \text{ min}^{-1}$. Before chemical analysis, each sample which has been dried at 105 °C for 4 h has been heated at 1000 °C for 2 h, and the decrease in mass has been taken as the loss on ignition (LOI).

The FT-IR spectra has been recorded with FT-IR Spectrophotometer Model 4400 (Shimadzu Corporation, Japan) with 1 cm^{-1} resolution within the range 400 – 4000 cm^{-1} . Solid clay has been mixed with KBr in 1:10 ratio. The mixture has been grinded till becoming very fine powder. The fine powder has been pressed under 10 ton pressure into pellet. The Infrared spectra has been obtained from solid samples and KBr pellets.

The CEC of samples is determined by three chloride cobalt hexamine [$\text{Cl}_3\text{Co}(\text{NH}_3)_6$] method at pH 7.0. The mixtures of three chloride cobalt hexamine

with bentonite sample have been kept at room temperature during 1 h under stirring. After centrifugation, the supernatant has been dosed calorimetrically at $\lambda_{\text{max}} = 470\text{nm}$, the amounts of adsorbed at flocculation point, referred to 100 g of clay. These values allowed the determination of both CEC.

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

Scanning electron microscopy (SEM) of the solid catalysts has been carried out at 15 kW using a Jeol scanning electron microscope, model JSM-630LV. Each sample specimen has been deposited on an aluminium stub and gold sputtered prior to analysis by SEM.

RESULTS AND DISCUSSIONS

Chemical composition

The chemical analyses of the natural and acid-activated bentonite powders are given in TABLE 1, as the mass in % of metal oxides. The bulk chemical analysis (wt. %) of the natural bentonite sample is: SiO_2 , 58.32; Al_2O_3 , 15.32; Fe_2O_3 , 2.23; MgO , 3.21; CaO , 0.95; Na_2O , 1.89; K_2O , 1.19; TiO_2 , 0.15; S_2O_3 , 0.1; P_2O_5 , 0.11; MnO_2 , 0.09 and loss on ignition (L.O.I.); 13.73. SiO_2 and Al_2O_3 are the major constituents of the clay with other oxides present in trace amounts. The results of TABLE 1 also show the changes in the chemical composition and the ratio of $\text{Si}/(\text{Al} + \text{Fe} + \text{Mg})$ of the bentonite clay as a function of acid concentration.

By increasing the hydrochloric acid concentration from 0.05 to 0.6 M, there has been an increase in SiO_2 content in bentonites, but the increase has been more at higher acid concentration. The same behavior is observed in the ratio of $\text{Si}/(\text{Al} + \text{Fe} + \text{Mg})$ which has increased in bentonite until treatment with 0.6M. Bentonite activation with hydrochloric acid has caused an increase of the SiO_2 content due to remobilization of octahedral cations^[21-23]. Octahedral cations have shifted

into the solution while the silicon, owing to its insolubility, remained and its content has increased with the increase of HCl concentration. After the treatment with 0.6M, the Al_2O_3 , Fe_2O_3 , and MgO content have decreased by 48.56%, 66.36%, and 84.42% respectively. TABLE 2 shows the changes of the CEC, the specific surface area and the bulk density of the bentonite clay as the function of acid concentration. With an increase in concentration of hydrochloric acid, the activated samples have showed a gradual increase in the surface area until treatment with 0.4M HCl. In treatment with 0.6 M HCl, a decrease of surface area has been observed in comparison with the surface area of the sample treated with 0.4 M HCl. This increase in surface area is as a result of the leaching of the octahedral cations from the inter layer of the samples, and this shows a relationship between the surface area and the amount of $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{MgO}$ in the samples, and the generation of micro-porosity during the activation process^[24]. The decrease observed at higher acid concentrations can be explained by the process of passivation^[25]. The octahedral sheet destruction passes the cations into the solution, while the silica generated by the tetrahedral sheet remains in the solids, due to its insolubility. Pesquera *et al.*^[25] suggesting that this free silica which is generated by the initial destruction of the tetrahedral

TABLE 1 : Chemical analysis and specific surface area of the natural, and acid activated Bentonite samples

Component (%)	Bentonite					
	Untreated	Treated with different concentrations of HCl				
		0.05M	0.15M	0.25M	0.4M	0.6M
SiO_2	58.32	59.66	61.32	63.10	65.32	69.66
Al_2O_3	15.82	14.85	13.24	11.85	9.79	7.88
Fe_2O_3	2.63	1.76	1.50	1.21	1.04	0.75
Na_2O	1.89	1.69	1.49	0.60	0.20	0.10
K_2O	1.19	1.90	1.85	1.65	1.83	1.82
MgO	3.31	3.19	2.80	1.86	1.60	0.50
CaO	0.95	0.70	0.50	0.15	0.10	0.05
TiO_2	0.15	0.12	0.11	0.10	0.07	0.07
S_2O_3	0.10	0.11	0.10	0.10	0.10	0.07
P_2O_5	0.11	0.10	0.11	0.11	0.10	0.10
MnO_2	0.09	-	-	-	-	-
L.O.I.	13.73	14.84	15.35	16.55	17.78	18.21
Total	98.29	98.92	98.37	97.28	97.93	99.27
$\text{Si}/(\text{Al}+\text{Fe}+\text{Mg})$	2.81	2.99	3.49	4.23	5.25	7.63

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sheet is polymerized by the effect of such high acid concentrations and is deposited on the undestroyed silicate fractions, protecting it from further attack and, thereby, resulting to a decreased surface area. The results of the bulk density measurement of clay show a decrease in density as acid concentration in bentonite acid mixture has increased. According to this trend, bentonite clay property is changed with the acid activation progresses.

The CEC values of the samples have also displayed similar behavior. With the increase of concentration of HCl, the samples have showed a gradual decrease in CEC until treatment with 0.4 M HCl. In treatment with 0.6 M HCl, an increase of the CEC has been observed in comparison with the CEC of sample treated with 0.4 M HCl and this can also be explained by the process of passivation^[25,26].

The variations of the relative content of metals (M/

M_0) in the bentonite with hydrochloric acid (HCl) are given in Figure 1 in which M_0 and M are the mass in % of the element oxides in the natural and acid-activated bentonite samples. The relative contents of the undissolved elements in the bentonite increase in the order of Ca^{2+} , Na^{1+} , Fe^{3+} , Mg^{2+} , Ti^{4+} , Al^{3+} , S^{3+} , P^{5+} , Si^{4+} , and K^{1+} by the increase in HCl molarities. The K^{1+} cations between 2:1 layers of illite and the Si^{4+} cations at tetrahedral sites of smectite and illite are not dissolved by acid activation. The increase in relative contents of these cations depends on the dissolution of other cations by the activation. The relative S^{3+} , P^{5+} content decreases slowly by the acid activation. It has been discussed that the S^{3+} , P^{5+} cations are located either on octahedral sites or tetrahedral sites. The increase in the relative content of S^{3+} , P^{5+} shows that these cations are located most probably at the tetrahedral sites in the 2:1 layers of smectite similar to Si^{4+} cations.

TABLE 2 : Effect of acid concentration on the bentonite surface are, mass percent of ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{MgO}$), bulk density, and CEC.

Component	Bentonite					
	Untreated	Treated with different concentrations of HCl				
		0.05M	0.15M	0.25M	0.4M	0.6M
S_{BET} (m^2/g^1)	508.27	580.32	600.57	715.64	837.11	544.37
Mass percent of ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{MgO}$) (%)	21,76	19,80	17,54	14,92	12,43	9,13
Bulk density (kg/m^3)	1026,9	997,7	976,3	950,1	896,5	927,6
CEC (méq/g)	74.32	70.56	62.33	46.75	40.15	70.56

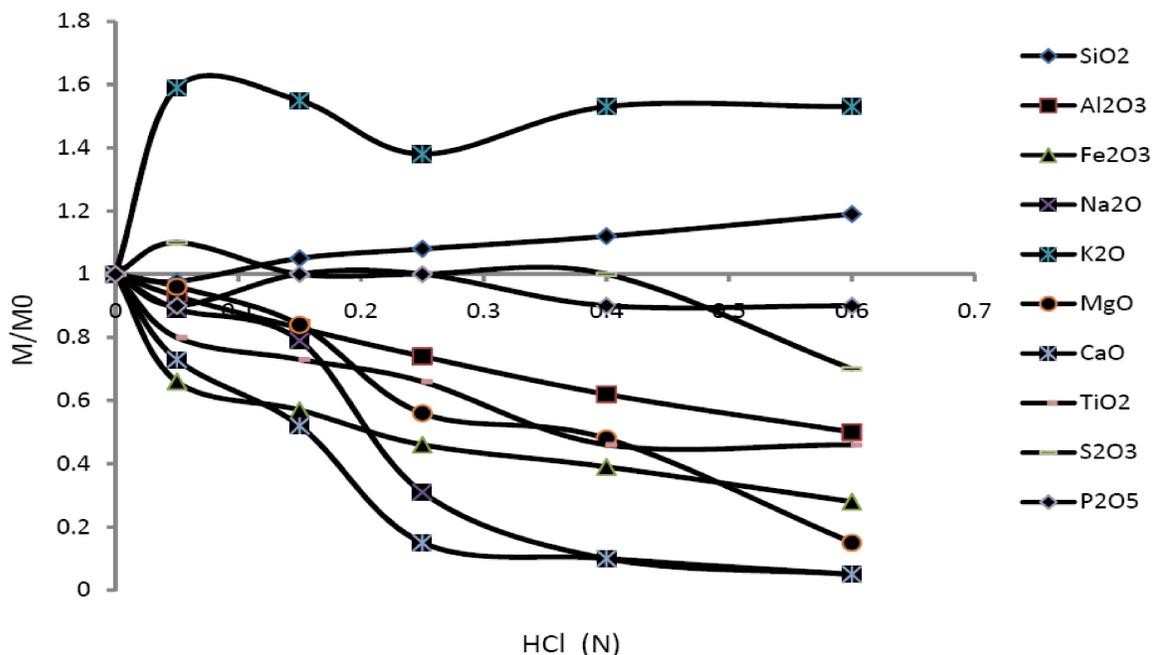


Figure 1 : The changes in relative metal contents (M/M₀) of the bentonite powders by HCl (M) in activation

Dissolution (%) of the exchangeable cations Ca^{2+} , K^+ and Na^+ from the bentonite structure is calculated and shown in Figure 2. It is expected that a significant amount of these cations is removed after leaching with 0.1M acid concentration. Dissolution of these cations remains almost constant by continuing the activation process with higher acid concentrations. However, a considerable amount of these elements is still found in the activated bentonite due to the presence of impurities, mainly feldspar that has calcium, sodium and potassium, and it is resistant to acid attack^[27,28]. It is presumed that at low acid concentration the attack on the structure is weak and that the exchangeable cations replaced by H^+ ions are few^[29].

Mineralogical composition

The XRD patterns of the samples are given in Figure 3. The bentonite contains a sodium-rich montmorillonite (NaM) with the $d(001)$ value of $15.56 [\text{\AA}]$ that is the dominant montmorillonite mineral which seems well crystallized in the sample. Other minerals were found to be quartz, orthodase, albite, and illite. Leaching of the sample with chlorhydric acid produces important mineralogical changes which can be seen from XRD patterns of Figure 3(b-f). The most pronounced modification occurs in the montmorillonite $d(001)$ peak (the first peak appearing at 2θ angle about 4°) which shows a reduction in intensity as a result of acid attack.

For concentrations of hydrochloric acid 0.05M and 0.25M the corresponding peaks are $d(002) = 12.71 [\text{\AA}]$, and $d(005) = 15.80 [\text{\AA}]$ respectively. It is clearly observed that hydronium cations can intercalate into

the interlayer spacing of the sodic bentonite by the mechanism of cation exchange, without the loss of layer structure. The hydrophilized bentonite exhibits rather broad diffraction peaks $d(005) = 15 [\text{\AA}]$ at 0.4 M of hydrochloric acid concentration. The reduction in intensity and increase in the width of $d(001)$ peak indicate that the crystallinity of the NaM is considerably affected by acid activation. This means that the process favours the production of amorphous phase by decomposing montmorillonite crystalline structure^[30]. This effect is more pronounced for activations with 0.6 M acid solutions, where the cebatite clay produced at $d006 = 10 [\text{\AA}]$. Similar results have already been described in the literature^[31]. It can be also observed that the characteristic peaks corresponding to quartz, orthodase, albite, and illite minerals disappear after acid activation under relatively mild conditions.

FTIR characterization

The FTIR spectra of the untreated and hydrochloric acid treated bentonite samples in the wave number range of $4000\text{--}500 \text{ cm}^{-1}$ are shown in Figure 4. The spectrum of the untreated bentonite exhibits absorption bands at 3422 and 1638 cm^{-1} this is assigned to the stretching and bending vibrations of the OH groups for the water molecules adsorbed on the clay surface, and a band at 3621 cm^{-1} which represents the stretching vibration of the hydroxyl groups coordinated to octahedral Al^{3+} cations^[27,32]. The spectra show sharp band vibrations in the region between 1000 and 400 cm^{-1} it is described in earlier papers^[33,34]. Namely, the most intensive band at 1035 cm^{-1} in the spectra of untreated

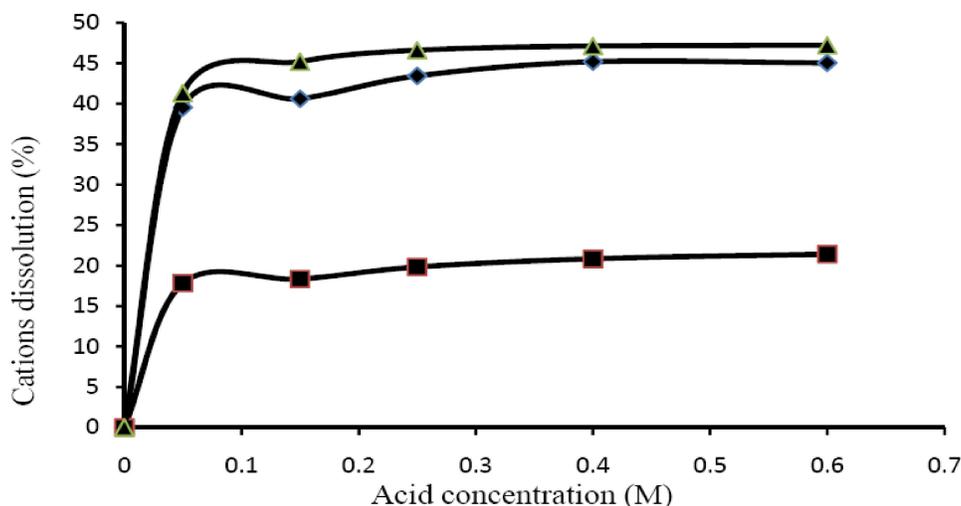


Figure 2 : Cation dissolution at different acid concentrations

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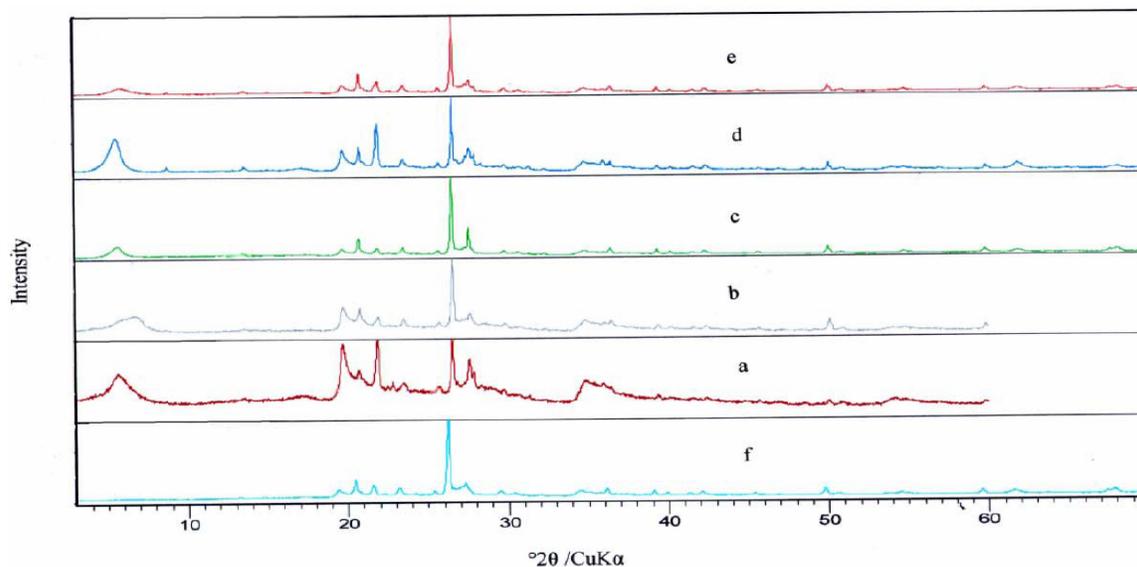


Figure 3 : XRD patterns of untreated bentonite (a), and activated with chlorhydric acid at different concentrations: (b) 0.05M; (c) 0.15M; (c) 0.25M; (d) 0.40M; (e) 0.6M.

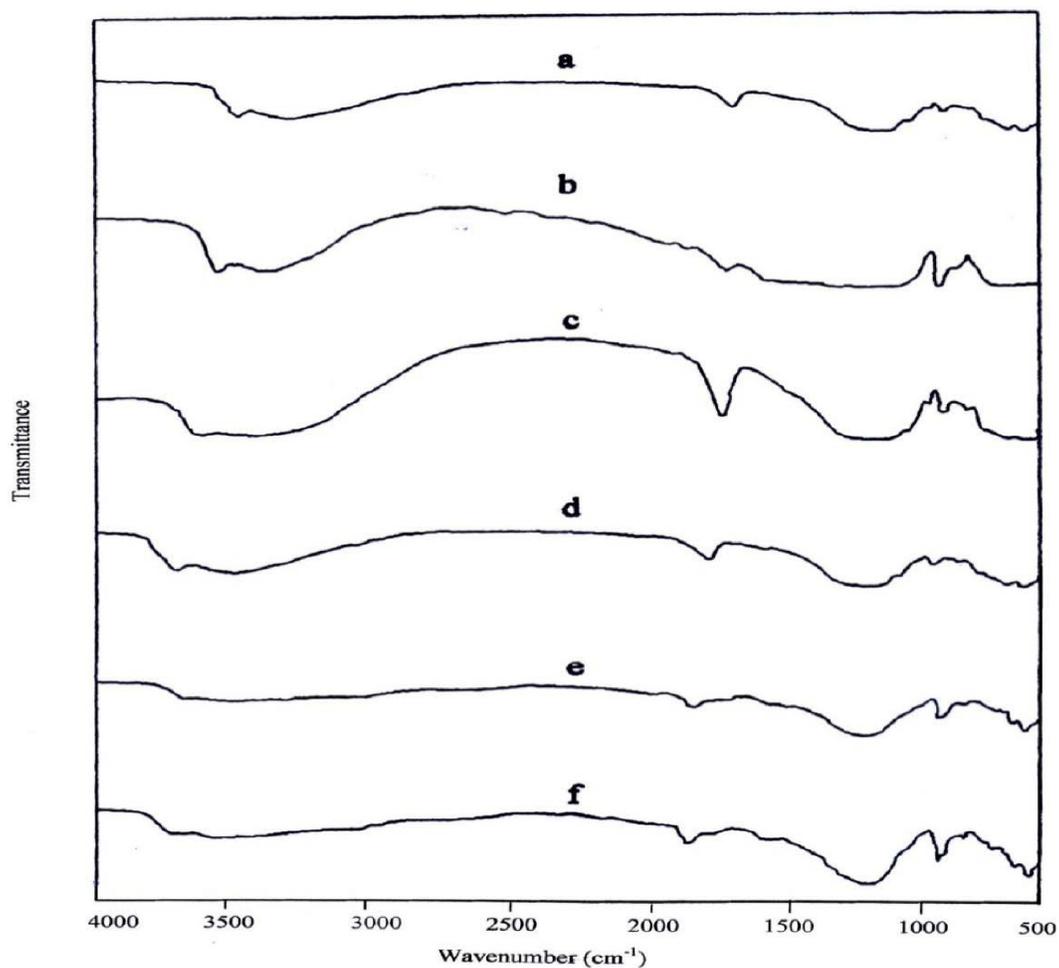


Figure 4 : FTIR spectrum of the natural (a) and, acid activated bentonite samples (b–f))

bentonite was attributed to Si-O stretching vibrations (in- plane) of the tetrahedral sheets, whereas the bands around 521 and 466 cm^{-1} are ascribed to Si-O-Al (where Al is the octahedral cation) and Si-O-Si bend-

ing vibrations, respectively^[35]. The intensive bands near 916 cm^{-1} , 845 cm^{-1} , and 521 cm^{-1} attributed to Al-Mg-OH, Al-Al-OH and Al-OH-O-Si stretching vibration respectively. The raw bentonite spectrum also contains a band between 796 and 693 cm^{-1} which are attributed to orthodase and quartz respectively^[27,36]. FTIR spectra of Figure 4(b-f) show the decreasing intensity as a result of acid activation bentonite which reflects the leaching of octahedral cations, such as Al^{3+} and Mg^{2+} from the bentonite structure. The reduction of the content of the octahedral cations is accompanied by a decrease of both OH bending vibrations at 916 and 845 cm^{-1} ^[37].

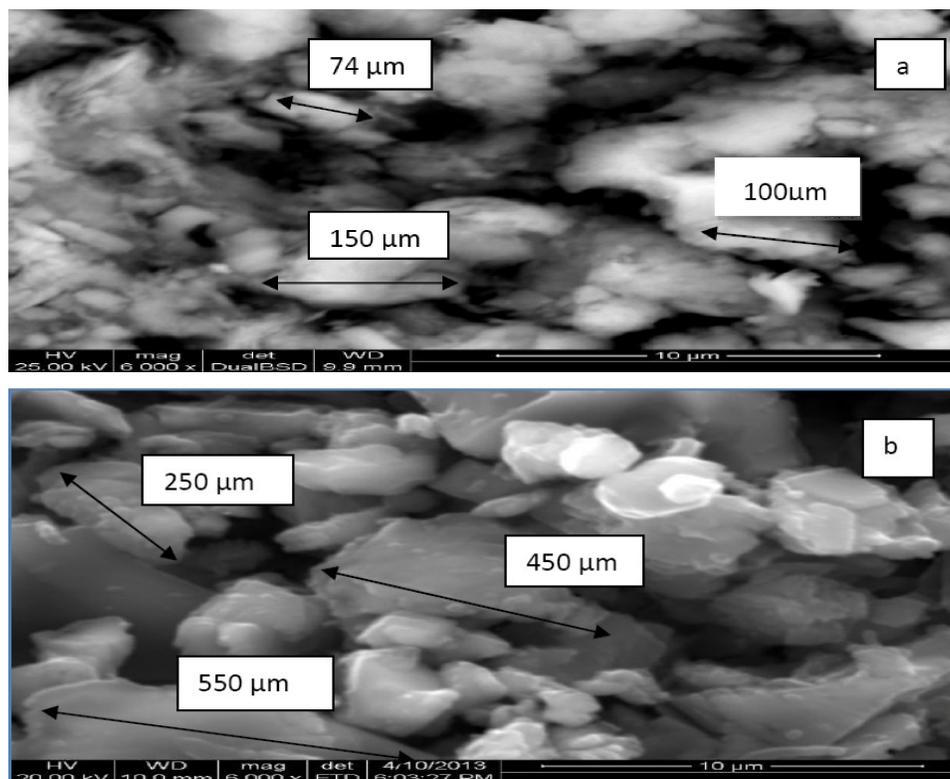
The FTIR result is in clear agreement with the XRF and XRD studies which indicates sequential degradation of the clay sheet upon acid treatment.

SEM analysis

Scanning electron micrograph of bentonite samples has been obtained and presented to an enlarging equal to 6000 X in the Figure 5. The micrograph of the untreated bentonite can be clearly observed from the Figure 5a which shows that the size bentonite grains is different, and their diameter is located between $29\mu\text{m}$ and $126\mu\text{m}$, and the aggregate mass of irregularly shaped

particles that appeared to have been formed by several flaky particles stacked together in form of agglomerates. The micro-graphs of acid treated bentonite indicate the disaggregation and decrease in size of clay structure on acid treatment (Figure 5(b-f)). When compared him with Figure 5a, it can be showed a clear distinction on visual analysis the microstructural differences. The diameter of particles acid treated bentonite varied from $250\mu\text{m}$ to $780\mu\text{m}$. These variations, thus, have led to decrease in the density of acid treated bentonite as the particulate volume automatically increases and therefore decreases the specific gravity. According to Amari *et al.*^[23], in the line with the previous results reported by Morgan *et al.* and Kheok and Lim^[37,38], state that the surface increases with the increase of acid concentration to the optimal value, beyond this acid concentrations the surface decreases.

The SEM micrograph of activated bentonite with HCl 0.6N shows the diminution of proportions of the different grains of size located between $60\mu\text{m}$ and $200\mu\text{m}$. The edges of the sheets are opened and separated, so the separation of layers are explained by the phenomenon of deshydrophilisation with the migration of hydronium ions towards the surface and the transformation of their crystal lattice (Figure 5f).



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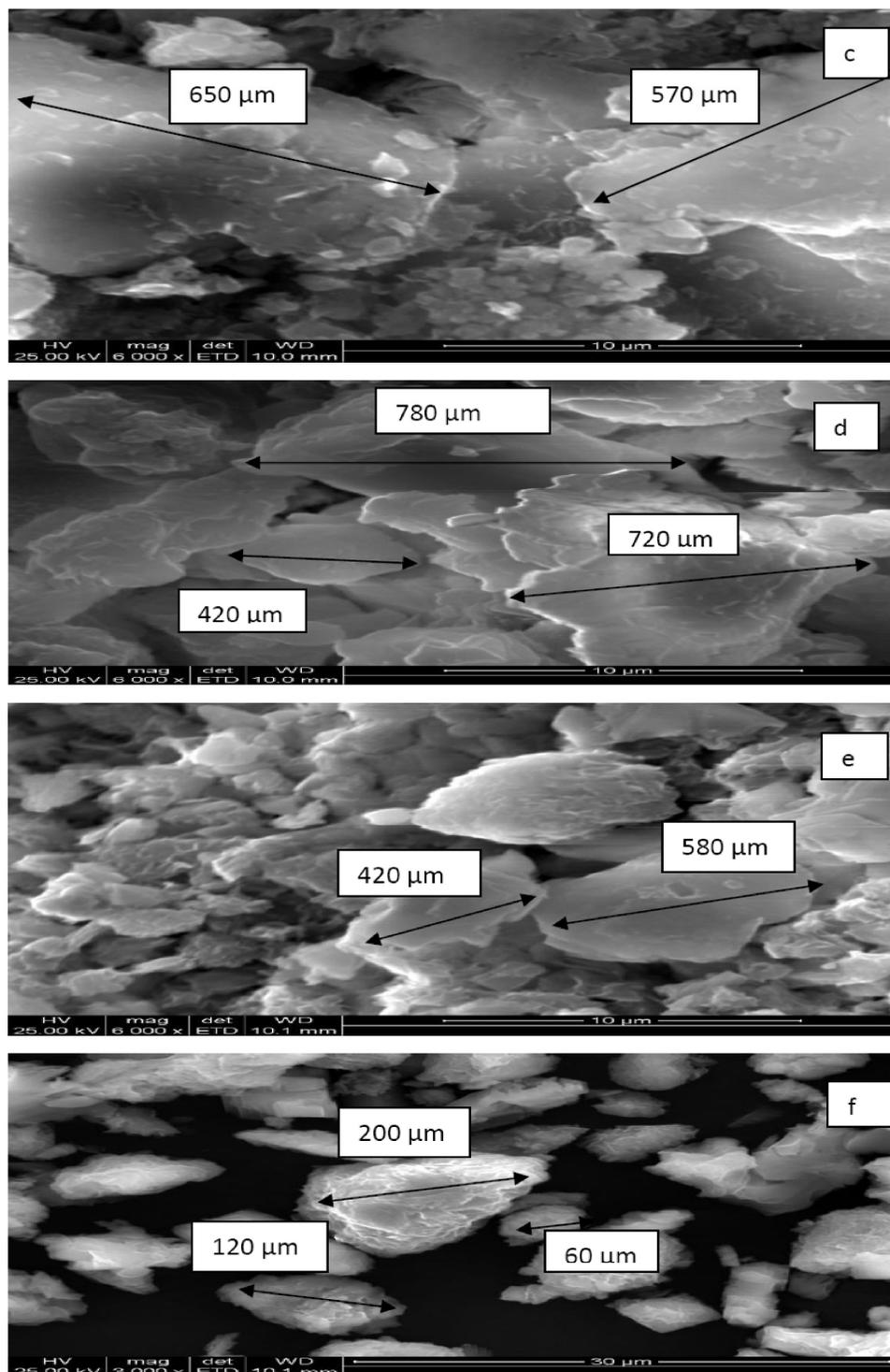


Figure 5 : SEM surface morphology of untreated bentonite (a), and activated with chlorhydric acid under different concentrations:(b) 0.05M; (c) 0.15M; (d)0.25M; (e) 0.4M; (f) 0.6M

CONCLUSION

The effect of hydrochloric acid activation on the structure of bentonite clay has been successfully investi-

gated. Natural bentonite which is used is of sodium-rich montmorillonite nature as confirmed by chemical composition and the XRD analysis. Acid treatment has partially altered the structure of the montmorillonite. The acid concentration plays an important role in the acti-

vation step which has been confirmed by XDR, FTIR, BET, and SEM analyses. This has led to increase a specific surface area of bentonite. The increase of acid concentration up to 0.1M has caused the increase of exchangeable cations dissolution after which it has remained almost constant.

The XRD results have pointed out that the activation has affected mainly d(001) (basal) reflections and has caused more changes in the interval between 0 and 40° of 2θ due to the decomposition of the structure and the deposition of amorphous silica. The intensities of the basal montmorillonite reflections (15.56 [Å°]) have been affected by acid activation. Acid-treated bentonites has greater SiO₂ contents and smaller contents of Al₂O₃, Fe₂O₃, MgO and CaO than the natural bentonite. The activated bentonite samples have contained substantially coarser particles than the original bentonite.

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