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Effect of acid leaching on the microstructure and adsorption properties of ground montmorillonite powder

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ABSTRACT

Montmorillonite powder was treated by grinding, and then, it was subjected to acid leaching with variable concentrations of HCl for different periods of time. The effects of these two activations on the crystal structure, specific surface area, pore structure, and adsorption properties of the clay were explored by Fourier transform infrared spectra, X-ray diffraction (XRD), Brunauer–Emmett–Teller, and UV/visible techniques. An increase in surface area from 78 to 490 m^2/g, specific micropore volume from 101.3 to 121.1 × 10^{-5} cm^3/g has been attained. Factorial design was used to determine main factors affecting microstructure and textural properties of the activated clay. Based on the analysis of the factorial design of experiments, acid concentration was the most significant factor for the amelioration of specific surface area. The adsorption efficiency of activated sample for phenol was tested. It showed that the adsorption followed Langmuir isotherms and it was enhanced owing to the increase in specific surface area.

Keywords: Acid activation; Grinding; Montmorillonite; Microstructure; Phenol removal

1. Introduction

Montmorillonites (MMT) are dioctahedral smectites composed of two silica tetrahedral (T) sheets bonded to a central alumina octahedral (O) sheet. The net negative electric charge of the (TOT) layers arising from the isomorphic substitution of Al^{3+} with Fe^{2+} and Mg^{2+} in the octahedral sites and Si^{4+} with Al^{3+} in the tetrahedral sites is balanced by the cations such as Na^+ and Ca^{2+} located between the layers and surrounding the edges. Industrial uses of smectite clay powders depend on their physicochemical properties, such as microstructure, cation-exchange capacity (CEC) and adsorption behavior [1]. Clay may be used naturally or after some physicochemical treatments, such as acid activation, ion exchange, or mechanochemical activation, by grinding according to the application areas [2–4].

Acid-activated smectite powders have been used in diverse applications, such as adsorbent, catalyst, and bleaching earth [5–7]. On the other hand, mechanochemical activation of clay minerals has for long been known to alter the solid material, not only by causing particles to fragment and by changing their specific surface area, but also by modifying their pore size distribution and inducing structural changes, such as complete or partial amorphization of the material, altered chemical reactivity [8–11]. Although most of

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the studies reported in the literature have been made by ball-milling [8–11], the mechanochemical activation by grinding using manual or mechanical mortar has been proved to be effective for clay minerals activation [12–14]. It was shown that in the early stage of grinding, kaolin crystals cleave and fracture and then split into fine crystals and as grinding progresses kaolin decomposes into a noncrystalline substance [14]. As shown by Mekhamer, the manual grinding of bentonite has effective reduction in the mean particle size and an increase in the specific surface in the first minutes of treatment [15]. Others effects, such as oxidation of structural Fe^{3+} in montmorillonite, have been reported to occur during manual grinding using mortar and pestle. Such oxidation has been attributed to adsorbed atmospheric oxygen induced by manual grinding [16].

Although mechanochemical modification of clay by acid activation or grinding has been widely studied and reported [5–9], the association of these two activations technique at the same time has been reported only for pyrophyllite, talc, and vermiculite minerals [17–19] and it was shown that the acid leaching of ground clay minerals ameliorates significantly microstructure and adsorption behavior. To the best of our knowledge, this activation technique has never been reported for MMT powder. Thus, the aim of this paper is to study the effect of acid activation of ground MMT powder on its microstructure such as surface area porosity and adsorption for phenol. A statistical analysis based on factorial design has been elaborated in order to evaluate the effect of these factors on textural behavior of clay.

2. Materials and methods

2.1. Preparation of purified Na^+-exchanged MMT

The MMT used in the present study is natural clay from Zaghouane in Tunisia. The raw sample contains quartz and calcite as major impurities (Fig. 1). Purified sodium MMT was prepared by purification of clay using standard procedures [20]. The protocol consists of the following three principals steps: (i) Decarbonation: carbonate is decomposed by the addition of dilute hydrochloric acid, taking care that the pH does not drop below 4.5 to avoid any attack on the clay mineral. Since the raw sample contains large amount of carbonate, this step requires significant time (4 d), (ii) Recupuration of the clay mineral fraction and exchanging and with Na^+: it consists of replacing the exchangeable cations with Na^+ followed by repeated washing and sedimentation with water. Washing and sedimentation allow the removal of impurities (organic materials, calcite, quartz, and hydroxides) and the recuperation of only the clay mineral fraction (<2 μm). The standard procedure is as follows: Na^+ exchanging: the raw clay is dispersed in 1 M NaCl solution by shaking of about 12 h and separated by centrifugation. This procedure is repeated several times (at least 5 times). (iii) Washing: The sediment of Na^+-exchanged clay mineral is washed with water and centrifuged several times until the clay minerals form a stable colloidal dispersion, and then, it is dialyzed until free of chloride. The dispersion is then allowed to stand and the <2 μm fraction is collected according to Stokes' law. The water is removed by drying at 60°C while the remaining purified clay mineral is freeze-dried, powdered in a mortar and pestle, and passed through a 60 mesh Sieve. As shown in Fig. 2, the presence of smectite was confirmed by the d_{001} spacing of the sample after air drying, calcination at 600°C for 2 h and glycol treatment. By means of lithium test, it was found that it constituted essentially of montmorillonite fraction. The chemical composition of the MMT is determined by atomic absorption spectrometer (AAS (Vario)) after dissolution of the purified exchanged MMT in hot solution of concentrated acid mixtures (HCl, H_2SO_4, and HNO_3) and the proportion of silica was determined gravimetrically. The chemical composition of the sample in mass % is as follows: 50.08% SiO_2, 3.95% MgO, 17.4% Al_2O_3, 0.2% K_2O, 0.08% CaO, 1.5% Na_2O, 6.3% (Fe_2O_3 + FeO), and 20.4% as loss on ignition.

2.2. Activation of MMT by grinding and acid treatment

Activation of MMT by grinding was performed by fine grinding of 1.6 g of purified Na^+-montmorillonite using handmortar for different periods of time. The acid leaching of the sample ground for 18 min has been achieved by immersion in 100 ml of hydrochloric acid (Sigma–Aldrich, St. Louis, MO, USA) with variable concentrations for different periods of time under reflux, and then, samples were washed with distilled water and finally dried at 80°C. Hereafter, different samples are denominated AMx,y (x refers to time of the acid treatment and y refers to HCl concentration).

2.3. Apparatus

The X-ray diffractograms (XRD) were obtained on a PANalytical diffractometer using Cu Kα radiation. Diffraction data were collected in the range from 2° to 80°. The IR spectra were obtained with a Nicolet

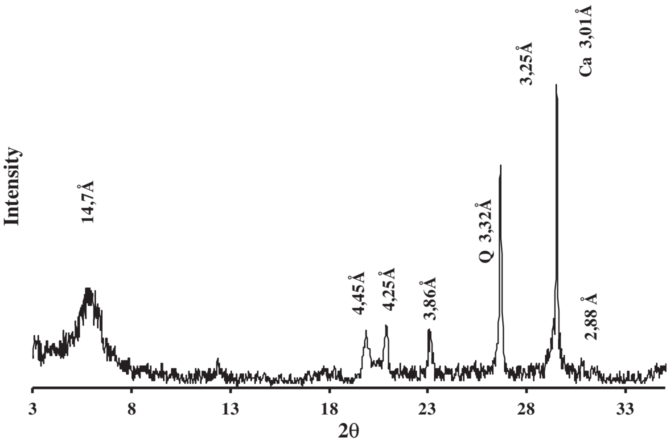

Fig. 1. XRD diffractogram of raw sample (Q: quartz, Ca: calcite).

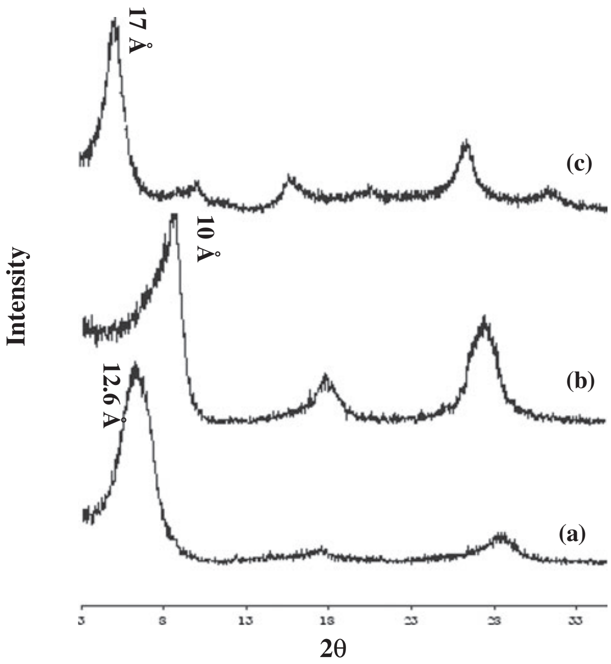

Fig. 2. XRD diffractograms of the purified sample (a) dried at air, (b) heated at 500˚C for 2 h, and (c) treated with ethylene glycol.

spectrophotometer, model 560, with a scanning range between 400 and 4,000 cm^{-1}, samples were prepared as tablets diluted in KBr, keeping constant the sample/KBr ratio and the total weight of sample. Fe^{3+}, Al^{3+}, and Mg^{2+} concentrations were checked by an atomic absorption spectrophotometer AAS (Vario 6).

The textural study and the measurement of the specific surface area of the clay were carried out with a study of the N_2 adsorption–desorption isotherm and application of the BET model. The equipment used was an Autosorb1 (Quantachrom). All textural parameters are given by the software connected to the apparatus (Autosorb for windows version 1.27). The Brunauer–Emmett–Teller (BET) is the method used by the software for the determination of the specific surface area and *t*-method for specific micropore volume.

The CEC of different samples has been determined using Kjeldahl method (UDK 149 Automatic Kjeldahl Distillation Unit).

The point of zero charge was measured using 0.01 M NaCl aqueous solutions at pH 3, 4, 6, 8, and 10. These solutions (5 mL of each) were brought into contact with 0.01 g of sample and the system was stirred for 48 h. The supernatant was then decanted and its pH was measured. The pH_{PZC} value was obtained from a plot of pH of the initial solution against pH of the supernatant. The pH_{PZC} is the point where the curve pH final vs. pH initial crosses the line pH initial = pH final [21].

Phenol (Aldrich) concentration was determined using PERKIN ELMER (model LAMBDA 20) spectrophotometer at 270 nm.

2.4. Adsorption experiment method

The equilibrium time for phenol adsorption was determined using different suspensions (0.2 g of the sample into 50 mL of 10^{-2} M phenol solutions). The effect of pH was varied from 2 to 10. Isotherms were determined using different phenol concentrations on the range of 10^{-4}–10^{-2} M. Freundlich and Langmuir models were used to modelize phenol absorption.

3. Results and discussion

3.1. Effect of grinding on microstructure and structure of MMT

3.1.1. Effect on the crystallinity

The XRD of the ground MMT are given in Fig. 3. The grinding has for effect the decrease of the intensities of the d_{001} basal spacing peaks. The grinding causes the diminution and gradually loss of intensity of the d_{001} and d_{060} spacing. The significance of this disruption means that the stacking between the layers is disrupted and lost. Thus, mechanochemical treatment has broken bonding between adjacent montmorillonite layers and has been gradually delaminated through the mechanical grinding process. After 60 min of grinding, the basal reflections totally disappear, and the ground material is completely amorphous.

3.1.2. Effect on textural properties

As shown in Table 1, the surface areas of the samples increase with grinding time in association with the decrease in particle size, reaching a maximum value of 101 m^2/g for grinding period of about 18 min then it decreases as grinding time increases to reach a minimum value of 80 m^2/g after 60 min of treatment. The increase in surface area is directly influenced by the formation of aggregates with small particle sizes at short grinding times and the decrease specific surface area obtained at the longest grinding time must be a result of the formation of larger stable large aggregates as shown by other workers [22]. In addition, it can be seen that micropore volume is slightly affected by grinding, and this behavior is similar to that reported when ball-milling SAz-1 bentonite [11]. For CEC, it can be seen that it increases rapidly with grinding to reach a maximum of 128 meq/100 g of MMT after 6 min of grinding then it decreases. The rise in CEC is a result of reduction in particle size of MMT, then as the grinding progresses, the decomposition of the crystal structure at some locations and the formation of large agglomerated particles cause the decrease in CEC.

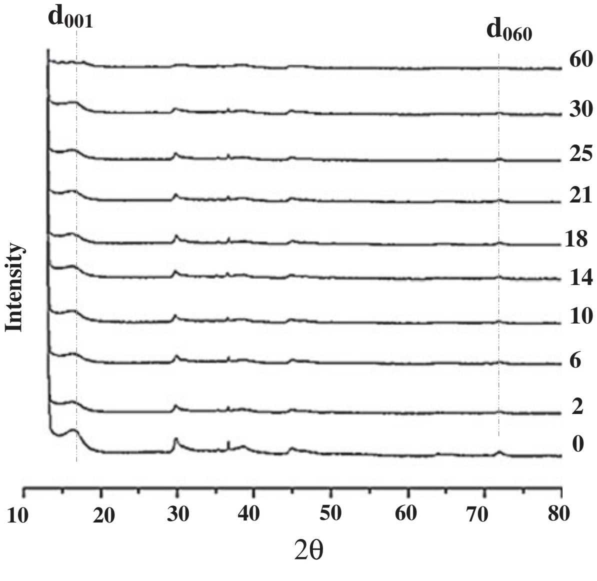

Fig. 3. XRD diffractograms of ground MMT for variable times (min).

3.2. Effect of acid leaching on the structure of ground MMT

3.2.1. Effect on the structure and the crystallinity

The sample ground for 18 min shows the highest surface area, and this was the reason for the selection of this sample for leaching studies. The XRD patterns of acid leaching of this sample with variable concentrations and times of acid attack are shown in Fig. 4. The XRD diffractograms show that acid activation caused structural changes in the ground MMT. In fact, acid activation affected mainly the 0 0 1 basal reflections; the d_{001} reflection completely disappeared after treatment with 2 M HCl for 6 h. On the other hand, the 0 6 0 reflection is affected only after 6 h of attack with 2 M HCl solution. In addition, it can be noted that the acid treatment effect the increase in the background in the interval between 20° and 30°. This change is due to the formation of amorphous silica caused by the attack of the octahedral layer and the exposure of the tetrahedral layer to the acid attack [23]. This has also been observed by other researchers for talc and vermiculite [17–19]. Moreover, the effect of both time under constant acid strength and acid strength under constant time on the smectite structure is similar, although it seems that the variation of time for the acid strength chosen (2 M) caused more drastic changes.

The effects of the acid activation process on the Fourier transform infrared (FTIR) spectra of the ground MMT (Fig. 5) are summarized as follows: The intensity of the absorption band at 3,640 cm^{-1} (A1–A1–OH stretching vibration) decreases with increasing severity of treatment to disappear after 6 h of 2 M acid treatment. With most severe treatments this band is almost eliminated. In addition, there is a slight effect on the Si–O stretching vibration localized at 1,050 cm^{-1}, the shape of this band changes with acid attack. This modification could be attributed to

Table 1
Variation of textural parameters of grinded MMT

Time of grinding (min)	0	2	6	10	14	18	21	25	30	60
Specific surface area (m^2/g)	78	91.64	96.19	96.41	98.28	101	94.92	91.16	85.19	80
Specific micropore volume (10^{-5} cm^3/g)	100	101	102.4	99.74	99.91	101.3	100.1	100	100	99.65
CEC (meq/100 g)	75	125	128	115	113	110	108	105	100	61

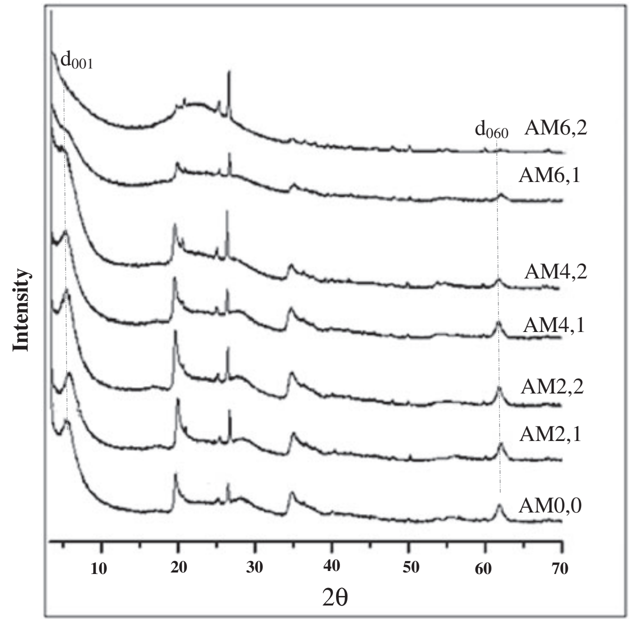

Fig. 4. XRD diffractograms of acid leached ground MMT for 18 min for variables periods and concentrations of HCl (AM*xy*, *x* notes time and *y* concentration of HCl).

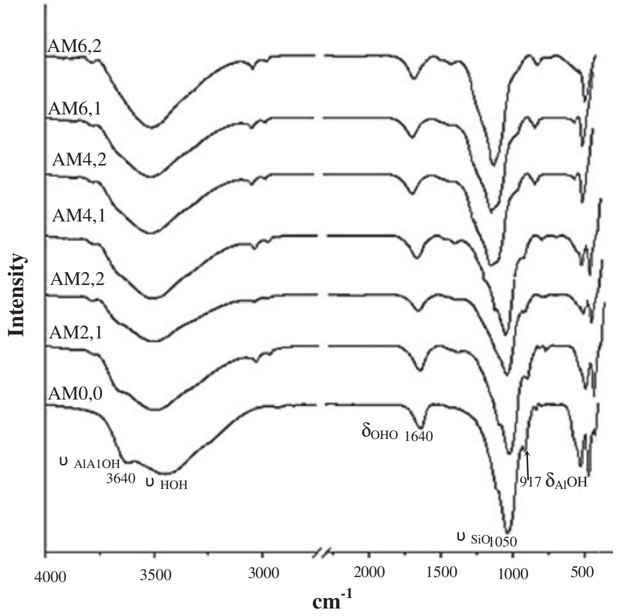

Fig. 5. FTIR spectra of acid leached of ground MMT (18 min) for variable periods of time and concentrations.

changes in Si environment after acid treatment [24]. Moreover, we noted the appearance of a new band at 800 cm^{-1} which can be assigned to the formation of three-dimensional amorphous silica [25] and which is in accordance with XRD results.

3.2.2. Effect on textural parameters

Table 2 shows the total surface areas and specific micropore volumes for the acid leached ground sample. The acid treatment produces an increase in these parameters as compared with ground montmorillonite without leaching. Best value of S_{BET} was obtained for the ground sample leached for 6 h in 1 M HCl solution (490 m^2/g). To visualize the effect of grinding, we have prepared acid activated sample in the same condition of acid attack without grinding (6 h in 1 M HCl). The S_{BET} of this sample is about 306 m^2/g without grinding. However, when grinding proceeds the acid leaching, the S_{BET} increases to attain 490 m^2/g with an enhancement of 184 m^2/g. This value is comparable to that obtained for acid leached ground vermiculite [10] (about 504 m^2/g). Thus, it seems that grinding before acid activation ameliorates the specific area.

To understand the origin of this enhancement, it is interesting to compare the crystal structural of acid leached sample with and without grinding. In Fig. 6, we have presented the XRD diffractograms of an acid-activated MMT by 1 M HCl for 6 h without grinding treatment and the one with grinding for 18 min. It can be seen that grinding causes the diminution and gradually loss of intensity of the 0 0 1 and 0 6 0 diffraction lines. This change in intensity means that grinding has broken bonding between adjacent MMT layers. On the other hand, since the 0 0 1 and 0 6 0 diffraction lines provide information, respectively, on the periodicity of the montmorillonite structure perpendicular to the layers, and within the layers, it can be concluded that

Table 2
Variation of textural properties of grinded and leached samples

Samples	AM0,0	AM2,1	AM2,2	AM4,1	AM4,2	AM6,1	AM6,2
Surface area (m^2/g)	101	247.9	311.3	374.7	423.9	490	389
Specific micropore volume (10^{-5} cm/g)	101.3	117.9	121.1	121.1	119.5	118.9	117.7

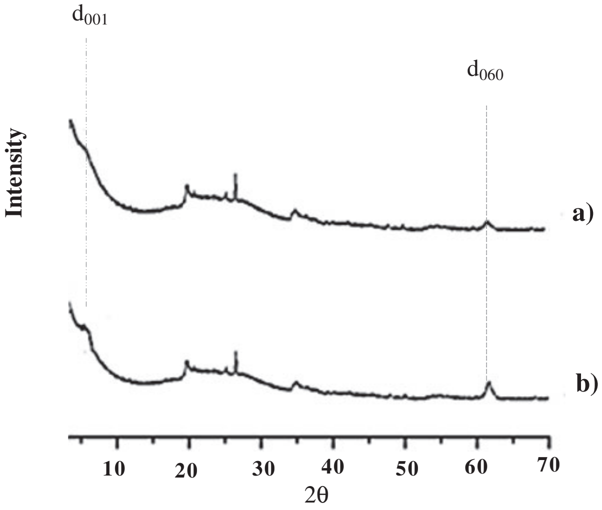

Fig. 6. Comparison of XRD diffratogramms of acid activated MMT (1 M HCl, 6 h) (a) with grinding (18 min) and (b) without grinding.

this disruption is manifested by glide movement of MMT layers in the *ab* plane (i.e. platelet delamination) and breakage in ac or bc planes as illustrated in Fig. 7. The distortion and breakage of MMT layers during grinding has for effect the expose of more surface of the mineral and could be the reason behind the increase in specific surface area for the ground-leached sample.

This conclusion could be strengthening by the determination the percentage of leached octahedral cations after grinding and acid attack. The amount of cations removed may be indicative of the proportion structure damage by grinding. Table 3 shows the percentage of leached Fe^{3+}, Mg^{2+}, and Al^{3+} cations. It can be observed that the grinding and acid treatments affect the breakdown of the layer, especially the exposed functional groups such as AlOH, SiOFe, and MgAlOH. After 18 min of grinding and after 6 h in 1 M HCl solution, the percentage of leached metals attains, respectively, 5.7, 12.7, and 2.9 for Fe, Al, and Mg cation. It is evident that the activation affects mainly the percentage of liberated cations. In fact, grinding facilitates the leaching caused by acid attack of the octahedral and tetrahedral cations. These changes in the chemical composition cause the formation of porous material.

3.3. *The effect of experimental parameters on textural properties of MMT evaluated by factorial design*

To well evaluate the effect of experimental conditions (time of grinding, time, and concentration of HCl acid) on textural and adsorption properties of treated MMT, it is interesting to use statistical technique based on 2^k factorial design. The factorial design 2^k is a two-level design [16] used to evaluate the influence of some experimental factors on results and their interactions. An experimental range was defined inside lower (−1) and upper (+1) limits of the three factors. In our study, the factors are defined as follow: acid concentration (min = 0.5 M, max = 4 M), time of grinding (min = 2, max = 30 min) and time of acid attack (min = 1 h, max = 6 h). The formalism of the factorial design according to a mathematical model indicates that an observable response Y can be expressed by Eq. (1):

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 + b_{123} X_1 X_2 X_3 \tag{1}$$

where X_1–X_3 are the main effect, $X_i X_j$ are the interaction effects between variables. The coefficients in Eq. (1) were calculated using NEMROD software [25]. A positive value of b_i coefficient associated with X_i factor indicates that on going from the low level to the high level of that factor the response is increased, whereas a negative value of a coefficient indicates a decrease in the response. The effects and interactions of the various investigated factors are represented in Fig. 8. This figure shows the following:

(1) The specific surface area is very influenced by the acid concentration which has a positive effect on the studied response. Therefore, the specific surface area increases with increasing HCl concentration.

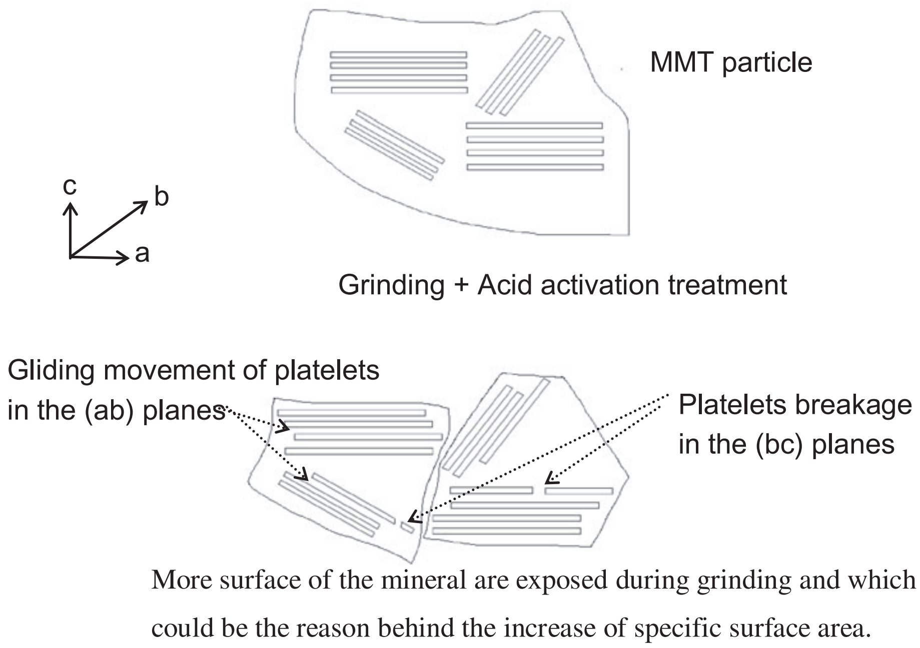

Fig. 7. Schematic representation of the reduction of particle size of clay, gliding movements and breakage of the MMT particles during grinding.

Table 3
The acid leaching of structural Mg^{2+}, Al^{3+}, and Fe^{3+} cations of different samples

Samples	% Fe_2O_3	% Al_2O_3	% MgO
AM2,1	3.1	6.9	1.4
AM2,2	3.5	7.8	1.6
AM4,1	4.5	10.3	2
AM4,2	5.4	11.7	2.3
AM6,1	5.7	12.7	2.6
AM6,2	5.9	13.2	2.9

(2) Only the grinding leads to an increase in the CEC; however, the acid attack has a negative effect of the CEC of the material.
(3) The time of acid attack is the second most significant factor on increase in specific surface area. Its effect is positive and the increase in the time of acid attack increases the specific surface area of the sample.
(4) Mechanochemical activation by grinding has a low effect on the specific surface area. However, as it can be seen, both the time of mechanical treatment and acid concentration affect positively specific micropore volume, while the time of the attack acid has a negative effect. Furthermore, a significant interaction b_{12} is significant; this result suggest that there is a synergy effect between grinding and HCl concentration.

3.4. Application of activated MMT as phenol adsorbent

This section is accorded to the study of the possibility of the application of activated MMT as phenol adsorbent from aqueous solution. Untreated MMT, ground MMT for 18 min and the sample ground for 18 min then acid leached with 1 M HCl solution for 6 h have been chosen for this study.

3.4.1. Effect of contact time

The results presented in Fig. 9 shows all the samples attain equilibrium retention after 6 h of contact time. It is also seen that the remaining concentration of phenol becomes asymptotic to the time axis after 6 h of shaking. These results also indicate that the sorption process can be considered very fast because of the largest amount of phenol attached to the sorbent within the first 6 h of adsorption, approximately 50 mg/L of phenol. Similar results were obtained with bentonite without modification [26], it seems that activation by acid and grinding treatment has no effect on the kinetic of phenol retention.

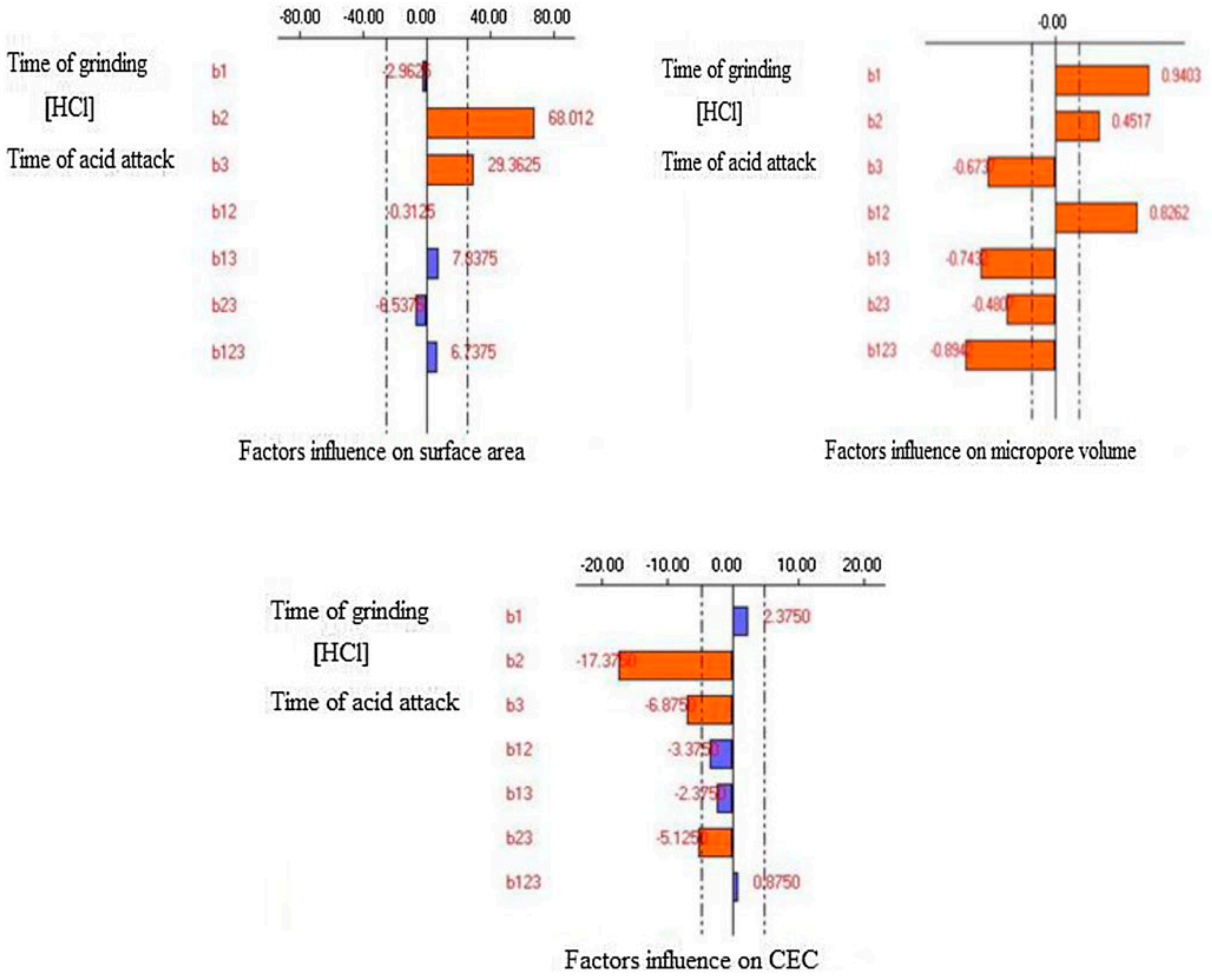

Fig. 8. Graphical analysis of the effect of: time of grinding, time and HCl concentration on CEC, specific surface area and specific micropore volume of MMT.

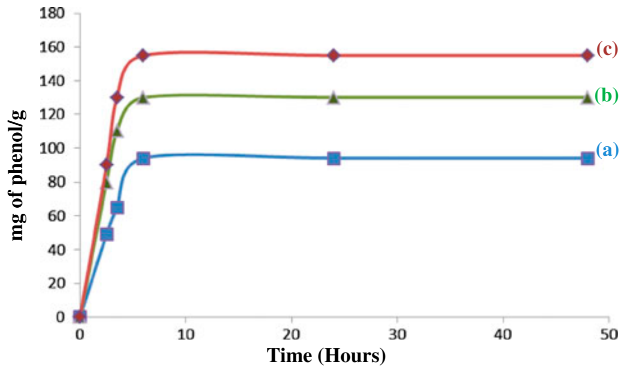

Fig. 9. Effect of time on the adsorption of phenol by (a) MMT, (b) ground MMT for 18 min, and (c) ground MMT and leached with 1 M HCl solution for 6 h.

3.4.2. Effect of pH

The effect of pH on phenol adsorption is presented in Fig. 10. Results show that adsorption increases with decreasing of pH values. To understand the origin of this trend, it is interesting to compare the pH_{PZC} of these adsorbents. The determined pH_{PZC} for MMT, ground MMT, and acid-leached ground MMT are, respectively, 6.2, 6.5, and 4.6. Thus, the reason behind the decrease in phenol retention with increase in pH could be attributed to the following two factors (i) phenol is a week acid ($pK_a = 9.8$), and for high-pH values, this adsorbent has a negative charge and (ii) for pH above the pH_{PZC}, the surface charge of adsorbents is negative, which create repulsion forces between the adsorbent and the aromatic compound.

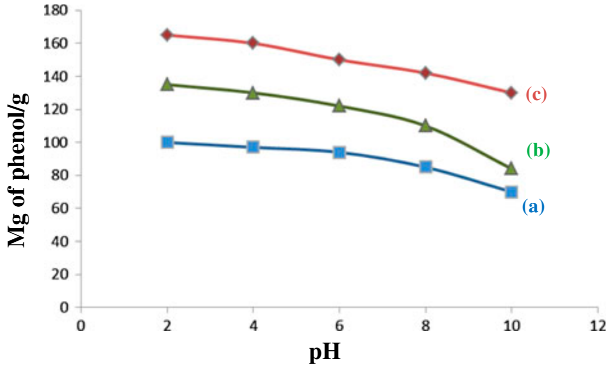

Fig. 10. Effect of pH on the adsorption of phenol by (a) MMT, (b) ground MMT for 18 min, and (c) ground MMT and leached with 1 M HCl solution for 6 h.

The same phenomenon has been reported for the removal of phenol by activated carbon [27].

3.4.3. Adsorption isotherm and modelization

Adsorption isotherm is represented in Fig. 11. Adsorption isotherm reflects the relationship between the amount of a solute adsorbed at constant temperature and its concentration in the equilibrium solution. It provides essential physiochemical data for assessing the applicability of the adsorption process as a complete unit operation. In this study, Freundlich and Langmuir models were used to describe phenol adsorption behavior [28]. The linear form of Langmuir model can be written as follows:

$$C_e/Q_e = 1/(Q_0 \cdot b) + C_e/Q_0 \qquad (2)$$

where C_e is the equilibrium concentration (mg/l), Q_e (mg/g) is the amount adsorbed at the equilibrium, Q_0 (mg/g) and b are Langmuir constants. The Langmuir isotherm was developed on the assumption that the adsorption process will only take place at specific homogenous sites within the adsorbent surface with the uniform distribution of energy level. Once the adsorbate is attached on the site, no further adsorption can take place at that site; which concluded that the adsorption process is monolayer in nature. Fig. 12 shows a linear relationship of C_e/Q_e vs. C_e using experimental data obtained, suggesting the applicability of the Langmuir model (R^2 = 1–0.99). The applicability of the model suggests monolayer coverage of the adsorbate at the outer surface of the adsorbent is significant.

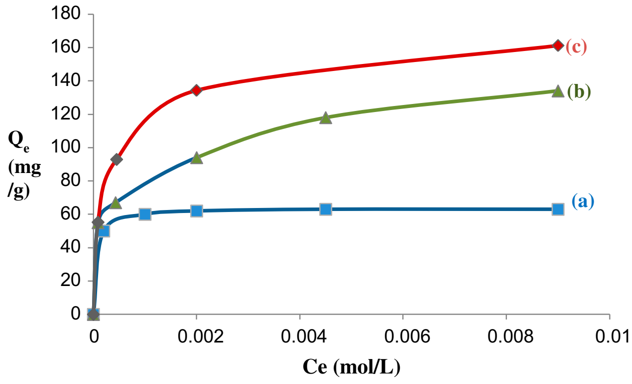

Fig. 11. Adsorption isotherm of phenol for (a) MMT, (b) ground MMT for 18 min, and (c) ground MMT and leached with 1 M HCl solution for 6 h.

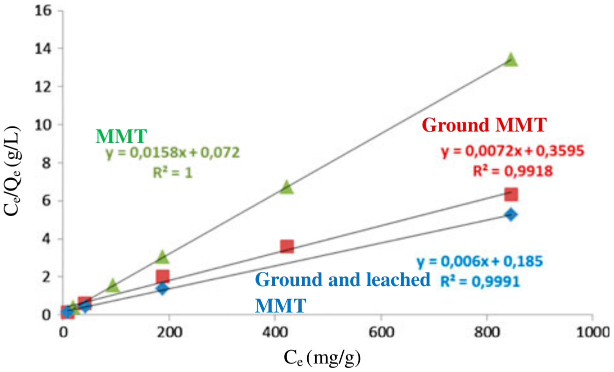

Fig. 12. C_e vs. C_e/Q_e of adsorbing phenol by various samples.

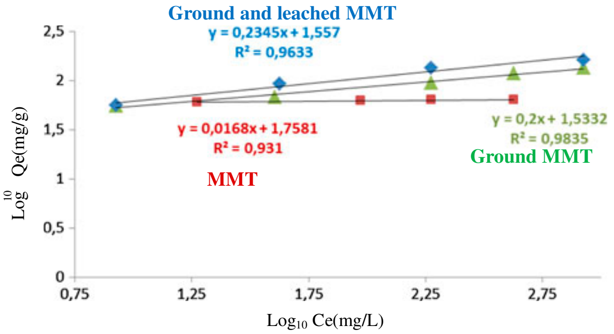

Fig. 13. $\log_{10}C_e$ vs. $\log_{10}Q_e$ of adsorbing phenol by various samples.

Contrarily to Langmuir, Freundlich isotherm was based on the assumption that the adsorption occurs on heterogeneous sites with nonuniform distribution of energy level.

The linear form of Freundlich model may be given by the following Eq. (3):

$$\log(Q_e) = \log(K_F) + 1/n \log(C_e) \qquad (3)$$

Table 4
Freundlich and Langmuir parameters

	Langmuir model			Freundlich model		
	Q_0 (mg/g)	b	R^2	K_F	$1/n$	R^2
MM	63	0.22	1	0.18	0.017	0.93
Ground MMT	138.9	0.02	0.99	0.19	0.2	0.98
Ground and leached MMT	166	0.03	0.99	0.24	0.23	0.96

where $1/n$ and K_F are Freundlich constants and will have a straight line with a slope of $1/n$ and an intercept of $\log(K_F)$ when $\log(Q_e)$ is plotted against $\log(C_e)$ (Fig. 13).

The Langmuir constants Q_0 and b and Freundlich constants K_F and $1/n$ for different samples are displayed in Table 4. It is obvious that the parameters Q_0 and K_F, which are related to the sorption capacity, increase with grinding and acid treatment. This is consistent with the experimental observation. Referring to these values it can be concluded that Langmuir explains better the adsorption of phenol and that phenol molecules are adsorbed until the formation of a saturated monolayer of molecules.

4. Conclusion

Mechanochemical treatment of montmorillonite effect the decrease in the crystallinity of clay by the reduction of particle size, breakdown and delamination of palatels clay. Grinding produces a loss of periodicity perpendicular to the layer plane and a decrease in the dimension of the crystallinity. After 18 min of grinding, the sample shows the highest surface area; for this sample, we have tested the effect of acid leaching on its textural and microstructure properties. Important differences have been obtained between unground and ground montmorillonite after leaching with 1 M HCl solution for 6 h which produce a material with a specific surface area of 490 m^2 g. Factorial design was used to evaluate most factors influence microstructure. It was shown that both concentration and time of acid treatment have a positive effect on specific surface area. Adsorption isotherm for phenol removal has been studied and it was shown that best retention is attained after 6 h and for lower values of pH. Adsorption analysis showed that the adsorption followed Langmuir isotherms.

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