Environmental Application of Acid Activated Kaolinite-Glaucnite Clay Assisted By Microwave Irradiation

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Abstract

Crude kaolinite-glauconite clay was active with hydrochloric acid for various times under variable microwave irradiation power. The influence of activation parameters (power and/or time) on the structural and textural properties of the treated samples has been studied. The modifications were evaluated by XRD, FTIR, XRF, SEM, BET, grain size and zetametry. The XRD and IR results show that acid activation reveals only weak changes on crystallinity of samples. However, HCl activation of clay assisted by microwave modifies morphology and size of grains with a little variation of the specific surface area values. The adsorbing power of the raw and activated clay was tested with methyl orange dye and the adsorption isotherms were modeled using Langmuir and Freundlich models. This study showed that the maximum adsorbed quantity of dye passes from 3.21mg/g for the untreated raw clay to 4.29mg/g for the activated clay irradiated 2 min under microwave at a power of 900W and that the Langmuir model is the most adequate to describe the adsorption process.

Introduction

Adsorption technology is the most widely used technology for waste water treatment. It was justified by several reasons including simplicity of design, rapidity, high efficiency and profitability. Although, this is a very proven technology for removing contaminants of different nature (heavy metals, organic molecules, dyes, etc.), it presents a major limitation to its application, which is the cost of the adsorbent [1–4]. In this context, natural clay minerals can be used as alternative adsorbents because they are inexpensive, friendly to the environment and available in huge quantities and notably can be easily accessible to improve their surface properties and therefore increase their adsorption capacities [5–7].

Glauconitic clay has been defined as green, iron potassium rich micaceous mineral of marine origin, with 2:1 dioctahedral sheets like illite structure. The octahedral sites in this clay were usually containing more Fe$^{3+}$ than Al$^{3+}$ and significant amounts of Mg$^{2+}$ and Fe$^{2+}$. Iron is mainly present in Fe$^{2+}$ form in glauconite structure. Glauconite structure is characterized by interstratications of expandable and non-expandable (10Å) layer (McRae, 1972) and low charge [8–9]. Some clays, such as, exhibit low reactivity and need some modifications to enhance their reactivities. Several modification processes (acid activation, thermal treatment, pillaring, organic functionalization...) have been proposed in order to obtain the desired properties [7, 10–12].

Clays modifications via acid activation aim to involve changing in physical and chemical properties of materials, by removal of different ions plugging the surface pores and to increase the surface area as well as the pore size and to obtain solids with high number of acidic sites from these minerals. Moreover, many Si-OH groups on the surface of clay appear as result of acid treatment. Acid activation has been a traditional method employed for improving the surface properties of clay minerals [13–14]. Actually, many chemical processes use microwave techniques for heating. The use of this technique in the activation of clay minerals offers some advantages comparing with the conventional method including a higher uniform heating rate in a shorter time. Also, this technique has proven successful for preparing new promising materials for water treatment by causing structural and textural changes that enhance the products’ adsorption capacity [10, 15–16].

In this study, we report the HCl acid activation assisted by microwave irradiation of crude kaolinite-glauconite clay. Structural and textural properties of activated clays will be evaluated then. This work will be closed by the study of adsorption of methyl orange on these obtained powders. An equilibrium adsorption isotherms’ analysis to obtain the Langmuir and Freundlich constants was realized.
Materials And Methods

2.1 Starting materials

A dark green clay mineral samples was used in this study. It was collected from Siliana region (north west of Tunisia). The clay was used in its crude form. The activating agent was hydrochloric acid (HCl, 98%). The anionic dye used as adsorbate is the methyl orange with the molecular formula \((C_{14}H_{14}N_3O_3S^-Na^+)\) and with the molecular weight \((327.34\text{g mol}^{-1})\).

2.2 Acid activation

Using the microwave irradiation method, the raw clay was activated with a hydrochloric acid (HCl) solution of 3M concentration. The ratio \([\text{solid (clay)} / \text{liquid (acid solution)}]\) used is 1/10. The suspensions prepared were irradiated in the microwave at different powers (630 and 900W) and at different times. After irradiation, the samples were centrifuged. The solids were washed several times with demineralized water to remove traces of chloride and then dried at 70 ° for approximately 24 hours. The materials obtained after drying were ground into a fine powder further subjected to characterizations. In the text, we note the samples activated as follows: Gpt where G is clay, p is the power (we note 6 if the power used is 630W and we note 9 if the power is 900W) and t is the activation time in minutes.

2.3 Adsorption

The concentration of dyes in the samples was determined during adsorption experiments by using UV-Visible spectrophotometer (PerkinElmer model LAMBDA 20) at 464nm. Adsorption tests were carried out by mixing 0.1g of clay with 50ml of methyl orange solution at various concentrations. The flasks were stirred for 2 h on a mechanical shaker at 2700 rpm. After the completion of the contact time, the suspension was centrifuged at 4000rpm for 15 min. The amounts of released dye were determined from the mass balance equation:

\[
Q_{\text{ads}}(mg/g) = \frac{(C_0 - C_{eq})V_s}{m} \quad [17]
\]

Were \(C_0\) and \(C_{eq}\) are respectively the initial and equilibrium concentrations of dye solution (mg/L) respectively; \(V_s\) is the suspension volume (L); and \(m\) is the amount of clay used (g).

2.4 Textural and structural characterization techniques

The identification of the different phases in the crude and activated clays was examined by X-ray diffraction technique by using X-ray diffractometer D8 ADVANCE BRUKER with CuK\(\alpha (\lambda = 1.54\text{Å})\) radiation over a range of angles from 5 to 80°. The FTIR spectrum of the clay mineral was recorded on a KBr disk, which contains 1% sample by mass, using a Perkin Elmer (model 783) spectrophotometer. For each sample, scans were measured in transmittance mode over the 4000 – 400 cm\(^{-1}\) range. The Chemical compositions of the studied materials were obtained by X-ray fluorescence (XRF) technique. The clay samples were prepared using the so-called fusion bead method. A specific amount of the analytical powder was first calcinated at 1050°C, and then added to lithium tetraborate. The mixture was introduced to the beader following a heating cycle. Finally, the transparent bead was analyzed using a BRUKER S8 TIGER. The zeta potential was measured by the Malvern Zetasizer Nano-ZS. Nitrogen adsorption–desorption isotherms at 77 K were performed in a Micromeritics ASAP 3000 sorptometer. Samples were out-gassed at 150°C in \(N_2\) flow with the residual pressure of \(10^{-5}\) mm Hg. Surface area values and pore size distributions were obtained from the adsorption branch of the isotherm by using the BET method. The morphology of the samples is analyzed
by scanning electron microscopy (MEB) by using FEG 650. The granulometric distribution of samples was measured by means of a Laser granulometer Microtrac S3500.

Results And Discussion

3.1 Mineralogical composition of starting materials

Figure 1 displays the X-ray diffractogram of the starting material. This diffractogram exhibits the characteristic reflections of illite (10.23 Å) and of kaolinite (7.11 Å; 3.56 Å). It also shows that the associated minerals are the quartz (3.33 Å), the calcite (3.03 Å) and the dolomite (2.85 Å) [18]. The chemical composition of starting clay, expressed as wt% of oxide, is given in Table 1. The relatively high percentage of iron oxide compared to aluminum oxide and the presence of $K_2O$ suggest that we are in the presence of a ferrous type mineral of illite called "glauconite" [13]. On the other hand, the high contents of $SiO_2$, MgO and CaO can be explained by the presence of quartz and carbonates associated with the clay. The infrared spectrum of clay (Fig. 2) reveals the presence of all characteristic vibration of phyllosilicates and these of associated minerals signaled by XRD [19]. The broad band at 3405 cm$^{-1}$ and the strain band at 1637 cm$^{-1}$ are attributed to the OH vibrations of the clay hydration water. The band at 1103 cm$^{-1}$ corresponds to the valence vibration of the Si-O group of the clay network, while the deformation bands appear respectively around 467 cm$^{-1}$ for the [Si-O-Al, Fe] group and at 991 cm$^{-1}$ for the Si-O-Si group. The two bands at 3636 and 692 cm$^{-1}$ reveal the presence of kaolinite. The bands at 778 and 1431 cm$^{-1}$ are attributed respectively to quartz and carbonate.

| SiO$_2$ | Fe$_2$O$_3$ | Al$_2$O | K$_2$O | MgO | CaO | Na$_2$O | P$_2$O$_5$ | SO$_3$ | TiO$_2$ | Cr$_2$O | MnO$_2$ | SrO | ZnO |
|--------|-------------|---------|-------|-----|-----|--------|-----------|-------|--------|--------|--------|-----|-----|
| 43.08  | 14.30       | 9.21    | 3.40  | 3.85| 8.36| 0.18   | 2.50      | 0.69  | 0.31   | 0.07   | 0.03   | 0.03| 0.02|

3.2 Characterization of activated samples

3.2.1 X-Ray diffraction

Figure 3 presents diffractograms of crude clay and these of treated with chlorhydric acid (3M) assisted by microwave irradiation at different times (1 ; 2 or 3mn) and various powers (630 or 900W). Only weak changes on cristalinity of samples have been detected after activation. All X-ray diffractograms recorded show the presence of the characteristic reflections of quartz, indicating their resistance to chlorhydric acid solution. Although, characteristic reflections of carbonates (dolomite and calcite) disappeared rapidly with acid activation treatment. On the other hand, we note that all reflections attributed to the glauconite remain at the same positions and with almost the same intensities whatever the power or time of activation used. However, it is shown that the kaolnic phase resists less and diffractograms indicate that 2 minutes is a sufficient time to disappear all their characteristic reflections. The base line of diffractograms is conserved with the same allure. The absence of amorphous phase indicates that the structural unit of the clay is partially affected without being destroyed.

3.2.2 Infrared spectroscopy

Figure 4 displays infrared spectra of crude clay and its derived acid activated materials. The most visible change introduce in these spectra after activation was the progressive decrease in the intensities of bands attributed to [HO-Al, Fe] (876 cm$^{-1}$) and [HO-(Al, Fe)] (3636 cm$^{-1}$) groups of kaolinite and glauconite clays. This decrease indicates...
the progressive destruction of octahedral cations as function of increasing acid activation. The band characteristic of carbonate is absent from two minutes of activation. However, all characteristic bands of silicate groups are conserved, which confirms the absence of amorphous silica.

### 3.2.3 Chemical analysis

The chemical composition of the resulting solids is given in Table 2. Following acid treatment, the content of iron and aluminum oxide decreased with increasing the treatment time and/or the power of microwave irradiation, while the relative amount of SiO$_2$ increased. This indicates the partial destruction of clays structures signaled by XRD and IR analyses. It was also revealed from these results that the percentage of K$_2$O decreases slightly indicating the resistance of glauconite to the acid activation. However, the highest decrease of the CaO content confirms the elimination of carbonates.

|                  | G$_0$ | G$_6$ - 1 | G$_6$ - 2 | G$_6$ - 3 | G$_9$ - 1 | G$_9$ - 2 |
|------------------|------|----------|----------|----------|----------|----------|
| SiO$_2$          | 43.08| 61.13    | 68.15    | 68.68    | 65.28    | 67.81    |
| Fe$_2$O$_3$      | 14.30| 12.31    | 8.75     | 8.57     | 9.76     | 8.40     |
| Al$_2$O$_3$      | 9.21 | 8.23     | 6.69     | 6.48     | 7.25     | 6.36     |
| K$_2$O           | 3.40 | 2.93     | 3.21     | 3.13     | 3.14     | 3.11     |
| MgO              | 3.85 | 2.57     | 1.83     | 1.81     | 2.06     | 1.73     |
| CaO              | 8.36 | 0.34     | 0.22     | 0.18     | 0.28     | 0.16     |
| Na$_2$O          | 0.18 | 0.16     | 0.13     | 0.13     | 0.14     | 0.16     |
| P$_2$O$_5$       | 2.50 | 0.12     | 0.19     | 0.16     | 0.11     | 0.09     |
| SO$_3$           | 0.69 | 0.16     | 0.17     | 0.33     | 0.17     | 0.12     |
| TiO$_2$          | 0.31 | 0.37     | 0.43     | 0.44     | 0.42     | 0.42     |
| Cr$_2$O$_3$      | 0.07 | 0.06     | 0.05     | 0.05     | 0.05     | 0.05     |
| Mn$_2$O$_3$      | 0.03 | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     |
| SrO              | 0.03 | 0.01     | 0.01     | 0.01     | 0.01     | 0.01     |
| ZnO              | 0.02 | 0.03     | 0.01     | 0.03     | 0.02     | 0.01     |

To evaluate more the decomposition and the change in dissolution characteristics of clay introduced by the activation, we used the proportion of reacted material value ($\alpha$) as a measure of the decomposition [20]. The $\alpha$ formula is:

$$\alpha = \frac{m_0 - m_t}{m_0}$$

where, $m_0$ and $m_t$ are respectively the amount of the oxide before and after acid treatment.

The exam of $\alpha$ values (Table 3) reveal that the relative amount of alumina extracted is lower than that of iron. This result can be correlated with the strength of the bond. In fact the Al-O bond is stronger than the Fe-O one ($E_{(Al-O)} = 507.5KJ mol^{-1}$ and $E_{(Fe-O)} = 408.8KJ mol^{-1}$) [21].
3.3 Textural properties of activated and non-activated clay

3.3.1 Granulometry

Crude clay displays a granulometry lower than 100 µm (Fig. 5). The particle size of this clay presents a bimodal distribution with two medium sizes 0.85 and 2.27 µm. However, activated clays showed a high particles sizes which can extended to 1000 µm. The particle size increases with acid activation assisted by microwave irradiation. The highest size (around 295 µm) is obtained by an activation during 3 min under a power irradiation of 630w.

3.3.2 SEM analysis

Figure 6 displays the scanning electron micrographs of crude clay G₀ and G9-2 activated sample. SEM Micrographs show that the textural of surface morphology of natural clay is different to these of G9-2 activated clay. In comparison with natural clay, G9-2 sample appears to be highly compact and an agglomeration phenomenon has been observed following the acid treatment assisted by microwave irradiation. These observations are in good agreement with the increase of particles sizes of activated clays signaled by granulometry.

3.3.3 Adsorption–Desorption Isotherms and BET Surface Area analysis

N₂ adsorption-desorption isotherms at 77K of crude and acid activated clay under microwave irradiation are presented in Fig. 7.

Adsorption-desorption isotherms of natural or acid activated clays at various microwave irradiations exhibit the classical type II shape of adsorbents with H₃ hysteresis loop according to the IUPAC classification [22–23]. H₃ hysteresis loop is observed for slit pores or in case of particles in the form of layers. The surface area values and total volume pore of studied samples are listed in table IV. As seen from this table, HCl activated clay assisted by
different microwave irradiation (630 or 900W) do not increase or increase little the surface area values. This can be correlated firstly to the low rate of amorphization signaled by XRD which can makes a very important contribution. Secondly, these results can be explained by the increase of particle sizes indicating by granulometry and SEM.

### 3.3.4 Zeta potential

The zeta potential of non-activated and activated clay is shown in Fig. 8. Compared to another clays, very limited literatures were interested to zeta potential on glauconite type. Herein, both for natural or acid activated kaolinite-glaucconite samples the zeta potential values are negative in all the field of pH. This indicates that surfaces of activated or non-activated samples have net negatives electrostatic charges and no iso-electric points are detected. These observations are similar to these observed by Khaled A. Selim et al. [24].

### 3.4 Adsorption studies

#### 3.4.1 Adsorption isotherms

Methyl orange adsorptions isotherms of the natural and prepared samples have been evaluated. To identify the interaction between adsorbent and adsorbate, the adsorption process was studied as a function of equilibrium methyl orange concentration (Ce) (Fig. 9). According to GILES classification [25] isotherms seem to be of the L type, revealing that methyl orange was rapidly adsorbed and has a good affinity for kaolinite-glaucconite clays surfaces. The exam of isotherms shows that only for G6-1 sample the form L of isotherm is conserved like the form of crude clay. For all other activated samples, all isotherms are similar in shape and they reveal the presence of two clear plateaus. This can be correlated to the existence of two types of reactive sites. These observations of two plateaus in adsorption isotherms were also obtained in some previous studies concerning the adsorption of quinalizarin onto acid activated palygorskite [26] and about the adsorption of organic molecules on silica surface [27] either about a sulphate adsorption on a volcanic ash soil [28]. According to the isotherms, the higher adsorption capacity was detected for G9-2 sample and Qmax is 4.29 mg/g (Table 5). This result is not correlated with values of specific surface area of sample indicating that this phenomenon was related essentially to the nature of the active sites created after acid activation assisted by microwave irradiation.

#### 3.4.2 Modelling Adsorption isotherms

| Samples | Q_{ads} (mg/g) |
|---------|----------------|
| G0      | 3.22           |
| G6-1    | 2.97           |
| G6-2    | 3.39           |
| G6-3    | 3.79           |
| G9-1    | 3.39           |
| G9-2    | 4.29           |
To describe solid/liquid adsorption process, two empirical models are tested, which are the Langmuir and the Freundlich isotherms (Fig. 10 and Table 6). Langmuir model assumes that adsorption occurs at specific homogeneous sites within the adsorbent and has found successful application in many studies of monolayer adsorption. The obtained adsorption data were fitted by the linearized Langmuir equation:

\[
\frac{c_{eq}}{Q_{ad}} = \frac{1}{KQ_m} + \frac{c_{eq}}{Q_m}
\]

[29]

Table 6

| Isotherm constants and correlation coefficients of methyl orange adsorption onto activated and non-activated clay |
|---------------------------------------------------------------|
| G0   | G6-1 | G6-2 | G6-3 | G9-1 | G9-2 |
| Langmuir model       | \(Q_{max}\) | 9.634 | 3.643 | 6.540 | 10.764 | 15.384 | 119.05 |
|                     | \(k\) | 0.183 | 0.103 | 0.147 | 0.108 | 0.053 | 0.007 |
|                     | \(R^2\) | 0.994 | 0.961 | 0.9713 | 0.9126 | 0.9309 | 0.9429 |
| Freundlich model     | \(K_F\) | 1.270 | 0.863 | 0.604 | 1.157 | 0.587 | 0.723 |
|                     | \(1/n\) | 1.768 | 1.607 | 1.324 | 1.597 | 1.060 | 1.264 |
|                     | \(R^2\) | 0.884 | 0.879 | 0.9445 | 0.897 | 0.913 | 0.940 |

Where \(Q_{ad}\) is the equilibrium capacity of adsorbate on adsorbent (mol.g\(^{-1}\)), \(c_{eq}\) is the equilibrium concentration of adsorbate solution (mol.L\(^{-1}\)), \(Q_m\) is the maximum adsorption capacity of the adsorbent (mol.g\(^{-1}\)), and \(K\) is the Langmuir constant (L.mol\(^{-1}\)) related to the adsorption energy.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. Its linearized form can be written as follow: \(\ln Q_{ad} = \ln K_F + n\ln c_{eq}\) [4]

Where : \(K_F\) (L.g\(^{-1}\)) and \(n\) (dimensionless) are the freundlich adsorption isotherm constants, being indicative of the extent of adsorption and the degree of non-linearity between solution concentration and adsorption respectively.

The correlation coefficients \(R^2\), calculated from the linear Langmuir and Freundlich equations, and the characteristic coefficients of each model are presented in Table 6. We can see from this table that for non-activated kaolinite-glaucnite the Langmuir model appears better than the Freundlich model to describe methyl orange adsorption process. However, these correlations are not satisfactory enough for the activated clay. N. Frini-Srasra and E. Srasra (2009) have attributed these observations in isotherms shape to the existence of two kinds of adsorption sites: the stronger and the weaker sites.

**Conclusion**

In conclusion, acid activation of Tunisian Kaolinite-glaucnite clay was successfully made in microwave by irradiation assistance. This method has the advantage of a short time of manipulation in comparison with the traditional heating activation method. The results show that acid activation under microwave irradiation does not increase the specific surface area but increases well the adsorbing power of crude clay and provide promising
materials for adsorption applications. Under the same conditions, the $Q_{\text{max}}$ value increases from 3.21mg/g for the untreated clay to 4.29mg/g for G9-2. This increase results from the existence of new active sites created by acid activation.

**Declarations**

**Author Declarations:**

**Credit authorship contribution statement:**

**Thouraya Turki:** Conceptualization, Methodology, Supervision, Investigation, Resources, Data curation, Writing - original draft, Project administration, Writing - review & editing, Validation.

**Najoua Frini-Srasra:** Conceptualization, Methodology, Supervision, Investigation, Project administration, Writing - review & editing, Validation.

**Ezzeddine Srasra:** Supervision, Investigation, Writing - review & editing, Validation.

**Conflicts of Interest:**

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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**Consent to participate:**

All authors of this research paper have directly participated in the planning, execution, or analysis of this study.

**Consent for publication:**

All authors of this paper have read and approved the final version submitted.

**Availability of data and materials:**

All data and materials are availables.

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Figures
Figure 1

XRD pattern of starting material
Figure 2

Infrared spectrum of starting material

Figure 3

X-ray diffractograms of starting and acid activated crude clay at different powers and times of activation
Figure 4

Infrared spectra of starting and acid activated crude kaolinite-glauconite clay at different powers and times of activation
Figure 5
Granulometry of crude and activated clays
Figure 6

Micrograph SEM of natural clay G0 and activated clay G9-2
Figure 7

Adsorption-desorption isotherms at 77K of crude and acid activated clays
Figure 8

Zeta potential of non-activated and activated kaolinite-glauconite

Figure 9
Adsorption isotherms of dye onto crude clay before and after activation

Figure 10

Calculated and measured adsorption isotherms for the Langmuir model