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STRUCTURAL CHARACTERISTICS OF THE EGYPTIAN CLAY AS A LOW-COST ADSORBENT

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ABSTRACT

A study of the characteristics of clay from El-Sheikh Fadl Village, El-Minia governorate in Egypt has been carried out. A crucial factor in the applying clay as a low-cost adsorbent, however, is the understanding of the physical, chemical, mineralogical, and colloidal properties of these clays. The characteristics of texture such as surface area, pore volume, porosity, pore size distribution, particle shape and density were determined. The pore size distribution results showed that natural clay is predominantly mesoporous. The thermal behavior of clay was studied using differential thermal analysis and thermogravimetric analysis analysis. The X-Ray diffraction analysis was performed in order to determine the main constituents of the materials. The X-Ray diffraction analysis verified the presence of kaolinite, montmorillonite and quartz in the natural clay. Then clay was tested for infrared spectra, it confirm the presence of the constituents mentioned above. The structure and chemical composition, exchangeable ion type and small crystal size of montmorillonite are responsible for several properties, including a large chemically active surface area.

Keywords: Egyptian clay, Low-cost adsorbent, Surface chemistry, Mineralogical analysis, Characterization.

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Contribution/ Originality

The paper's primary contribution is finding that the structure, chemical composition and exchangeable ion type of montmorillonite are responsible for several properties, including a large chemically active surface area. and low-cost adsorbents might be a suitable local alternative for elimination of heavy metal ions and basic dyestuffs from aqueous solutions

1. INTRODUCTION

Clays may be considered of the most distributed elements in the earth crust. Clay are composed of the octahedral (Al^{3+}, Fe^{2+} , Fe^{3+}, or Mg^{2+}) and tetrahedral (Si^{4+}) structures depending on the type of clay [1]. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite [2]. Clays are composed by hydrous aluminum, silica, magnesium and iron, it may also contain calcium, potassium and other ions, which are non-clay minerals. Both clay and non-clay minerals influence the properties of a clay materials. In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and Fuller's earth for their capacity to adsorb not only inorganic but also organic molecules. In particular, interactions between dyes and clay particles have been extensively studied [3-

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16]. Clays are among the cheapest, abundant, environmentally friendly, ion exchangeable and non-toxic adsorbents that can be used to substitute the expensive commercial activated carbon in tackling environmental pollution problems [17]. There are three basic classes of clays: kaolinite, micas (such as illite) and smectite (for ex. montmorillonite).

2. LITERATURE REVIEW

Some investigations were carried out to study the clay as low-cost adsorbent and its microstructural and mineralogical characteristics. Egyptian natural clay was characterized using DTA, TGA, XRD, and chemical analysis. Montmorillonite clay has the largest surface area and highest cation exchange capacity. Its current market price (about US$ 0.04–0.12/kg) is considered to be 20 times cheaper than that of activated carbon [18]. An experimental study of clay characterization conducted with the aid of MB test, which yields a semi-quantitative evaluation of the activity of a geo-material based on the type and quantity of clay minerals contained in it was illustrated. Reference [19] studied surface chemistry of clay. The negative charge gives clay the capability to adsorb positively charged species, their sorption properties also come from their high surface area and high porosity. Clay was characterized through FPIA, SEM-EDX, XRD, N_2 (77 K) adsorption, and FTIR [20]. Bentonite clay minerals belonging to the smectite group have a wide range of chemical and industrial uses. Clay was studied by some physico-chemical methods. Results of XRD, chemical analysis, IR, TGA and DTA, specific and total surface area confirm the general smectite character of the collected sample [21]. A study of the characteristics of clay samples from different locations in Nigeria has been carried out [22]. Instrumental characterizations of the clay were performed by different techniques such as XRF, XRD and FTIR. XRF shows the chemical compositions of the clay where Al-oxide and silica oxide are present in major quantity whereas XRD confirms the presence of these minerals in clay. FTIR studies show the presence of quartz, alumina, hematite and different mineral matters [23]. Reference [24] tested the applicability of the MB method for the determination of cation exchange capacity and specific surface area of Egyptian smectitic clay deposits and hence to estimate their content of expansive clays. It has been concluded that the MB test can be used as a reliable and rapid method for the characterization of smectitic clay deposits and soils containing smectite. These properties are important for engineering and environmental geological assessments of sites for different construction purposes.

Two clays taken from Tunisia [25] was characterized, the research has been carried out by using XRD, IR, TGA and DTA, observations with SEM and analytic techniques. The Langmuir isotherms fit better the experimental data. The results which were obtained can be introduced in data base for designing an adsorption process using clay, as a low-cost adsorbent for the treatment of the Cr (VI) rich wastewater. Reference [26] characterized Ball clay for its morphology, surface area, porosity, functional groups identification and testing of its adsorptive capacity as low cost adsorbents for MB. Reference [26] characterized natural clay containing kaolinite, chlorite, illite and illite/smectite mixed layered clay minerals and used as a potential adsorbent for the removal of Rhodamine B (RB) dye from aqueous solution. A maximum dye uptake of > 90% was achieved at 313 K employing an initial dye concentration of 4.8×10^{-6} M, a pH value of 2 and an adsorbent dosage of 1 g/l. the textural, mineralogical and chemical composition of the smectitic clays from Fayum, Egypt was studied. The clay has good heat capacities and their pastes can be applied in different treatments. The trace elements present in the clay stones, namely, As, Pb, Cu, Zn, Co, Ni and Cr are within the normal ranges of average natural mud [27].

The objective of the present study is to characterize Egyptian natural clay in terms of its surface area, pore structure (total pore volume, pore size distribution and porosity). Also other physical properties (density, particle shape) which have an important role in industrial applications, especially handling and packing in fixed and fluidizing bed have been studied. The second objective was to study the thermal behavior (DTA and TGA) in order to investigate the thermal stability and thermal behavior of adsorbents. The work also investigates the usefulness of (IR and XRD) analysis for more a knowledge of constituents and chemical structure as well as understanding the mechanism of adsorption of any adsorbate on the adsorbents. These properties are directly related to the effectiveness of using of the clay as a low-cost adsorbent; also these properties are important to the commercial utilization of the adsorbent.

3. EXPERIMENTAL TECHNIQUES

The characterization of clay is carried out with a number of experimental approaches in order to investigate all the adsorptive features. Clay was obtained from El-Sheikh Fadl Village, El-Minia governorate in Egypt. Specific surface area by gas adsorption was performed using gas sorption analyzer model (NOVA 2200, version 6.10, Quanta Chrome Corporation, Japan), pre-weighted samples are prepared and degassed by applying combination of heat (120 °C) and vacuum for 3 hr, this process removes previously adsorbed contaminants from the surface and the pores, adsorption isotherms were analyzed by the BET method to determine surface area. Pore size distribution was calculated from the gas adsorption isotherm using (Barrett, Joyner and Halenda (BJH)) method [28]. Specific pore volume was calculated from the amount of nitrogen adsorbed at the highest relative pressure examined [29] which was $P/P_o = 0.99$, surface texture experiments were carried out in Faculty of Science, Elmina university. The investigating of the particles shape was carried out using the large toolmaker's microscope. XRD analysis was carried out by means of a (JSX-60PA Joel diffractometer) equipped with a source of Ni-filtered CuK_α-radiation. For the sake of identification (I/I_o vs. d-spacing Å) obtained was matched with ASTM standards [30] XRD experiments were carried in the Central Lab., El-Minia University. DTA and TGA were performed using an automatic recording Shimadzu (model 60H) thermal analyzer. DTA and TGA curves were recorded by heating a definite mass of the materials up to 1000 °C at a rate of 10 °C min^{-1}, in a dynamic atmosphere of air (40 ml/min). Platinum was used as a reference material for DTA measurements. The thermal behavior experiments were carried in the Thermal Analysis Lab., Faculty of Sciences, Asuit University. The pH was measured by placing 5g of the adsorbent in 100 ml of distilled water (the pH of distilled water is 5.8), this value was adjusted by adding dilute solution of alkali (NaOH)), being checked vigorously and left for 24 hr, then the pH of the solution was measured. IR analysis was carried out over the frequency range 4000-500 cm^{-1} at a resolution of 2 cm^{-1}, using Spectrophotometer [model 580B Perkin-Elmer (U.K.)], the spectrum was taken for a thin (20mg/cm^{-2}) lightly loaded, (1%) KBr-supported disk of each sample, IR experiments were carried in Faculty of Sciences, El-Minia University.

4. RESULTS AND DISCUSSION

4.1. Physical Analysis

4.1.1. Brunauer Emmett Teller (BET) Analysis

Typical result of N_2 adsorption/desorption isotherms for the clay is shown in Figure (1). According to (B.D.D.T) classification, the adsorption isotherm of natural clay is of type IV which is generally associated with capillary condensation in mesopore structures. Also it can be seen, that the hysteresis curves of adsorption isotherms of N_2 of natural clay onto the surface of the adsorbents of type (b) [31] which is commonly interpreted as evidence for slit-shaped meso- or macropores [31].

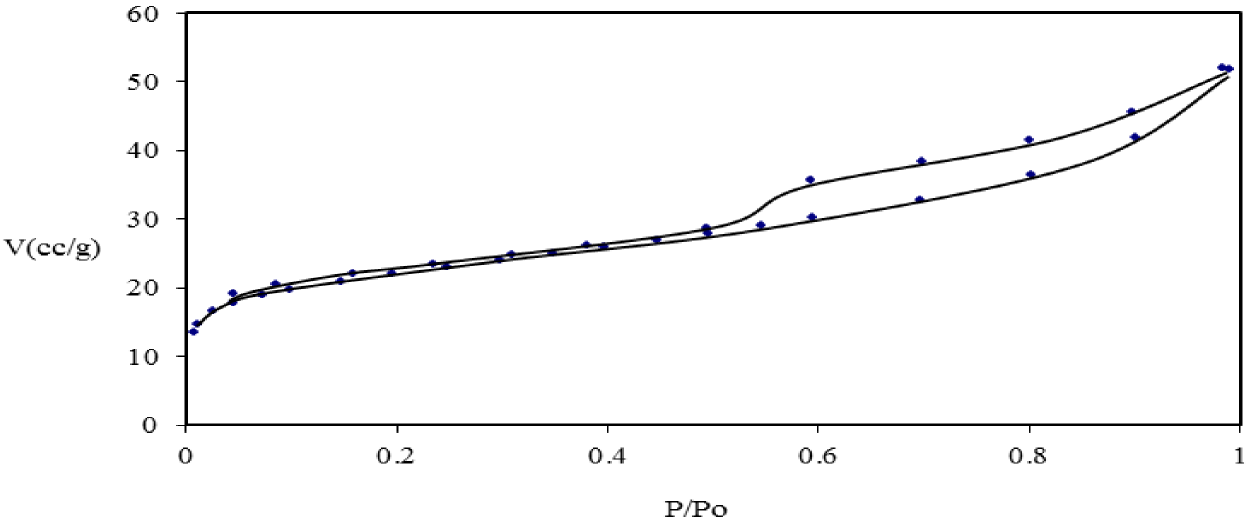

Figure-1. N2 Adsorption/Desorption Isotherms for Natural Clay.

Table-1. Surface characteristic of clay

Materials	Specific surface area (m^2/g)	TPV (cc/g)	Particle porosity
Natural clay	78.4	0.056	0.37

4.1.2. The Characteristic of Clay Surface Texture

As shown in Figure (2), the natural clay consists mainly of kaolinite and montmorillonite, due to the isomorphic substitutions: Si^{4+} can be replaced by Al^{3+} or Fe^{3+} in tetrahedron sites and Al^{3+} by Mg^{2+}, Fe^{2+}, and Mn^{2+} in octahedron sites [32] Montmorillinite has an excess of negative charge on its lattice, the presence of this negative charge on the clay surface enhance the adsorbent capacity to adsorb dye ions such that clay has an affinity for cationic species [10]. A second source of charge on the minerals is the broken bonds found at the mineral edges. The structure cannot extend infinitely, so at some point there will be oxygen without all charges satisfied by associating with cations. The structure and chemical composition, exchangeable ion type and small crystal size of montmorillonite are responsible for several properties, including a large chemically active surface area.

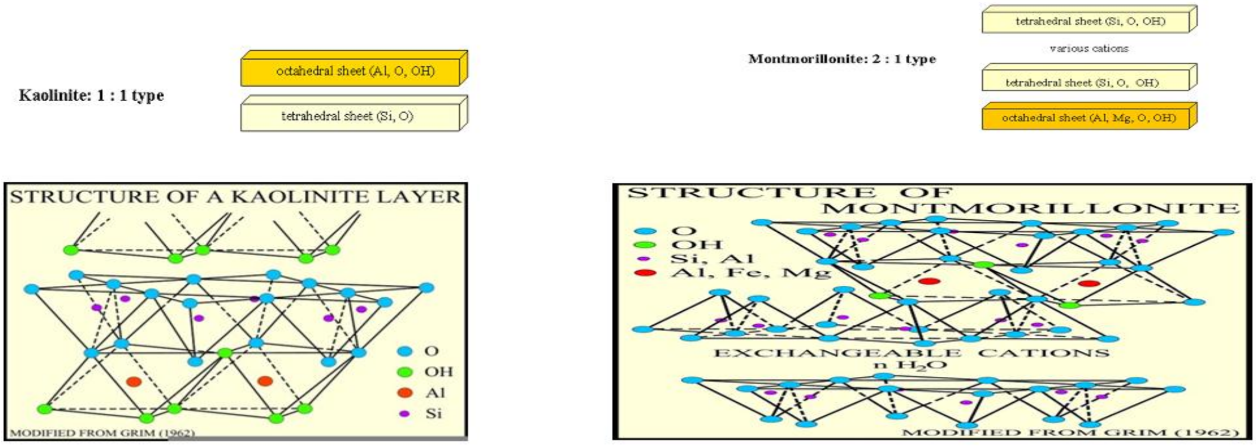

Figure-2. Chemical Structure of Kaolinite and Montmorillonite [33].

4.1.3. Pore Size Distribution

Pore size distribution (PSD) was represented in Figure (3) by the derivative (dv_p/dr_p) as a function of r_p, where V_p and r_p are the volume and radius of the pores. The size in question is here the radius, which implies that the pores are known to be, or assumed to be, cylindrical. In other cases r_p should be replaced by the width. As shown in

Figure (3), PSD of natural clay displays only one characteristic peak in mesopores region at r_p=23.52 Å, which suggest that much of the pores are of the same size. Based on these results, this natural clay can be classified as a mesoporous material.

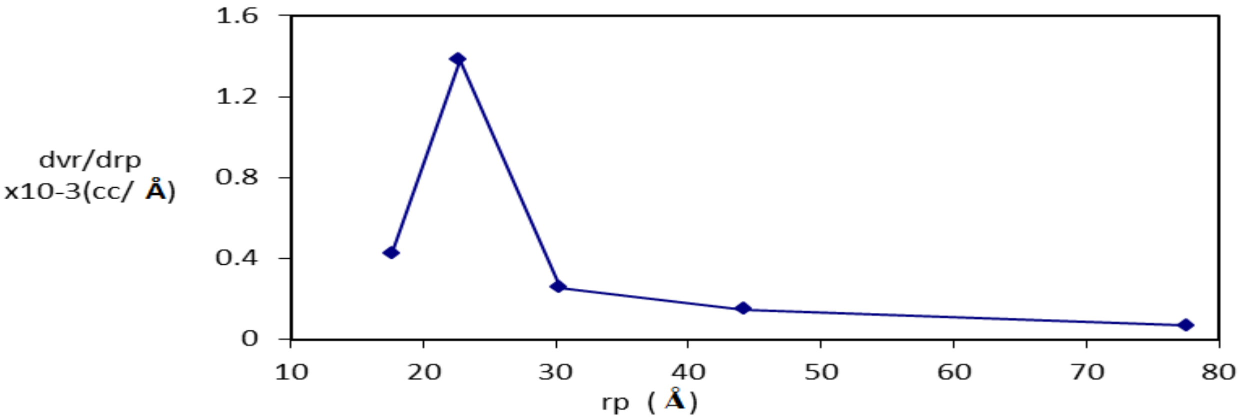

Figure-3. Pore Size Distribution of Natural Clay

Mesopores, which branch from the macropores, serve as passages by which molecules reach the smaller micropores. The pore structure should be such that the adsorbate molecules enter the pores and adsorb onto the inner surface of the pores. If the adsorbate molecules are larger than the pore diameter, lesser adsorption will take place because of stearic hindrances. According to the classification of IUPAC, the hysteresis shape of natural clay is of type H3 indicates the existence of the aggregates (assemblage of particles which is loosely coherent) of adsorbent containing parallel plates, slit shape pores or wide capillaries.

4.1.4. Density

4.1.4.1. Apparent Particle Density (ρ_p)

The physical properties of natural clay change from place to another even in the same place from a depth to another. However the major constituents of the clay are montmorillonite and Kaolinite. Particle density of Kaolinite is 2.6 g/cm^3 (Ceramic Materials Database). Particle density of montmorillonite varies from 2.3: 3 g/cm^3 (Amethyst Galleries, Inc), which close to the results of the clay under study (2.34 g/cm^3).

4.1.4.2. Bulk Density (ρ_b)

As shown in Table (2) for clay under investigation, as the particle size increase, the bulk density also increases. Amirbahman, et al. [34] studied the relationship between particle size and bulk density for crab-shell chitosan particles, where for dp = 0.425- 0.85, 0.85- 2 and 2- 4.75mm the bulk density was 1.16 , 1.33 and 1.07 g/cm^3, respectively. The Cain-Lairmore model which was based on the Hausner ratio, mean particle size, and the angle of repose was found to be an accurate predictor of bulk material cohesiveness. Thalberg, et al. [35] used a modified Hausner ratio for evaluating the flowability of different formulations. They used a compressed bulk density instead of tap density, as it required less power to achieve a maximum packing condition. In conclusion, the change of particle size has an effect on bulk density, but it is not only the controlling parameter

Table-2. Bulk density of natural clay, ρ_b (g/cm^3)

Materials	(180-250 μm)	(250-355 μm)	(500-710 μm)
Natural clay	0.818	0.899	1.183

4.1.5. Particle Shape

The milling of natural clay was necessary in order to achieve better performance for dye removal (they used in their milled form in adsorption purposes). Examination of the particles under a microscope provides a two-dimensional image. The particles of the clay appeared irregularly shaped under a microscope but approximated more closely to spheres than to cylinders or parallel pipes.

4.2. Mineral Analysis (XRD Analysis)

Mineralogical analysis was performed in order to determine the main constituents. The natural clay is composed of montmorillonite (58%) and kaolinite (42%). As shown in Figure (4), XRD pattern of clay displays the characteristic peaks of kaolinite that is characterized by its strongest d-lines (6.97, 5.44, and 2.53 Å) and others (ASTM card no. 14-0164); montmorillonite that is characterized by its strongest d-lines (3.59, 2.53 , 1.53 and 1.29 Å) and others (ASTM card no. 13-0135); quartz (which is the non clay mineral in the clay) is characterized by its strongest d-lines (3.31, 4.19) and others (ASTM card no. 5-049).

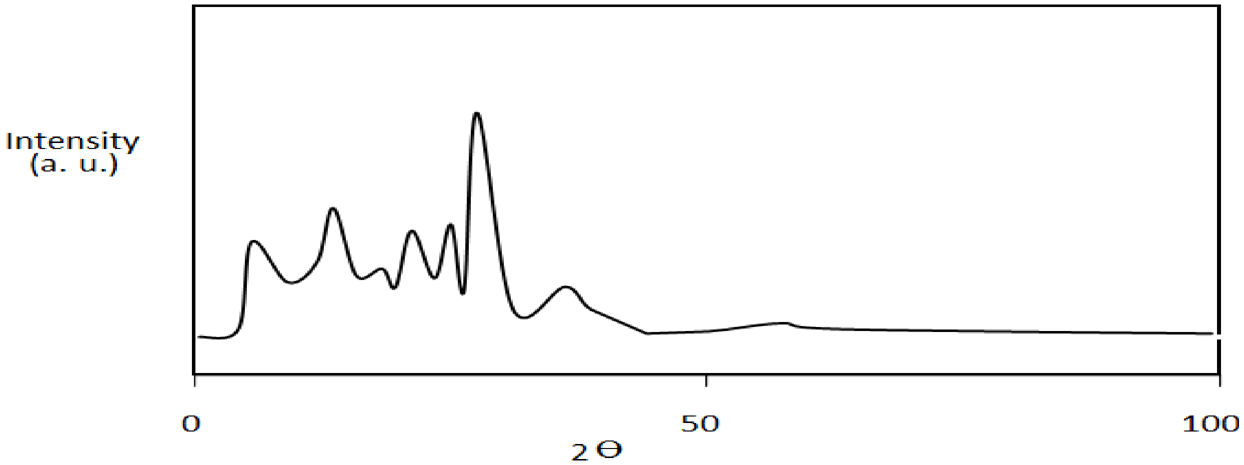

Figure-4. XRD Pattern of Natural Clay

4.3. Thermal Analysis (DTA and TGA)

From Table (3), it was found that the weight loss of natural clay is 6.297% occurred at 28-120 °C as a big endothermic peak, as shown in Figure (5), and weight loss (3.156%) which appears as small endothermic peak at 121-187 °C , this is may be due to the loss of sorbed water, which largely existing in the interlayer spaces of montmorillonite structure. The size and the shape of peak as well as the position of endothermic temperature are depend on the type of exchangeable cations held with water in the interlayer spaces [36]. An exothermic shoulder noticed at about 374 °C could be related to the oxidation of minor amounts of organic materials. The second weight loss is (6.805%) occurred as an endothermic peak at 404-550 °C, this is loss in weight could be related to the dehydroxylation ; elimination of hydroxyl group of clay crystals. The formation of S-shaped peak at 761-1001 °C could be due to the formation of a new phase due to the breakdown of the structure and formation of new phase at this high temperature, such as mullite, $3Al_2O_2.2SiO_2$ [37] from the heated kaolinite mineral. The amount of adsorbed water <200 °C may be used as distinctive parameter for determining the nature of the clay mineral. The amount of structural water associated with the unit weight of adsorbed water is referred to as W_a, could be used for such determination. If $W_a \geq 5$, then the clay contains kaolinite in significant proportion, while for montmorillonite or illite, $W_a < 2$. It was found that the clay has 1.26 [$W_a = (21.338-9.453)/(9.453) = 1.26$], indicating the predominance of montmorillonite in its composition.

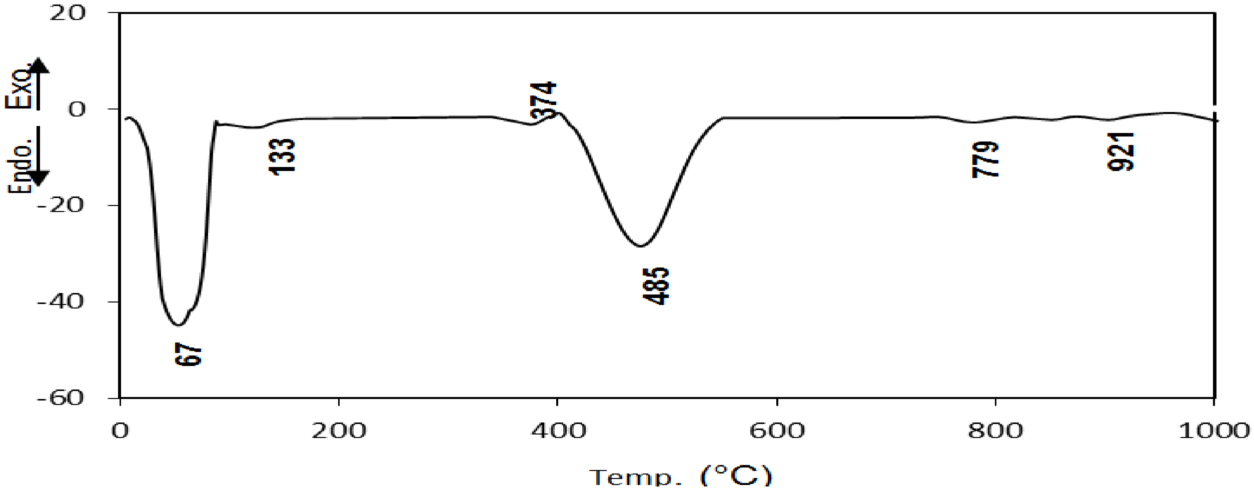

Figure-5. DTA Thermogram of Natural Clay.

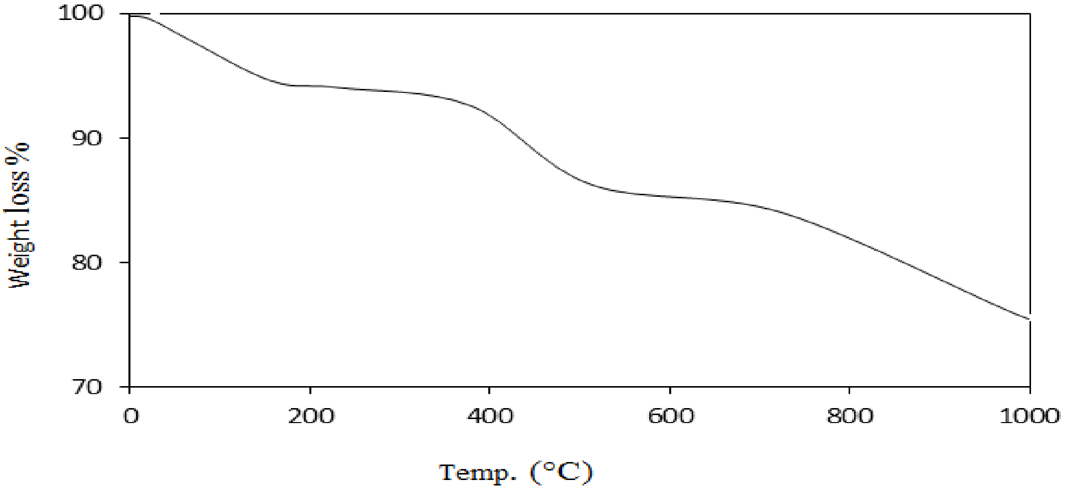

Figure-6. TGA Thermogram of Natural Clay.

Table-3. Thermal Analysis Results for Natural Clay

Event	**Characteristic**
First:	
Type of peak	Endothermic
T_{range}	28-120°C
T_{max}	67°C
WL	6.297%
Second:	
Type of peak	Endothermic
T_{range}	121-187°C
T_{max}	133°C
WL	3.156%
Third:	
Type of peak	Endothermic
T_{range}	404-550 °C
T_{max}	485°C
WL	6.805%
Fourth:	
Type of peak	S-shape
T_{range}	766-1001°C
T_{max}	921 °C
WL	5.8%

4.4. Chemical Analysis

4.4.1. pH Measurements

Adsorption capacity of the adsorbents is strongly influenced by the presence of functional groups at the surface. Natural clay under investigation (SiO_2 = 56.72%) is neutral (pH= 7.02), which agrees well with Ulasoglu [38] Table (4), who concluded that the pH of the clay depends on its SiO_2 content (% wt).

Table-4. pH of Natural Clay according to Ulasoglu [38].

SiO_2 Content (% wt)	pH
< 45	Ultrabasic
45-52	Basic
52-66	Neutral
> 66	Acidic

The major component of natural clay is silica (58%), its pH_{zpc} =2.5 [39] a negative charge will be developed above this value. The other constituent is alumina (42%), which develop a positive charge below pH_{zpc} =8.2, consequently, a net negative charge on the clay surface along the pH of experiments. This explanation can be supported by the study of the effect of pH of the medium on zeta potential of natural clay, which showed that zero point charge (IEP) of clay lay at pH=1.8 [40].

Table-5. Important IR bands of clay along with their possible assignments

Observed Frequency (cm^{-1})	Assignment	Remarks
3700	(Br,OH)	
3650	(Br,OH) (Al, Al-OH)	(Al, Al-OH) [40]
3424	(OH)	OH- of the water molecule adsorbed on the clay surface [21]
1660	(OH)	OH- of the water molecule adsorbed on the clay surface [21]
1119	Si-O-Si	[41]
1033	Si-O-Si	[41]
1100,1000	SiO	[21]
921	Si-O Al, Al-OH	[41]
536	Kaolinite SiO , Si-O-AL	[21]

4.4.2. IR Spectra Analysis

FTIR studies of the adsorbent help in the identification of various forms of the minerals present in the clay. The coupled vibrations are appreciable due to the availability of various constituents. As shown in Figure (7), infrared absorbance at 3650, 921cm^{-1} confirms the dominant presence of dioctahedral smectite with (Al, Al- OH) stretching and bending bands [41]. The absorption bands at 3700, 3650, 3424 and 1660 cm^{-1} correspond to (OH) frequencies for the water molecule adsorbed on the clay surface [21]. Bands at 536 cm^{-1}can be assigned to (Si-O), (Si-O-Al). The (Si-O) bands are strongly evident in the silicate structure and can be readily recognized in the infrared spectrum by absoption bands in the 1100, 1000 cm^{-1} region.

As shown in Table (5), the characteristic bands of kaolinite appear at 3700, 3613, 1119, 1033, 921, 767, 706 and 536.4 cm^{-1}.The characteristic bands of montmorillonite appear at 3650, 3613, 3424, 1660, 1119, 1033, 809, 921 and 536.4 cm^{-1}.

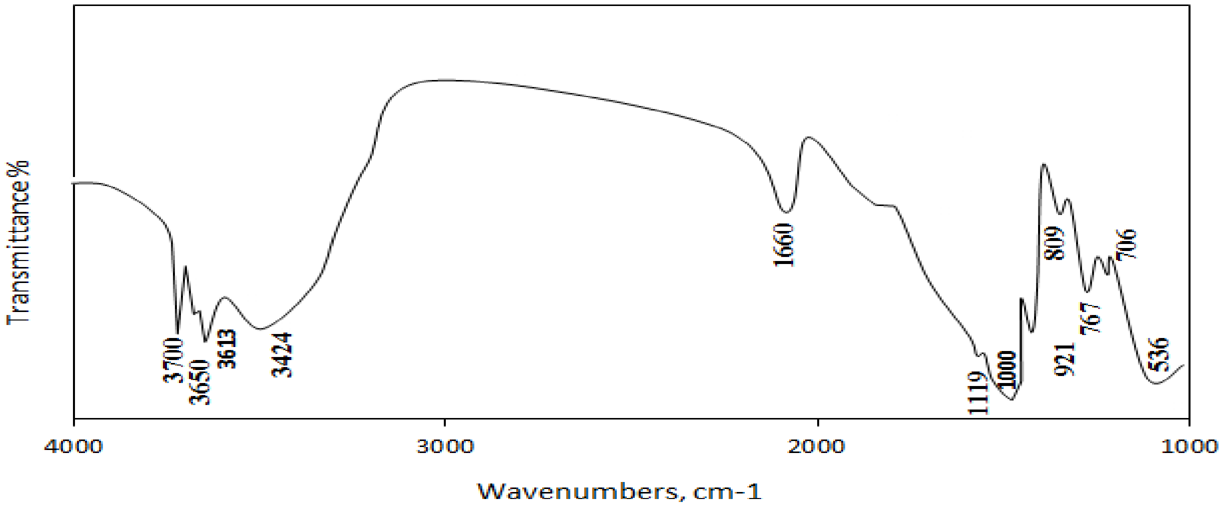

Figure-7. IR Spectum for Natural Clay.

5. CONCLUSION

From this work, we characterized clay from El-Sheikh Fadl Village, El-Minia governorate in Egypt. The clay has a Specific surface area 78.4 m^2/g and particle porosity 0.37. Based on PSD results, this natural clay can be classified as a mesoporous material, with reasonable density (2.34 g/cm^3). As it was discovered in some of the characterization parameters, the sample can be considered a good material for adsorption applications. The loss on ignition value indicates that clay has lower carbonaceous matter and higher mineral matter contents. X-ray diffraction study shows the presence of kaolinite, montmorillonite and quartz as major phases. The presence of above minerals was further confirmed by FTIR analysis. The presence of the negative charge on the clay surface enhances the adsorbent capacity to adsorb dye ions such that clay has an affinity for cationic species. Based on the results of the present study, one could conclude that clay being a natural, eco-friendly and low-cost adsorbents might be a suitable local alternative for elimination of heavy metal ions and basic dyestuffs from aqueous solutions.

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Competing Interests: The authors declare that they have no competing interests.

Contributors/Acknowledgement: All authors contributed equally to the conception and design of the study.

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