



Study of Efficacy Adsorption of Methyl Green by Attapulgite and Modified Attapulgite Clay from Aqueous Solution

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Abstract

This paper includes the modification of the attapulgite by precipitation of iron and aluminum compounds. Attapulgite (Atta) and modified attapulgite (Atta-m) clays are characterized by many techniques (FTIR , XRD ,SEM with EDX). The attapulgite clay before and after modification were used as the adsorbents for adsorption of methyl green (MG). The results indicate, that the percentage of removal (MG) at equilibrium by using (Atta) and (Atta-m) clay were reached to 94% and 97% respectively. Indicating that the clay modification process was in addition to a relative improvement in the adsorption potential of the clay after modification.

Keywords: Methyl green, Attapulgite, Modified Clay ,Adsorption.

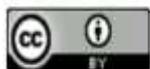
1. Introduction

The waste water disposed by textile industries is causing major hazards to the environment and drinking water due to presence of large number of contaminants like acids, bases, toxic, organic, inorganic, dissolved solids and color. In effect the discharge of contaminants such as dyes in the environment is warring for both toxicological and esthetical reasons as damage the quality of the receiving streams and is toxic to food chain organisms. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight into the stream and reducing the photosynthesis reaction. Since many organic dyes are harmful to human beings, the removal of color from process or waste effluents becomes environmentally important [1].

Conventional methods to treat contaminated effluents can be classified into several categories: adsorption [2], precipitation [3], physico-chemical techniques (e.g. solvent extraction and membrane separation) [4,5] and biological techniques (e.g. biosorption, phytoextraction) [6,7].

Adsorption is, however, more popular among all these methods because of its low cost, simple design, easy operation and the possibility of adsorbent recycling [8].

Some researchs proved to treatment using natural materials such as clays for removing dye pollutants treat the wastewater has been gaining more attention because the materials are cheap



and available and their high specific area, and a variety of surface and structural properties. Adsorption is a method of treatment, although adapted to remove a variety of toxic compounds in our environment [9, 10].

Several studies in this field are mentioned, the clay minerals have already been extensively investigated to remove various organic pollutants and metal ions, and how to improve their adsorption capacity is critical to practical application. In the paper, raw attapulgite clay was modified by hydrochloric acid to improve its adsorption capacity for dye. The adsorption properties of methylene blue (MB) from aqueous solutions onto modified attapulgite clay were further evaluated. The maximum adsorption capacity is 217.4 and 271.7 $\text{mg} \cdot \text{g}^{-1}$ at 298 K and 318 K, respectively. The Kinetic experiments show that the adsorption follows the pseudo-second-order kinetic model well. Considering its high adsorption capacity and low cost.[11]

Palygorskite (PAL) (another name of the attapulgite) was activated via a simple hydrothermal process (with ammonium sulfide) , The hydrothermal process evidently improved the dispersion of PAL crystal bundles, increased surface negative charges and built more active –Si–O– groups served as the new “adsorption sites”. The activated PAL exhibited a superior adsorption capability to the raw PAL for the removal of MV (from 156.05 to 218.11 mg/g). The kinetics for MV adsorption followed pseudo second-order kinetic models. The structure analysis of PAL before and after adsorption demonstrated that electrostatic interaction and chemical association of –X–O– are the prominent driving forces for the adsorption process.[12] The aim of this work is studied and characterization of attapulgite clay modification and evaluated the adsorption capacity of adsorbents (Atta) and (Atta-m) in removing methyl green from aqueous solutions in batch system.

2.Experimental

2.1 Adsorbate Methyl green dye properties

It was used simulated waste water as adsorbate, the chemical formula $\text{C}_{26}\text{H}_{33}\text{N}_3\text{Cl}_2$, molecular weight = 458.5 g/mol , $\lambda_{\text{max}} = 618\text{nm}$ (measured by UV-vis Spectrophotometer ,Double beam, Shimadzu. 1800), the chemical structure of Methyl green is shown as in figure (1).



Figure1. Chemical structure of Methyl green dye

Stock solution (100 mg/L) was prepared by dissolving 0.1 g of methyl green dye in distilled water (1 L), and then dilutes the stock solution to give the appropriate concentration.

2.2. Adsorbent

2.2.1 Properties of attapulgite clay

This study includes use attapulgite clay which obtained from the general company for geological survey and mining, Baghdad, Iraq. It was obtained from Akashatt area in Iraqi western desert. It was collected from an opened mine. It is a buff material (yellow-light orange powder) and is practically insoluble in water, organic and inorganic acids and in solutions of the alkali hydroxides. The chemical analysis of attapulgite was obtained by same company mentioned above and listed in **Table (1)**.

Table 1. The chemical analysis of Attapulgite

Compounds	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	L.O.I	Total
Wt%	49.0	12.6	6.2	6.2	6.0	1.5	11.6	93.1

The ore of the attapulgite clay was broken and crushed by a domestic mill To a fine powder to ensure the quality of the washing process after that the clay powder was washed with sufficient quantity of Distilled water seven times to remove the material Exotic substances are soluble in water and then dried in an oven(Daihan Labtech Oven LDO- 060E) at a temperature of (80°C) for 72 hours. was grinded dried clay with a domestic mill for the purpose of obtaining soft particles after sieving powder using sieves for particles sizing (150 µm) is required in all experiments related to this study

2.2.2 Modification of Attapulgite (Atta-m):

The modification method includes adding (300ml) of the ferric chloride solution (0.05M) in a suitable flask and then add (50 ml) of ammonium hydroxide solution (1M) as a single batch and then gradually add 25g of the prepared ethylene clay with constant stirring (Hotplate Daihan Labtech Co., LTD, Stirrer) for two hours Then the mix is dispersed by ultrasound(Ultra sonic Cleaner POWER SONIC - 0405S) for one hour. The filtration and washing process will be done with distilled water and drying at 100 ° C and grinding. The first part of the second surface shall be modified with the iron element.

The second part is to be modified by mixing the 300 mL of the hydrolytic aluminum sulphate 18-hydrate solution (0.01M) with 50 mL of the sodium carbonate solution (0.2M). Then add the mixture to the sample in the first part gradually with continuous stirring, the mixture is then dispersed in ultrasonic dispersion and then washed with distilled water, filtration, drying, milling and sieve to obtain a particle size (150 µm) from the second surface of the Atta-m clay. This clay is diagnosed before and after modification using several techniques (EDX, SEM, XRD and FTIR).

2.3. Adsorption Procedure (Batch System)

Adsorption experiments carried out by placing a constant mass of clay or modified clay (0.01 g) with 10 mL of (MG) dye solution (50 mg/L) in glass bottles in constant agitation shaker (Shaking Water Bath , Labtech) at temperature 25°C . when the adsorption process reached to equilibrium. After that samples were separated by centrifuge (6000rpm, Hettich (EBA-20) then absorbance measured using by UV-vis Spectrophotometer .The amount of (MG) dye adsorption on the adsorbents calculated as follows:-

$$Q_e = \frac{(C_o - C_e)V}{m} \dots\dots\dots(1)$$

Where, C_o and C_e is the initial and final or equilibrium concentration of (MG) dye in solution (mg /L) respectively, m is the clay mass in grams (g) and V is the solution volume in liters (L). The percentage amount: [13] of adsorbate adsorbed on the adsorbent was calculated by equation (2).

$$E\% = \frac{(C_o - C_e)}{C_o} \times 100 \dots \dots \dots (2)$$

Where E% Percentage adsorption of the adsorbate.

3. Results and discussion

3.1 Characterization of Adsorbents

Attapulgite (Atta) and modified attapulgite (Atta-m) were characterized by FTIR spectroscopy (Shimadzu. I Raffinity-1(8400s) , X-ray diffraction (6000 shimaduz) ,SEM (Inspect S50 ,FE) and EDX (XFlash 6110,Bruker) techniques. Figure (2) shows a number of distinctive peaks of [attapulgite clay formation (2800-3700)cm⁻¹, which is a set of compact peaks, the most prominent of which is 3641 cm⁻¹, which is due to the stretching vibration of the structural hydroxyl aggregates of the attapulgite structure, is due to the bending vibration of the absorbed water molecules At 1650cm⁻¹ and a sharp peak at 1041 cm⁻¹ due to the stretching vibration of the Si-O group, Alongside it, there is a top that is due to the bending vibration of the Si-OH group at 918cm⁻¹,figure (3) for (Atta-M) shows a variable change in the positions of a number of peaks with the same value for both surfaces. On the other hand, a significant change in the intensity and shape of most peaks, as well as the absence or disappearance of new peaks. Deposition of hydroxides of both aluminum and iron with the presence of attapulgite has led to changes or occurred a physical connections to the surface by pressing the clay structure without distortion to produce the surface (Atta-M).[14,15]

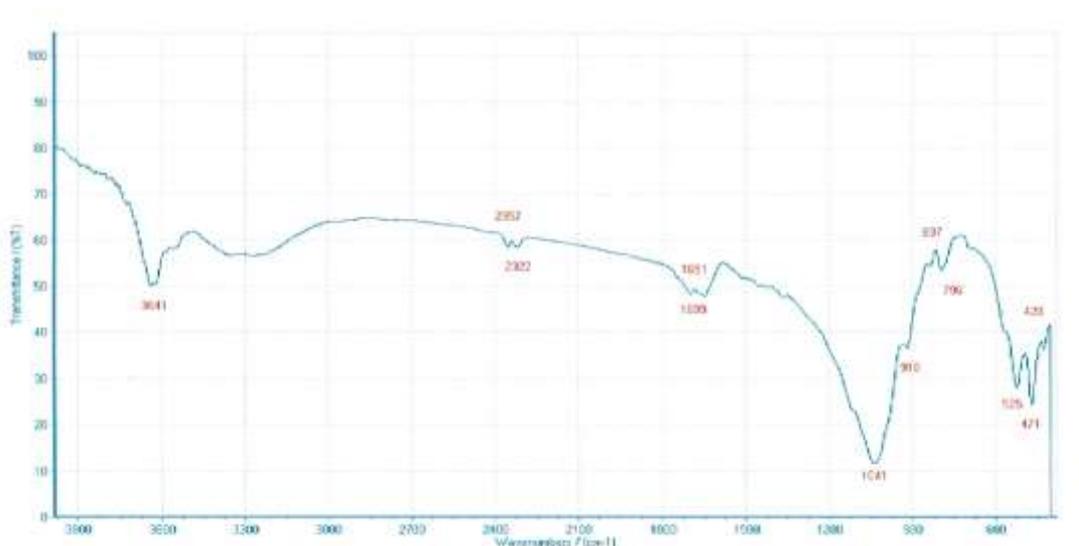


Figure 2 . FT-IR spectrum for (Atta) surface

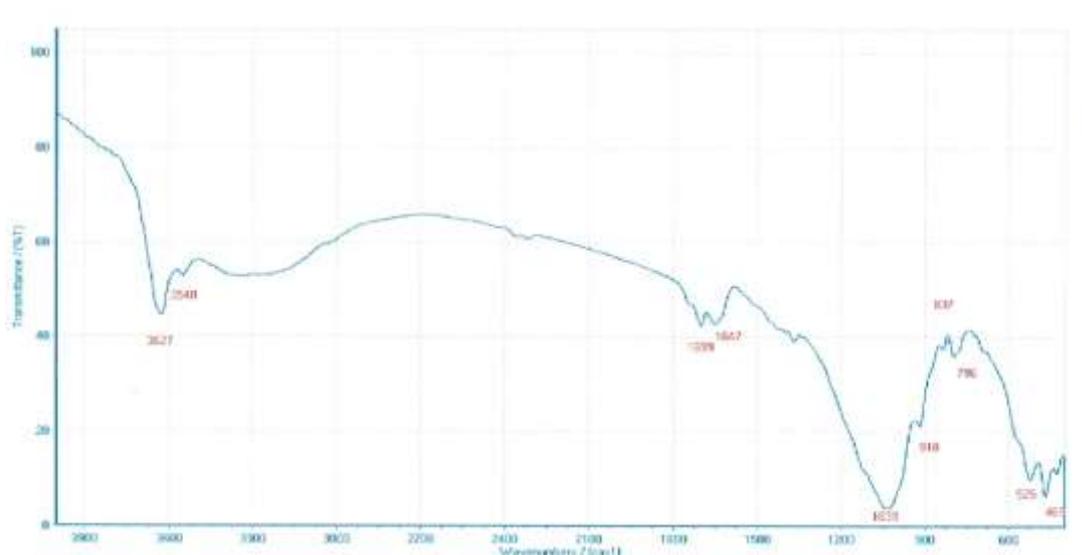


Figure 3. FT-IR spectrum for (Atta-m) surface

Figures (4) and (5) show that the distinctive peaks are characterized by their high intensity with a relative change in the shape of the peaks of the attapulgite clay before and after the modification. This confirms the slight relative effect on the crystals of all surfaces. On the other hand, (2 θ) and the intensity of all the distinctive peaks of the attapulgite clay and this is due to the modification of iron and aluminum hydroxides in certain proportions as the stage of modification and inclusion to produce the surface (Atta-m), these additions have involved the introduction and bonding of these elements (such as aluminum and iron) and their electronic effects on the surface and inside gaps and pores and between the crystalline levels of the attapulgite clay, which causes pressure on it without distorting or destroying its crystalline structure. This is confirmed by all spectra of x-rays of the surfaces all through do not show or disappear new peaks after adjustments.[16]

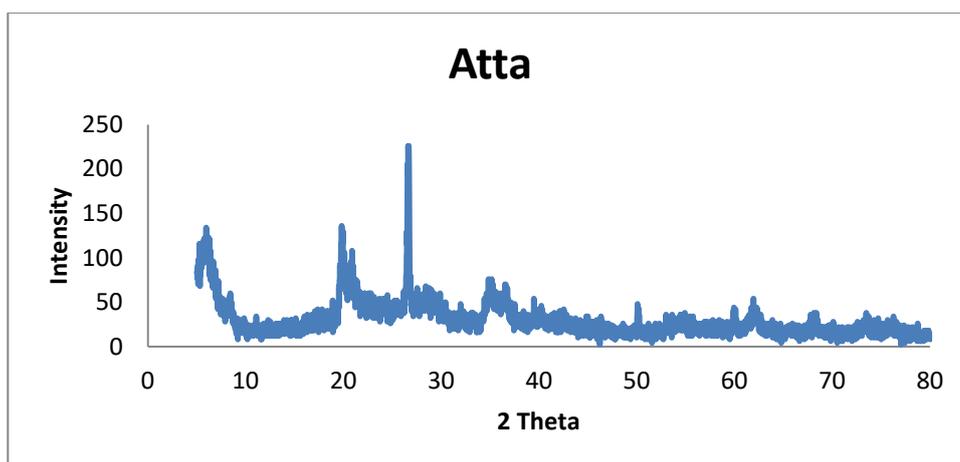


Figure 4. XRD spectrum for (Atta) surface

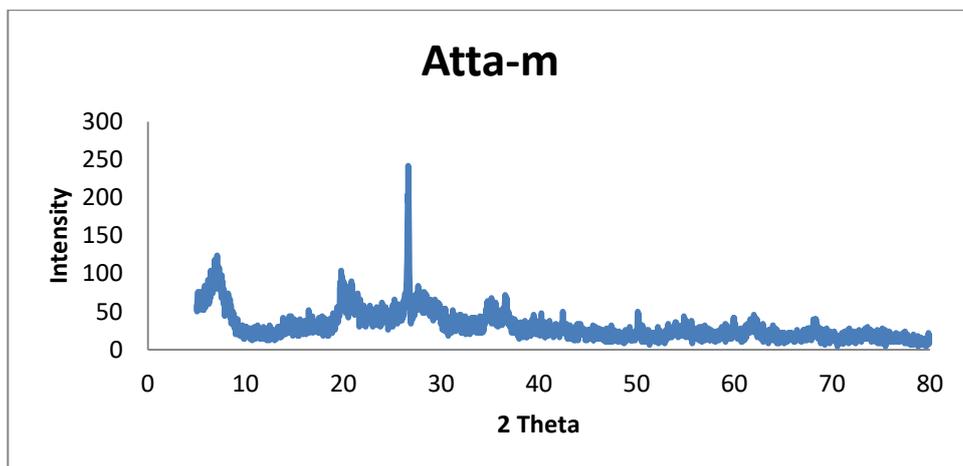


Figure 5. XRD spectrum for (Atta-m) surface

We observe from the **Figures (6) and (7)** the result observed two SEM images of the attapulgite clay before and after the adjustment with a magnification force (10 μ m) to see the clusters and the homogeneity of the surfaces. The process of addition of iron and aluminum hydroxides worked to dissipate the assemblies of the attapulgite molecules into smaller clusters with less sharp endings by the adjustment, giving a more homogeneous image. [17]

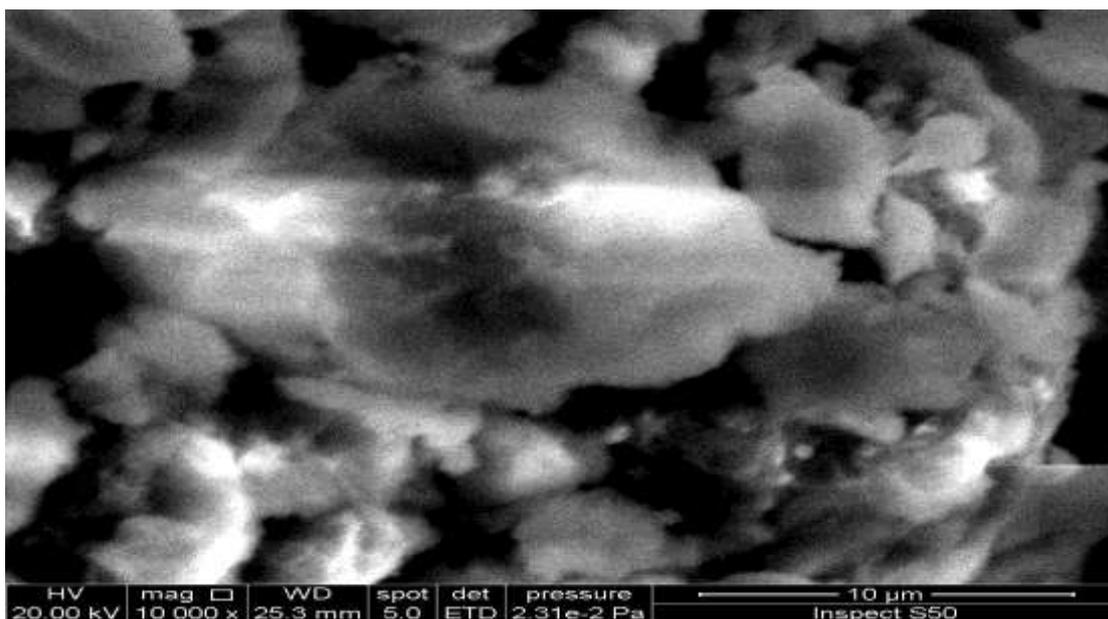


Figure 6. SEM images of (Atta) surface

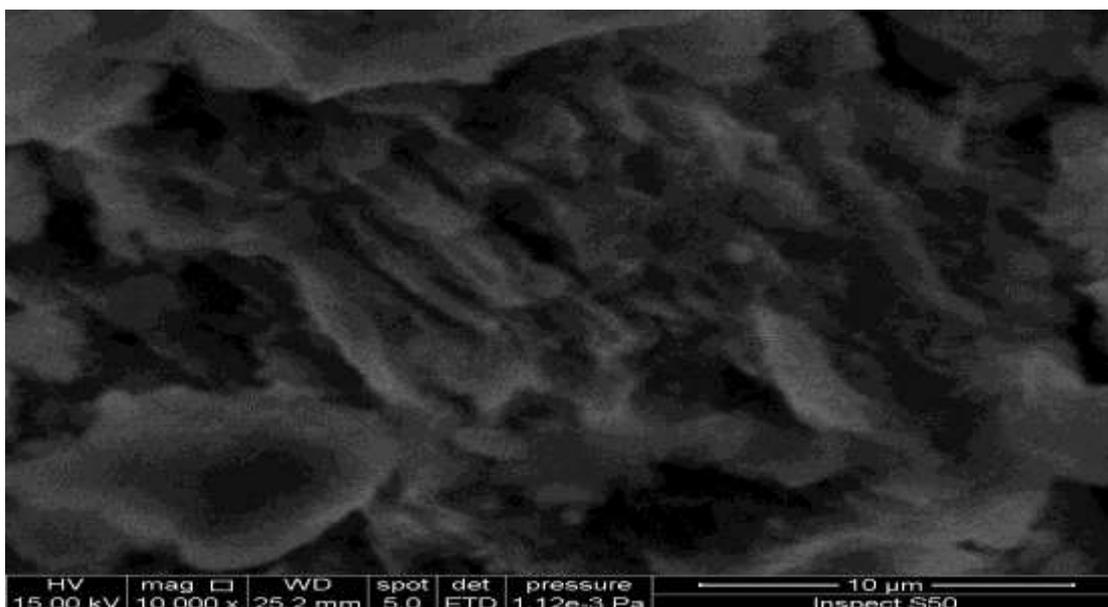


Figure 7. SEM images of (Atta-m) surface

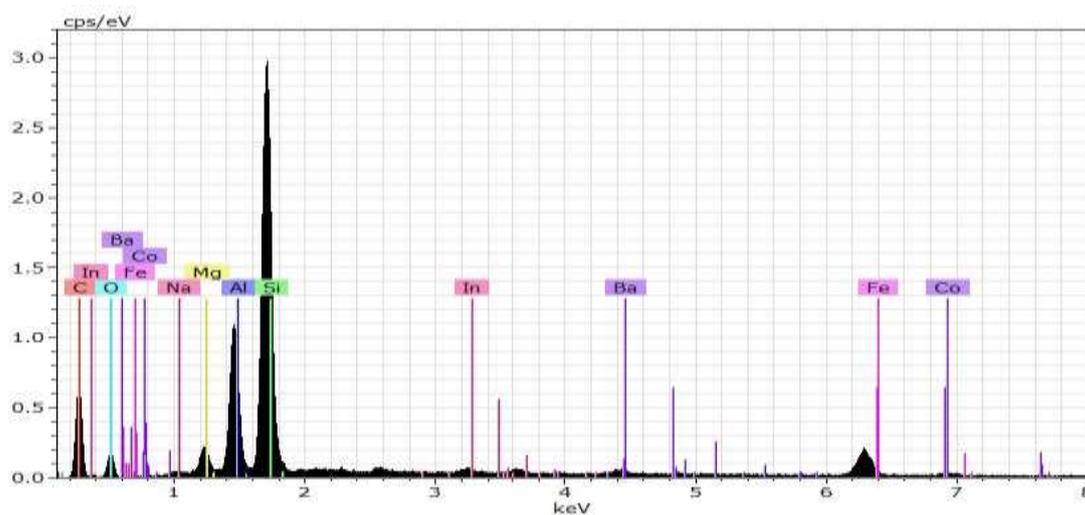


Figure 8. EDX spectrum for (Atta) surface

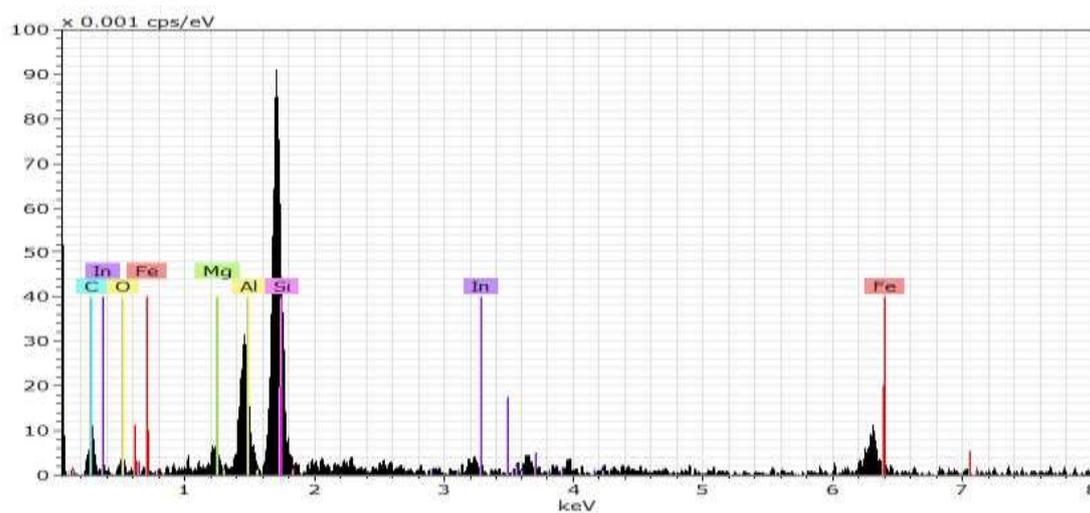


Figure 9. EDX spectrum for (Atta-m) surface

Table 2. Weight ratios of constituents of the attapulgite surface before and after modification

Surface	Elements	Si	Al	Fe	Mg	Ba	Co	In	Na	O	Total
Atta	W _t %	27.509	13.353	4.283	3.286	1.344	1.382	1.178	0.666	46.998	100
Atta-m		29.880	14.586	4.713	1.076	-	-	1.132	-	48.613	100

Figures (8), (9) and Table (2). We note that the EDX analysis of the ratio of elements in the pre-modified attapulgite clay shows that the highest components are oxygen and secondly the elements of silicon, aluminum and iron, and then other elements in lower proportions where these elements or the groups that are responsible for producing And the differentiation of some properties of the clay, including adsorption ability, but with the process of modification of the attapulgite clay through the inclusion of molecules of iron hydroxides and aluminum prepared, we notice a change in the proportions of both iron and aluminum and oxygen with the disappearance of some elements such as barium, cobalt and sodium, which did not have the minimum energy in order to Sensitive EDX spectrum, which will change the properties of the modified mud (Atta-m) [18]

3.2. Studying the adsorption properties of the adsorbent surfaces

After most conditions, the weight and particle size of the adsorbents surface (Atta, Atta-m), the concentration of the adsorbate (MG) and the temperature were fixed for the purpose of studying the adsorption of the (MG) dye of both surfaces. The application of the practical results of the adsorption process in equations (1,2) where both the amount of adsorption (q_e) were calculated and represented by **Figure (10)** and the percentage of adsorption (%E) It was represented in **Figure (11)**.

From the **Figures (10) and (11)**, the amount of adsorbate (MG) or percentage of adsorption increases of time and is quick at the beginning to provide a large number of adsorption sites that are not do but with time the process begins to slow down with the decrease in the number of sites not occupy, On the other hand, the speed of this process is greater at the modified surface than the first surface In total, the average surface access to saturation (absence of vacant sites) (97%) is faster than the first surface (94%), Reflecting an improvement in the adsorption properties of the modified surface. The modification process is expected to provide an increase in the number of adsorption sites, an increase in surface area or a reduction in adsorption energies, which facilitates greater adhesion of the adsorbed material to the surface. This is in line with the diagnostic tools mentioned above .[19,20]

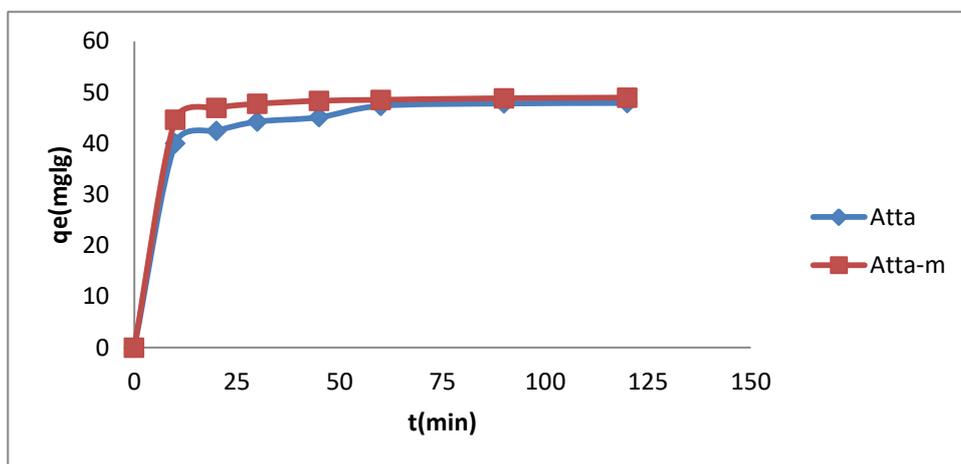


Figure 10. Effect of contact time on adsorption of (MG) by Atta ,Atta-m surfaces

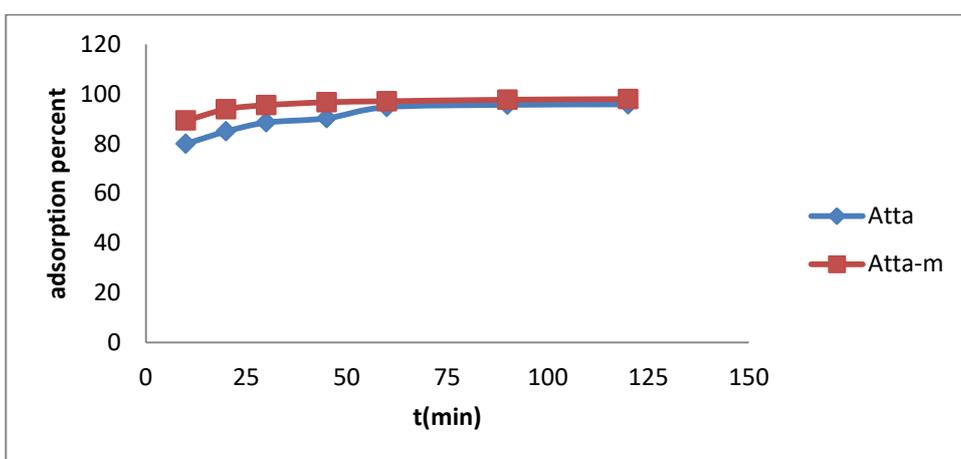


Figure 11. adsorption percentage of (MG) by Atta ,Atta-m surfaces

4. Conclusions

We conclude from this study that the process of modification of Atta clay by Iron and aluminum hydroxides have been done without breaking the structure of the clay or crystalline structure and was diagnosed with several techniques (FT-IR ,XRD and SEM with EDX) on the one hand and on the other hand the modification process to improve the relative properties of adsorption of clay after modification (Atta-m) .

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