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Preparation and Characterization of Graphene Oxide – Attapulgite composite and its use in kinetic study of Alizarin Dye Adsorption from Aqueous Media

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ATTAPULGITE clay was modified in this study by the graphene oxide sheets and the clay was diagnosed before and after modification using several techniques (Fourier-transform infrared spectroscopy FT-IR, X-ray powder diffraction XRD, Scanning electron microscope SEM , energy dispersive spectroscopy EDX) ,The surface of the attapulgite clay (before (Ata) after modification by graphene oxide (Ata-GO)) was applied to adsorption of the Alizarin dye from its water solutions through the application of several kinetic models (pseudo first-order model , pseudo second -order model , intraparticle diffusion model),It was found that the practical results follow pseudo second -order model. The process of modification on the surface of the mud has improved the adsorption properties where the quantity dye adsorbed is equal to (55,81) mg/g by the surfaces (Ata ,Ata-GO) respectively.

Keywords: Attapulgite, Graphene oxide, Modified Adsorbent , Alizarin Dye.

Introduction

Industries that use dyes are waste water discharged into the rivers and this is a major environmental problems, where the small amounts of dyes can contaminate large areas of water, and this affects the aesthetic environment and obscures light and photosynthesis, as most of the dyes may be toxic and mutagenic and carcinogenic [1]. For these reasons, the removal of dyes from process residues or effluents becomes environmentally important traditional waste water treatment plants that are not suitable for the removal of dyes because of their non-degradable properties [2]. Therefore, alternative methods have been developed to remove dyes from wastewater,

Which coagulation and flocculation [3], membrane separation [4], oxidation or ozonation [5], electro-coagulation [6], and adsorption. Among these methods, depending on cost, ease of application and efficiency, adsorption seems to be the best treatment option [7]. A highly efficient absorbent material in wastewater treatment is activated carbon, but it is very expensive and has high operating costs due to the high price of activated carbon and high water flow rate.

The adsorption process offers great features such as lowcost, efficiency and ease of operation. Low-cost materials can be used as a promising dyeing pipette to make the adsorption process less expensive. In this area, several low-cost materials have been used as absorbent surfaces to treat wastewater containing dyes. Among them, clay minerals were used as a potential absorbent for this application ,Natural clay is available in most continents of the world. Clay materials have a kind of layer and are classified on the basis of their layered structures. This clay is much cheaper than activated carbon , Attapulgite clay is a magnesium aluminium phyllosilicate with the general chemical formula $\{(Mg,Al)_4Si_8(O,OH,H2O)_{24}.nH_2O\}$ which has several properties such as porous structure, high surface area, fibrous morphology , high adsorption capacity and moderate cation exchange capacity [8-10].

Graphene oxide (GO) is typically obtained by oxidation or sonication of graphite, and it possesses

oxygen-containing functional groups, including hydroxyl groups (–OH), epoxy groups (–C=O), and carboxyl groups (–COOH). In addition, GO also possesses a high specific surface area [11]. Oxygen-containing functional groups can be used as the adsorption sites for heavy metal ions in wastewater [12].

Graphene oxide (GO) is used in several applications for the purpose of having effective groups such as hydroxyl, epoxy and acidic carboxyl groups, which make their dispersion high in water.

Several studies dealt with the subject of adsorption of which, polyaniline/attapulgite (PANI/APT)- reinforced nano particals zero-valent iron (nZVI) composites which used for the removal of two kinds of dyes (azo, non-azo). The results showed that the adsorption property of the composite materials on azo dyes (alizarin yellow R, methyl red, chrome black T, methyl orange) is obviously better than that on non-azo dyes (methylene blue, rhodamine B) . The study showed that nZVI/PANI/APT were effective against adsorption of azo dyes from wastewaters.[13]

Another study included A comparative study was conducted between graphene oxide (GO) and bare graphite powder (BGP) When Alizarin Red S (ARS) dye adsorption under ideal conditions (initial concentration of ARS, pH solution, absorbed dose, contact time) , The adsorption kinetics well fitted using a pseudo second-order kinetic model. It is, Therefore, it is clear that GO can be used as a high-intensity agent for anionic dye adsorption and can be reused for the fourth time of adsorption[14].The objective of this study was to conduct the modification on the Attapulgite surface to diagnose it and then to conduct a kinetic study for adsorption of the Alizarin dye from its Aqueous solution.

Material and Methods

Materials

Alizarin (Aliz) also known as 1,2-dihydroxyanthraquinone , M.wt :240.21 g/mol , Empirical Formula : $C_{14}H_8O_4$ as in figure (1) was supplied by Merck company . A stock solution of Aliz dye was prepared (40 mg/L) by dissolving a required amount of dye powder in deionized water. The stock solution at (Ph = 4) was diluted with deionized water to obtain the desired concentration ranging from 5 to 40 mg/L.

The concentration of Aliz in the experimental solution was determined from the calibration curve prepared by measuring the absorbance of different known concentrations of Aliz solutions at λ_{max} = 567 nm using a UV–vis spectrophotometer (Shimadzu, Japan). Graphene oxide (GO) was obtained from a previous study [15]
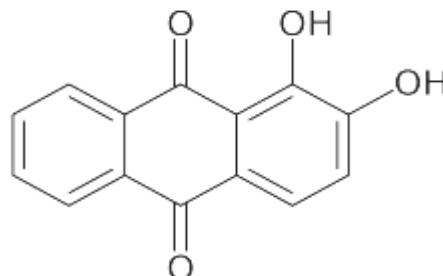

Fig. 1. Structure of Aliz Dyes.

Methods

a-Preparation of Attapulgite clay (Ata)

The clay was obtained as a fine powder from the geological survey company and then washed with distilled water several times to get rid of the soluble materials and impurities. It was then dried by oven at 100 ° C for (3hour) .the clay was grinded by a domestic mill and then cleaned to get (150 μm), which was adopted for the experiments of this research, so that the first surface is the (Ata) Attapulgite before the amendment .

b-Attapulgite clay modification (Ata-GO)

(10 g) of the attapulgite clay was taken before modification and activated by heating it by oven (Muffle Furnace LabTech) at 300 ° C and then added to the clay suspension solution in a circular flask (500 ml) containing an appropriate amount of distilled water and subjected to ultrasonic device ,For the purpose of dispersing particles of clay in the solution for 30 min and then gradually add to the appropriate amount of the grapheme oxide (60 min) with simple heating to ensure the propagation and full homogeneity of the minutes of the graphene oxide sheets between the particles of the clay and then the process of decantation, Filtration and drying at a temperature of 100 ° C, grinded by a domestic mill and then sieved to obtain an equivalent particles size (150 μm). The second surface is produced by the attapulgite after the amendment with the particles of the (Ata-GO).

c-Adsorption experiments Procedure

The influence of the contact time on the adsorption capacity of Aliz dye by both of clay and modified clay were conducted through batch experiments to achieve the equilibrium time, this

procedure achieved by adding 0.01g of adsorbents (Ata or Ata-GO) into 10 ml dye solution, with initial concentration (40 mg/L) under shaking at temperature rang (20,25,30,35) ℃ with a thermostatic shaker (LabTech LSB-series Shaking Water Bath). After different time intervals, the solutions were centrifuged (Hettich EBA 200) and volumes of 3ml supernatant were taken for spectrophotometrically measurements of Aliz dye content at its λ_{max}.

The adsorption capacity of Aliz dye (q_e) was calculated from the difference between the initial and equilibrium adsorbate (dye) concentration which as follows:[16]

$$q_e = \frac{(C_o - C_e)V}{m} \quad \text{---------------------(1)}$$

m : weight of adsorbent (g), C_o : initial concentration (mg/l), C_e : equilibrium concentration (mg/ l) , V : volume of solution (L).

Results and Discussion

Diagnosis of the surface of attapulgite before and after modification (Ata , Ata-GO) involves several techniques, as follows:

a-FTIR analyses

The FT-IR spectra of the studied surfaces were recorded by figures (2) and (3) ,The figure (1) shows a wide peak at 3691.76 cm⁻¹ returning to a range of sites to the to stretching vibrations of each of the hydroxyl groups with positive aluminum ions in the consistency of dioctahedral (AL₂-OH) and to the hydroxyl grouping of the water molecules consistent with the magnesium element with iron or aluminum (Fe, Mg) -OH or (Al, Mg) -OH along the crystalline structure of the clay, A small and weak peak at 1338 cm⁻¹ belongs to the group of carbonates, which are considered to be impurities in the mud, A sharp

bilateral peak at 1029,1002 cm⁻¹ belongs to the silica conglomerate , A sharp peak at 910 cm⁻¹ is due to the vibration of the silanol group which is associated with the amorphous silica which refer to vibration bending (Si-OH), medium bilateral peak at 792,750 cm⁻¹ returns to the Si-O-Si vibration in the silicate group formed (SiO₂),while figure (3) shows the We note the disappearance and appearance of new peaks in addition to a change in the intensity and shape of all peaks due to the process of thermal activation and modification of the graphene oxide sheets, where we note the emergence of three new separate peaks in the region (3600-3700 cm⁻¹) one may return to the vibration of the group of OH or Carboxyl graphene oxide and attapulgite clay in addition to the disappearance of the site of carbonates group due to the thermal activation of the impact of sites peaks in the region 1000-1050 cm⁻¹ by vibrations aggregates C-O-C of the graphene oxide sheets which operating in this site.[17,18]

b-XRD analyses

The XRD spectra of the studied surfaces were recorded by figures (4) and (5), Note from figure (4) the XRD spectrum of the attapulgite clay before and after modification that the characteristic peaks of the attapulgite clay prior to the modification were (2θ) at (59,50,26,25,20,12 °). However, after thermal activation and modification of the graphene oxide sheets figure (5), there was a change in the location and intensity of the peaks (Increase or decrease) and the absence or disappearance of peaks indicating that the process of activation and modification has occurred, but did not affect the crystal structure of the clay or the occurrence of strong links between the molecules of graphene oxide and the structure of attapulgite clay.[19]
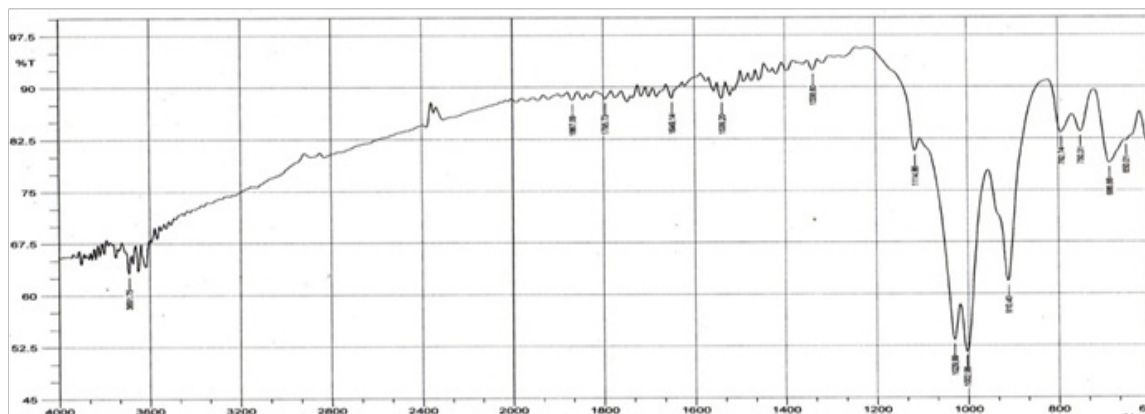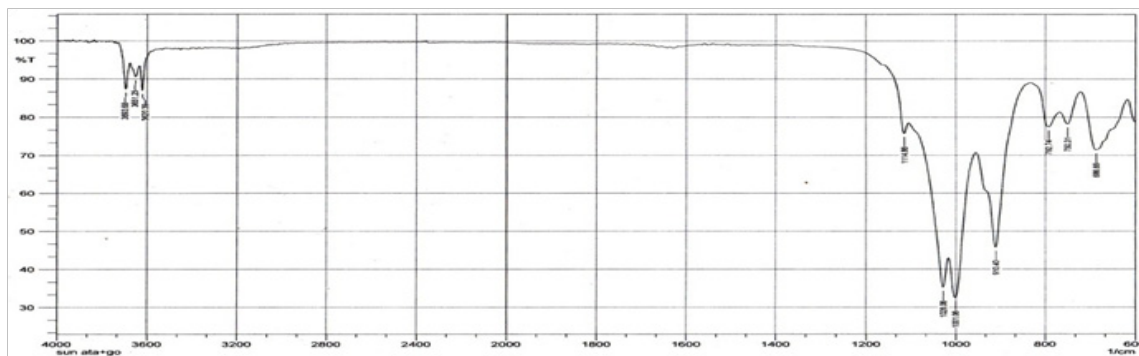

Fig.2. FT-IR spectrum for Ata surface .

Fig.3.FT-IR spectrum for Ata-GO surface.
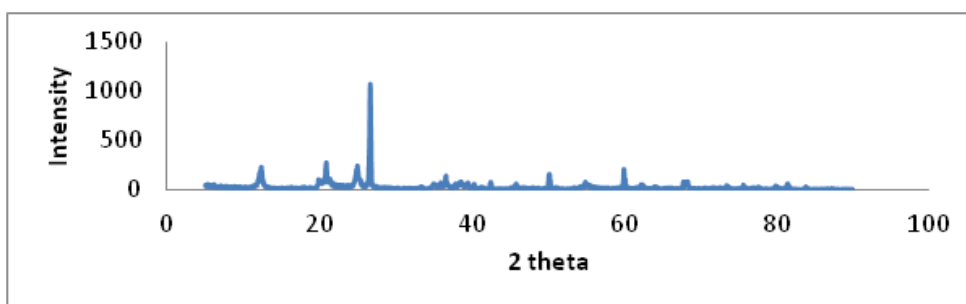

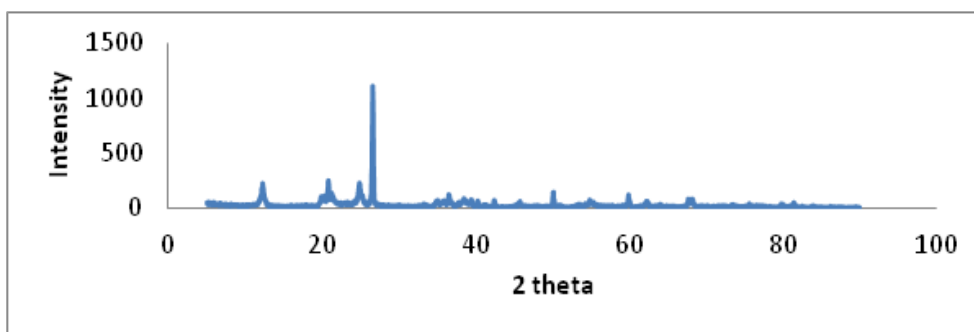**Fig. 4. X-ray diffractograms (powder specimens) of natural attapulgite.**

Fig.5. X-ray diffractograms (powder specimens) of natural attapulgite after modification with graphene oxide.

c-SEM analyses

SEM images were taken before and after the adjustment of the attapulgite clay with a magnifying force (5000 x) represented by figures (6) and (7), figure (6) show the clusters of different sizes have heterogeneous ends. However, after the thermal activation and modification of the graphene oxide sheets figure (7), the aggregates become larger and more uniform, giving a more homogeneous surface. Causes a change in the surface properties of the clay after activation and modification.

d-EDX analyses

The EDX spectra of the studied surfaces were recorded by figures (8) and (9), From figure (8) show the several peaks of elements (Ru, Al, C, Si, O, Se, Fe, Ba, Co) in the spectrum analysis of the elements of the attapulgite clay but after the activation and modification of the carphene oxide sheets This led to a reduction in the weight ratios of most elements and some of them to zero such as (Co, Se),While the increase in the ratio of oxygen (5.6-6.2) and carbon (6.5-12.8), which confirms the occurrence of the process of modification of the graphene oxide, as shown in Figure (9) shows that several peaks of Ru, Al, C, Si, O, Fe, Ba), within the spectrum of elemental analysis of the attapulgite clay after activation and modification . [20]

Kinetic Studies of Adsorption

It is necessary to study the kinetics of adsorption in batch systems in order to determine the rate limiting step in the adsorption process. To evalute the effectiveness of an adsorbate, the adsorption of Aliz dye on Ata and Ata-GO adsorbents with the initial dye concentration (40 mg/L) at range temperatures (293,298,303,308) K were studied as a function of contact time, and the results are shown in Figures (10) and (11). Figures (10,11) shows The adsorption rates of dye onto Ata and Ata-GO adsorbents are observed to be very fast within the first few minutes and gradually decrease and become almost constant after a period of 90,45min and maximum Aliz dye adsorbed (55, 81) mg/g. for Ata and Ata-GO adsorbents respectively. Note that the amount of dye absorbed on the (Ata) surface increases with the increase of temperature, indicating the endothermic of the process, while noting the decrease in the amount of dye absorbed on the surface with increasing temperature, which indicates the exothermic nature of process .[16]
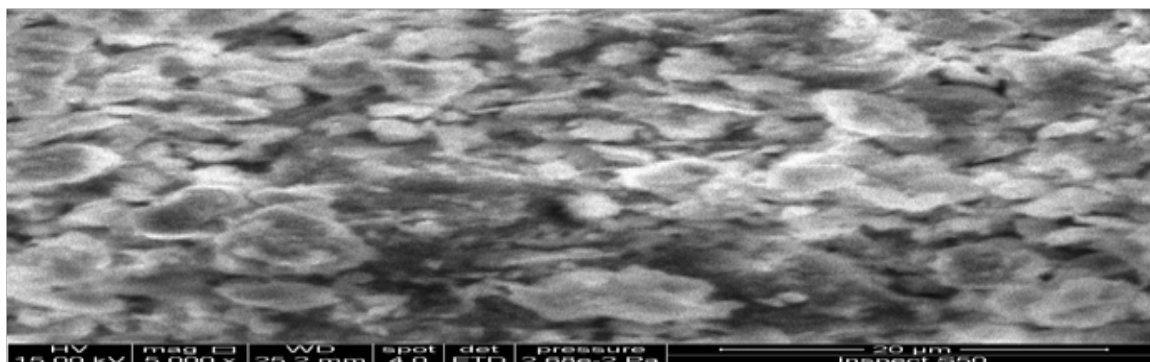

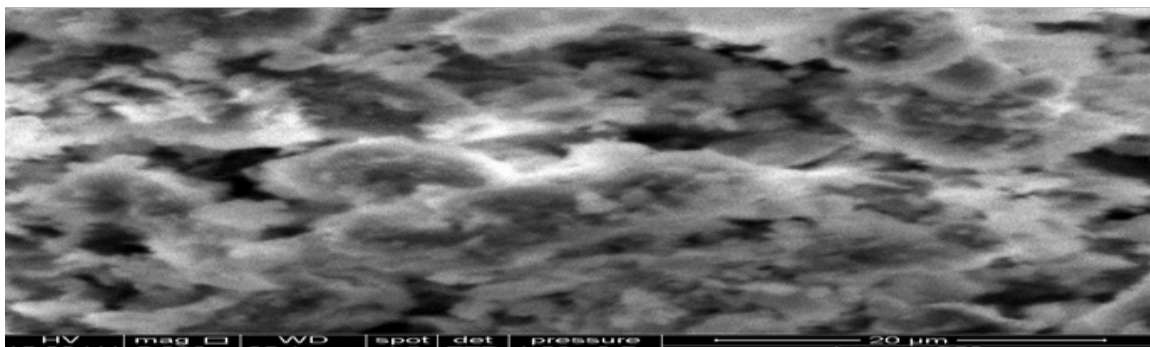
Fig.6. SEM micrography of attapulgite structure.

Fig.7. SEM micrography of attapulgite structure after modification with graphene oxide.
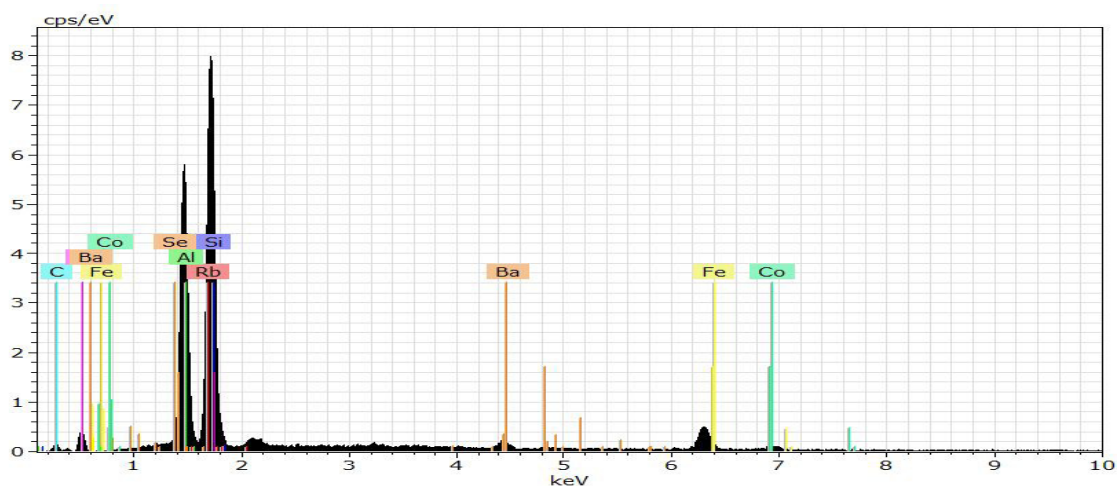

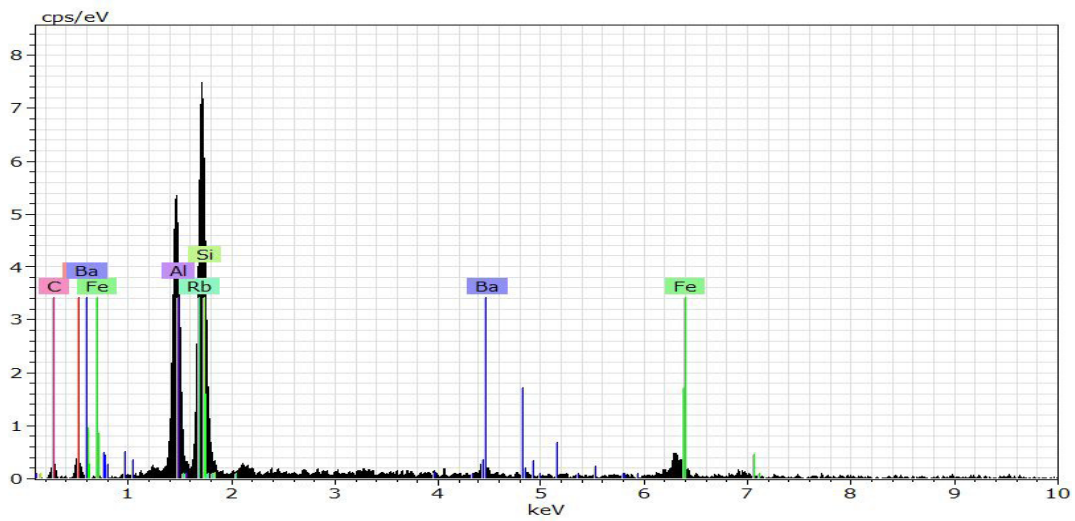**Fig.8. EDX spectrum of attapulgite structure .**

Fig. 9.EDX spectrum of attapulgite structure after modification with graphene oxide .
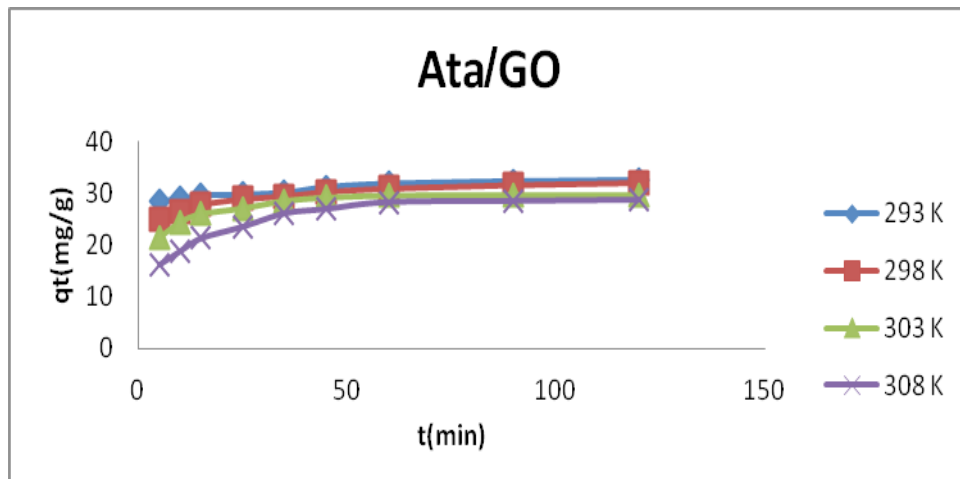

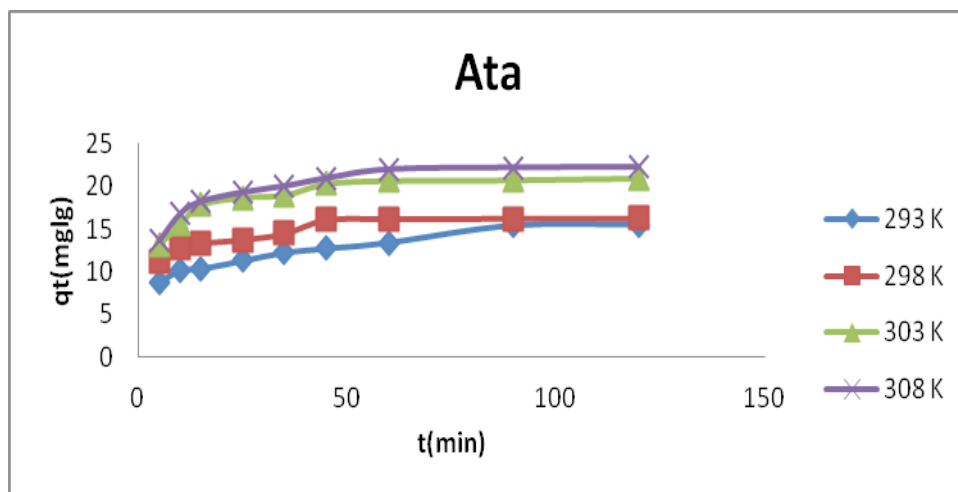**Fig.10. Adsorption of Aliz dye on Ata surface at different temperatures.**

Fig.11. Adsorption of Aliz dye on Ata-GO surface at different temperatures.

The kinetic data for the adsorption of Aliz onto Ata and Ata-GO adsorbents with the initial dye concentration (40 mg/L) were tested with the well-known kinetic models namely pseudo first order , pseudo second order , Intraparticle diffusion .The lagergren first order rate equation was used to fit the experimental results. The integral form of the model is [21]:

$$\ln(q_e - q_t) = \ln q_e - (K_1)t \quad \text{-------------(2)}$$

Where q_t (mg/g) is the amount of dye adsorbed at time t (min), and k_1 is the equilibrium first-order constant. Values of k_1 and q_e were obtained from the slope and intercept of the plot of $\ln(q_e\text{-}q_t)$ vs.t (Figure (12)). The adsorption kinetic parameters from Figure (12) are recorded in Table (1).

The second order rate equation was used to fit the experimental results. The integral form of the model is[22]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{-----------------(3)}$$

where k_2 (g/mg min) is the equilibrium rate constant of pseudo second-order adsorption. Values of q_e and k_2 were obtained from the slope and intercept of the plot of t/q_t vs.t (Figure (13)). The adsorption kinetic parameters from Figure (13) are recorded in Table (2).

The intraparticle diffusion equation is given as: [23]

$$q_t = k_i t^{1/2} + C \quad \text{-----------------------(4)}$$

k_i is the intraparticle diffusion rate constant (mg/g min$^{1/2}$), C: gives the idea on the thickness of the boundary layer. Values of k_i and C were obtained from the slope and intercept of the plot of qt vs.t$^{1/2}$ (Figure (14)). The adsorption kinetic parameters from Figure (14) are recorded in Table (3).
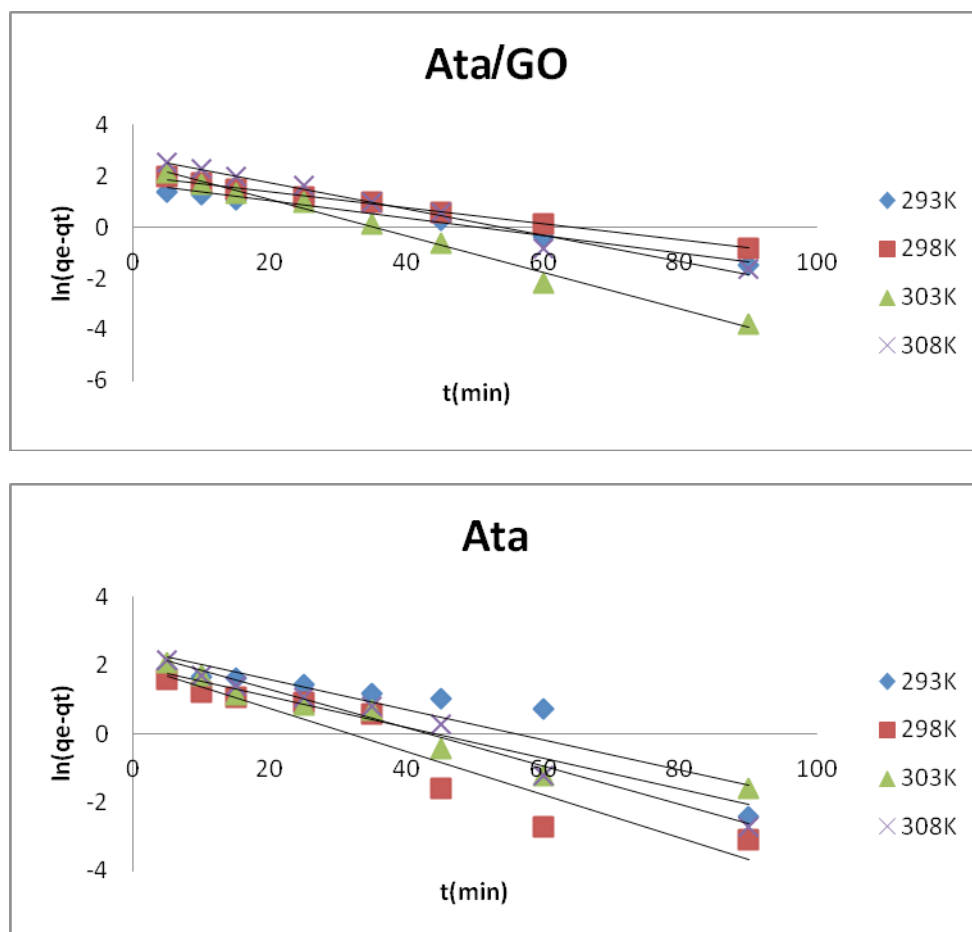

Fig.12. The applicability of the first order kinetic model to Aliz dye adsorption on (a) Ata and (b) Ata-GO surfaces.
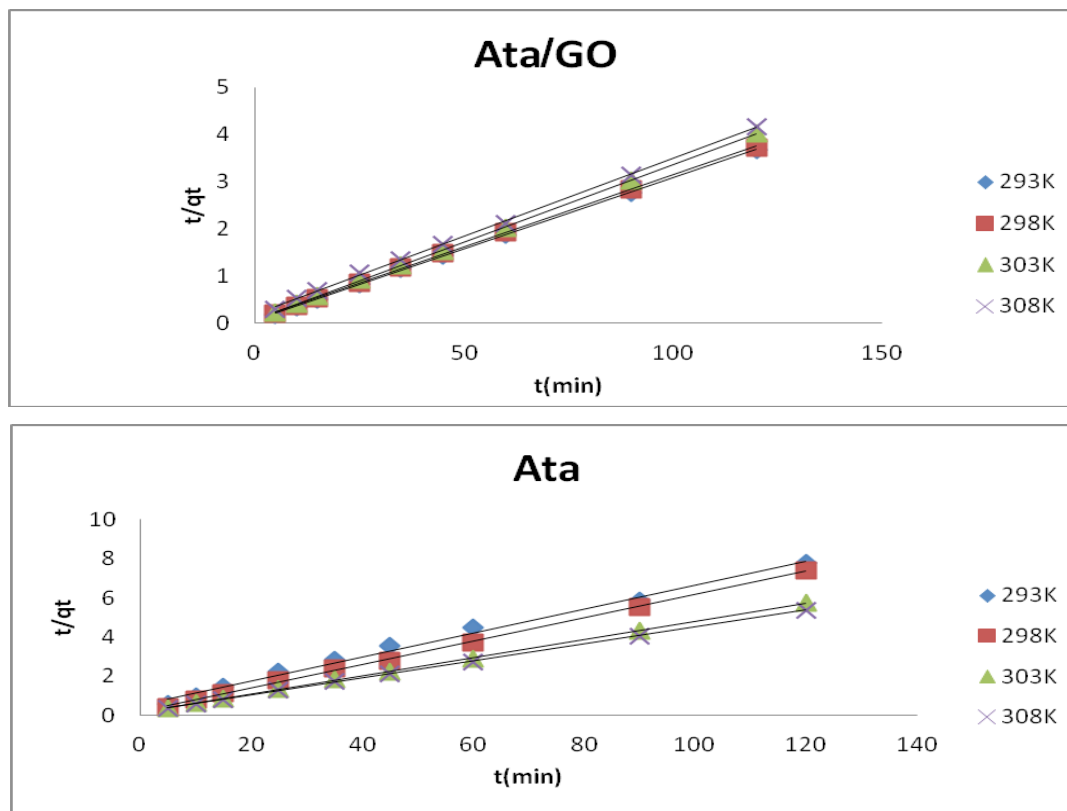
Fig.13. The applicability of the Second order kinetic model to to Aliz dye adsorption on (a) Ata and (b) Ata-GO surfaces
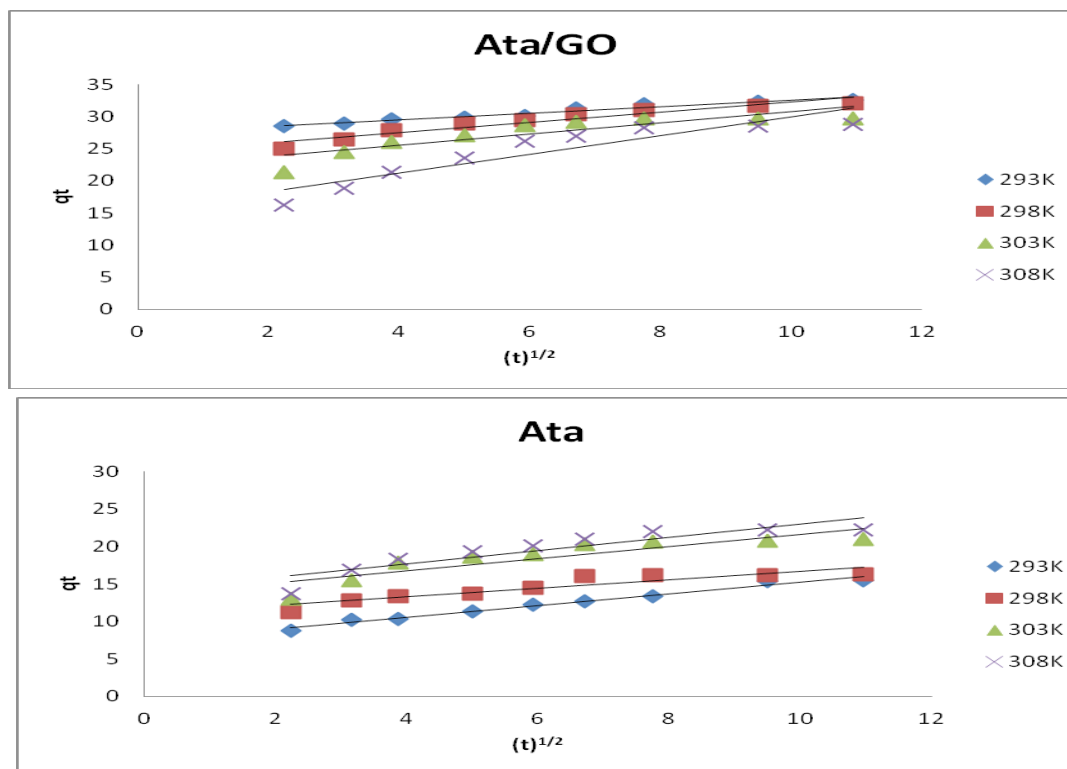

Fig.14. The applicability of the intraparticle diffusion model to to Aliz dye adsorption on (a) Ata and (b) Ata-GO surfaces.

Table (1): Parameter of the First order kinetic model to to Aliz dye adsorption on (a) Ata and (b) Ata-GO surfaces

Surface	Ata			Ata/GO		
T/K	$k_1(min^{-1})$	$q_e(mg/g)$	R^2	$k_1(min^{-1})$	$q_e(mg/g)$	R^2
293	0.0440	11.699	0.830	0.0342	5.637	0.968
298	0.0628	7.271	0.896	0.0317	7.603	0.995
303	0.0452	7.392	0.931	0.0712	12.034	0.990
308	0.0562	11.372	0.977	0.0515	16.126	0.978

Table (2): Parameter of the second order kinetic model to to Aliz dye adsorption on (a) Ata and (b) Ata-GO surfaces

Surface	Ata			Ata/GO		
T/K	k_2 (g/mg min)	$q_e(mg/g)$	R^2	k_2 (g/mg min)	$q_e(mg/g)$	R^2
293	0.0068	16.370	0.992	0.0156	32.979	1.000
298	0.0165	16.800	0.999	0.0111	32.675	1.000
303	0.0129	21.591	1.000	0.0142	30.465	1.000

Table (3): Parameter of the intraparticle diffusion model to Aliz dye adsorption on (a) Ata and (b) Ata-GO surfaces

Surface	Ata			Ata/GO		
T/K	k_i (mg/g min$^{1/2}$)	C (mg/g)	R^2	k_i (mg/g min$^{1/2}$)	C (mg/g)	R^2
293	0.7802	7.427	0.981	0.5014	27.512	0.958
298	0.5699	10.997	0.841	0.7945	24.354	0.919
303	0.8109	13.547	0.772	0.8712	22.017	0.764

Tables (1,2,3) shows The value of R^2 for the second order equation is higher for all studied systems than for the other kinetic models. The values of q_e calculated according to the second order equation are close to the q_e experimentally values of the process with little or no Which corresponds to the other models. This indicates the applicability of the second-order equation to the adsorption of Aliz dye on all studied surfaces [24,25]where the following order is taken:

second order kinetic > first order kinetic > intraparticle diffusion

Conclusion

We conclude from this work that the process of activating and modifying the attapulgite clay with the graphene oxide sheets has Completed and diagnosed through several techniques (FTIR,XRD,SEM,EDX) and this process have improved the adsorption of the Ata surface (55 mg / g). The process was of a endothermic nature while the Ata-GO surface was equal to (81 mg /g) The process is of a exothermic nature, The process of adsorption Aliz dye on both surfaces follows the second order kinetic model more than the other models studied (first order kinetic , intraparticle diffusion).

Acknowledgement

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تحضير وتشخيص متراكب اوكسيدالكريفين /اتابلكايت واستعماله في دراسةحركية لامتزاز
صبغة اليزارين من محاليلها المائية

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في هذه الدراسة تم تعديل طين الاتابلكايت بصفائح اوكسيد الكريفين حيث تم تشخيص الطين قبل وبعد التعديل
بعدة تقنيات (FT-IR, XRD, SEM , EDX) , سطوح طين الاتابلكايت قبل التعديل (Ata) وبعد التعديل
(Ata-GO) طبقت في امتزاز صبغة البزارين من محاليلها المائية من خلال تطبيق عدة نماذج حركية (مرتبة
اولى كاذبة , مرتبة ثانية كاذبة , الانتشار الضمني الدقائقي) .وجد ان النتائج العملية تتبع نموذج المرتبة الثانية
الكاذبة ,عملية تعديل على سطح الطين ادت الى تحسين الخواص الامتزازية حيث كانت كمية الصبغة الممتزة
مساوية الى (mg/g 81,55) على سطوح (Ata-GO,Ata)على التوالي .

الكلمات المفتاحية : الاتابلكايت ,اوكسيد الكريفين ,السطوح المازة المعدلة ,صبغة اليزارين .