Kinetic Study for Janus Green Dye Adsorption from Aqueous Solutions Using Iraqi Bauxite Clay and its Composite

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Abstract— Clays are considered important natural materials in the field of water purification, including bauxite clay (BAU) and its prepared and activated composite (BAU/CMC-AC) with carboxymethyl cellulose polymer. The adsorbent surfaces are characterized by FTIR and XRD techniques. The adsorption of green janus (JG) from an aqueous solution with bauxite and its composite were studied under the influence of different conditions of the weight and size of adsorbed surface particles, contact time and temperature. The results were found to be: contact time (90, 45) min for maximum quantity adsorbed of (JG) dye on bauxite and its composite respectively. The experimental data were tested on pseudo 1st- and 2nd-order kinetic models. It was shown to apply more with the pseudo-2nd order kinetic model for both adsorbents. It also showed that the highest removal percentage were (78%, 88.5 %) for the bauxite surface and its composite (BAU, BAU/CMC-AC) at the preferred temperature

Keywords— Bauxite, carboxymethyl cellulose, Composite, Adsorption, Janus green.

1. Introduction

Water bodies are important for the life of living organisms on Earth, as groundwater is the main source of drinking water. Unfortunately, this water is exposed to various types of pollutants, which include toxic organic acids and bases, heavy organic materials, and colored materials [1], Especially dissolved dyes, which are thrown into the environment as waste from the textile and leather industries and other industries that use dyes. This leads to their remaining in the water clearly even at low concentrations, in addition to their non-disintegration and toxicity, which makes this water undesirable for living organisms [2]. Thus, this is a major environmental problem that puts the world in a great challenge. In order to solve it, a variety of methods were used, including physical, chemical and biological methods, to remove the color from the liquid waste [3]. Among these methods, the adsorption technology has proven to be an effective and economical process for treating dyes. The efficiency of this technology depends on the selection of adsorbent surfaces in terms of availability, cheapness, ease of use, in addition to being environmentally friendly.

Among these materials are clays, including bauxite, because of its composition containing aluminum and silicon oxides, hydroxyl compounds, and varying proportions of mineral elements that make it capable of ion exchange and adsorption, in addition to the possibility of using it in the form of compounds to increase its adsorption efficiency for organic pollutants, especially dyes, as it included several studies that used bauxite and bentonite clays. flint [4-6], bauxite composite - carbon nanotubes [7], bauxite composite - surfactants [8] and bauxite - urea [9],

The study aims to use bauxite and its compound with carboxymethyl cellulose to remove the green janus dye from its aqueous solution and to study the kinetics of the adsorption process.

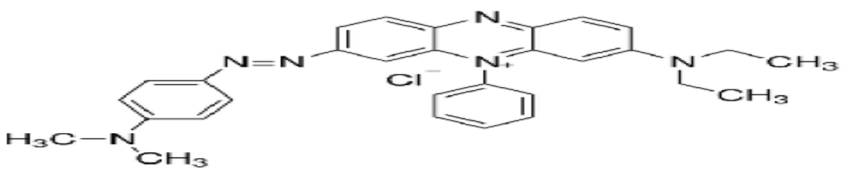
2. Experimental

2.1 Instruments

1-Uv-visible spectrophotometer (shimadzu UV-1800) 2- Labtech shaking water bath, 3- Centrifuge tubes. Hettich (EBA-20).4- Balance, Sartorius Lab. L420 B, +0.0001. 5- PH-meter (pHep) HI 98107, Hanna Instruments . 6- Daihan Labtech Oven LDO - 060E 7- QA9010X - Hot Plate Stirrer, Ceramic Surface 8- iraffinity-1 FTIR spectro-photometer (shimadzu 8400 s) 9- XRD-6000 shimadzu .

2.2 Materials

Carboxymethyl cellulose (CMC) (BHD) , NaOH (BDH) ,H_2O_2 (PanReac AppliChem) Janus Green B (JG) dye Figure (1) (BDH) (figure1), The bauxite clay used in this work is an Iraqi local clay sourced from the Ministry of Industry and Minerals from Al-Anbar Governorate in the western region in Trefawe district. According to the analysis of the processing company, bauxite clay includes the following compounds; oxides = (1.5 CaO : 0.1 MgO : 64.2 Al_2O_3: 15.7 SiO_2: 0.9 Fe_2O3 : 1.3 TiO_2 : 0.3 SO_3 : 16 LOI).



Fig(1). The chemical structure of Janus Green dye

2.3 Preparation of Clay Powder (BAU).

A certain amount of clay was washed by immersing it in an appropriate amount of distilled water for a number of times to remove foreign substances and water-soluble substances, then it was dried in an oven at (80) oC for (48) hours. The crushed powder using suitable sieves (Seives) to obtain the required size. The size (75 µm) was chosen in all experiments related to this study. As for the sizes (250 and 150 µm), they were used for the purpose of studying the effect of particle size on the adsorption process. The raw bauxite surface was diagnosed after conditioning by adopting techniques (XRD and FT-IR).

2.4 **Surface preparation and activation of CMC-bauxite modified**

This surface was prepared, as a 500ml beaker was taken and (30g) of crushed and dried bauxite was placed in it with (5g) of CMC polymer. We add (100ml) of diluted NaOH (0.1M), then add (100ml) of H_2O_2 gradually and put it in a hot stirrer For two hours , after that, the beaker was placed in an ultrasonic clear device, and for an hour after the completion of this process, the solution was placed for a whole day and washed with distilled water three times, then the modified clay was dried using a laboratory oven with a temperature of (80) ^{0} C for a period of 48 hours until that Dries completely. After that, it was ground using a mortar mill, and then the crushed clay was sifted using sieves (Particle Size 75µm), and the surface of the modified bauxite was identified after preparation by adopting techniques (XRD and FT-IR).

2.5 **Adsorption Experiments**

The process of adsorption of the Janus green (JG) dye from its aqueous solutions was carried out using bauxite clay and modified bauxite in a batch system, and the dye adsorption was followed up through the spectrometer at a maximum wavelength (λ_{max}) (611nm) , Experiments were carried out to determine the equilibrium time, kinetic study, and the effect of temperature by using shaker (120 rpm) , by fixing all the factors with changing one of them, and by measuring the difference before and after adsorption of the dye concentration by spectrophotometry . The quantity of (JG) dye adsorbed can be calculated by using the following equation [10]:

$$q_e = \frac{(C_\circ - C_e)V}{m} \qquad (1)$$

m: mass of (BAU and BAU/CMC-AC surfaces (g). C_o: concentration (JG) dye be for adsorption (mg/*l*). C_e: concentration of (JG) at equilibrium after adsorption (mg/*l*). V : volume of dye solution through adsorption (L).

2.6 Contact Time and Kinetic study

Equilibrium time and kinetic study experiments were conducted for the adsorption of Janus green dye with concentration (45 mg/l.) , weight (0.04 g) and surface particle size (75 µm) at time intervals within the range (5,10,15,25,35,45,45,60.90,120,150,180) min and pH (7) and for both surfaces (BAU and BAU/CMC-AC) by batch adsorption,

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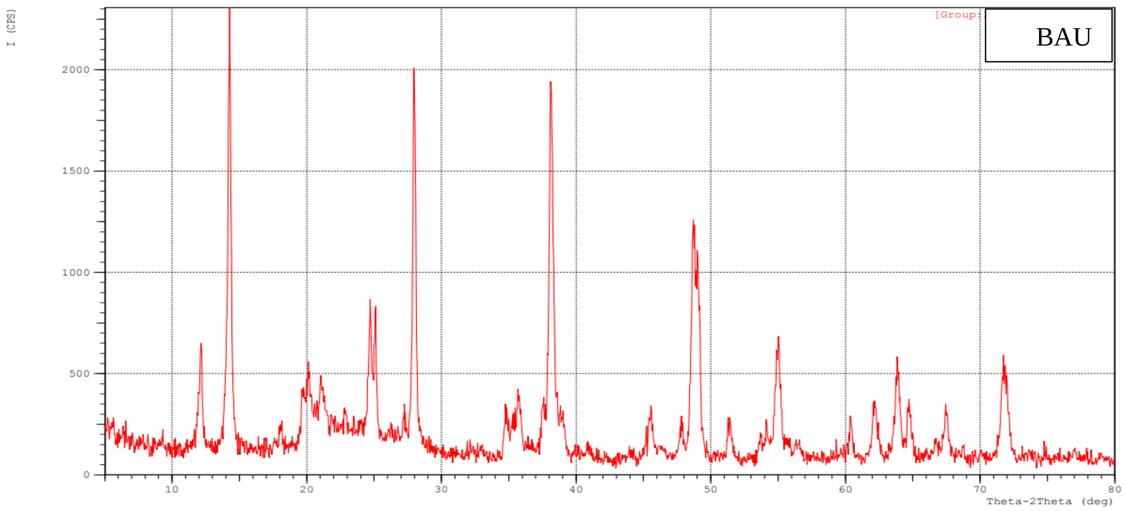
2.8 Temperature Variation

The equilibrium time experiments were repeated for the adsorption of Janus green dye from its aqueous solutions within a thermal range (15, 25, 35, 45 °C) to clarify the effect of temperature on the adsorption process and its kinetics.

3. Result and Discussion

3.1Characterization of Bauxite (BAU) and modified Bauxite (BAU/CMC-AC)

Figure (2 - BAU) XRD pattern of bauxite before modified Where we notice that most of the characteristic peaks of the first surface (BAU) belong to the minerals bohemite and kaolinite, and to a lesser extent both gibbsite and calcite , We also notice a great agreement in terms of the positions of the characteristic peaks of the above figure with the X-ray diffraction spectrum of bauxite clay in the study [11],Which indicates that it is this bauxite clay on the one hand, and on the other hand, we notice the sharpness and intensity of the distinctive peaks, which indicates that it is of a crystalline nature. . Figure (2 –BAU/CMC-AC) XRD pattern of bauxite after modified , which we notice from the figure that the process of loading the bauxite surface with CMC polymer particles and its activation led to a change in the locations and intensity of the characteristic peaks of the bauxite surface, and this was reflected on the adsorption properties of the surface.[12]



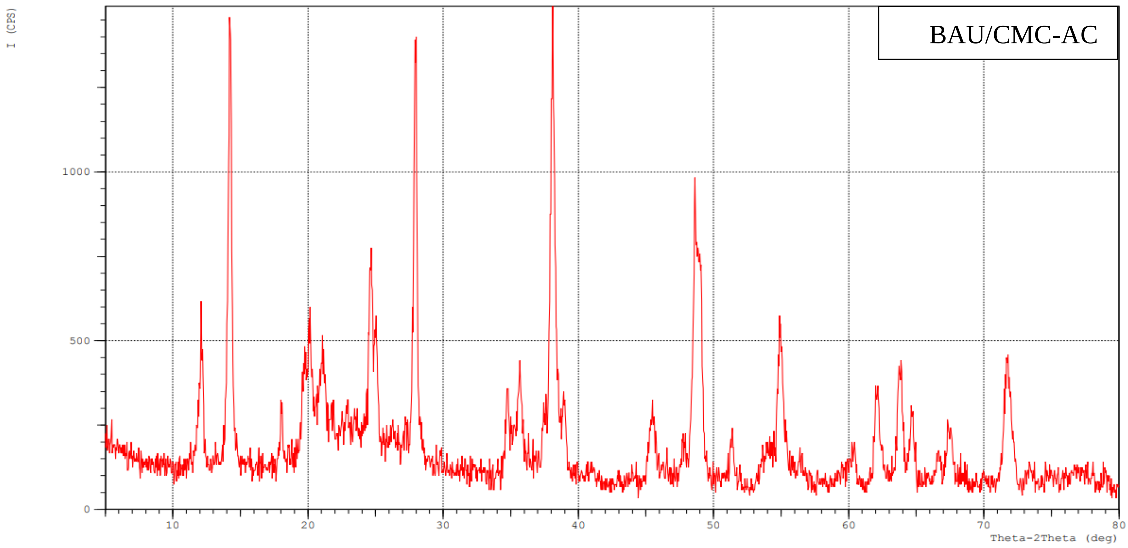
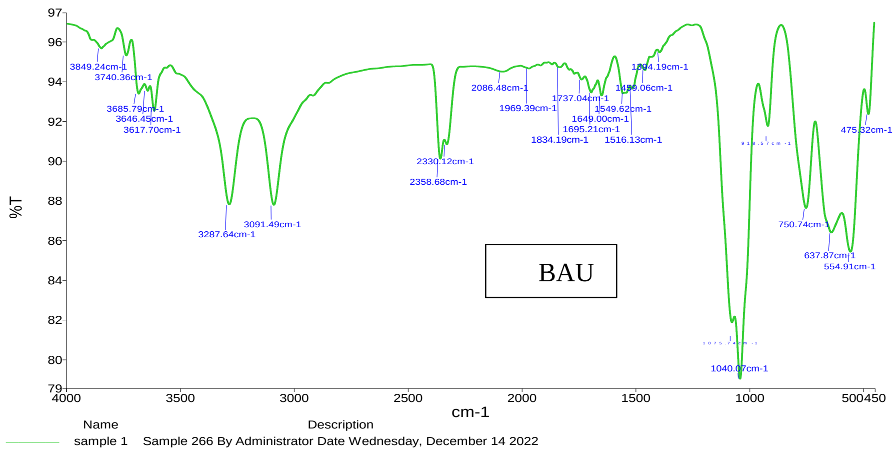


Fig. (2) X-ray diffraction of bauxite surfaces (BAU, BAU/CMC-AC)

Figure (3- **BAU, BAU/CMC-AC**) FT-IR spectra of bauxite and modified bauxite , bauxite has peak at 475.32 cm^{-1} is assigned to Si-OH-Al stretch , at 750.74 cm^{-1} is assigned to Al-OH bend , at 1074.07 cm^{-1} is assigned to Si-O stretch , at 3617.70 cm^{-1} is assigned to Al-OH stretch , After loading the bauxite surface with CMC particles and activating them, this led to a relative change in the bauxite peaks, in addition to the appearance of a peak at 1618.10 cm^{-1} is assigned to C=O stretch and at 2921.89 cm^{-1} is assigned to C-H stretch duo to CMC molecules , data of XRD and FT-IR of bauxite and modified bauxite be compatible[13,7] .



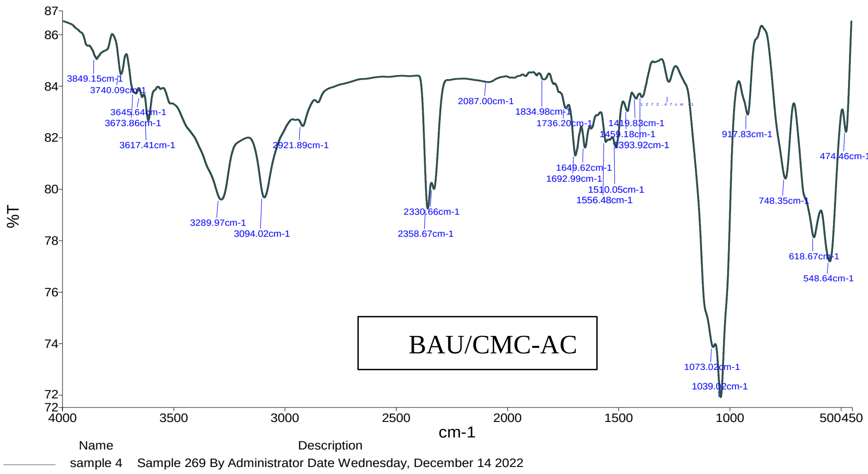


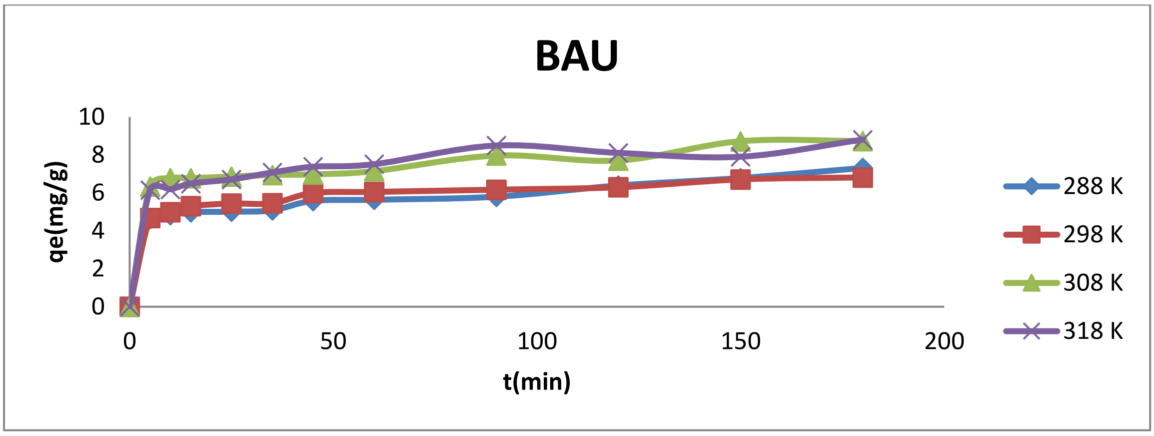
Fig. (3) FTI R spectra of bauxite surfaces (BAU, BAU/CMC-AC)

3.2 Study of contact time of adsorption process

The adsorption of Janus green dye (JG) on bauxite surfaces (BAU, BAU/CMC-AC) were studied as a function of contact time, and draw q_e versus t in Figure (4) at different temperatures . from Figures (6) are shown The adsorption rates of (JG) dye onto bauxite surfaces (BAU, BAU/CMC-AC) are observed We note that the adsorption process is fast during the first minutes, and this is due to the fact that the adsorption sites are not occupied, but with the passage of time, the adsorption speed begins to decrease, reaching the equilibrium time (90,45) min for (BAU and BAU/CMC-AC) surfaces respectively , which represents the saturation of the adsorbent surface of the green janus dye. On the other hand, we notice an increase in adsorption with the increase in temperature, for molecules The adsorbent dye penetrates the inner surface of the adsorbent surfaces by the energy gained from the temperature increase [14], and these results similar with result of The percentage adsorption of (JG) dye on bauxite surfaces (BAU, BAU/CMC-AC) were calculated using the equation **:**

$$Adsorption\ \% = \frac{(C_\circ - C_e)}{C_\circ} \times 100 \qquad (2)$$

Figure (5) are shows the percentage adsorption of (JG) dye on bauxite surfaces (BAU, BAU/CMC-AC) Nearly 78%, 88.5% respectively at favorite temperature within range (288, 298 ,308 .318) K, We also notice an increase in the percentage of adsorption with the increase in temperature, which indicates that the process has an endothermic nature [15]



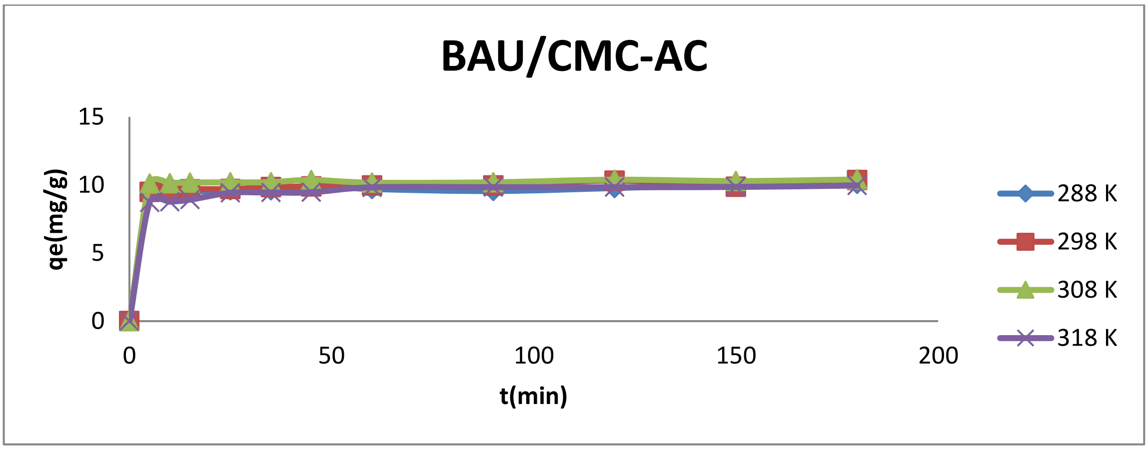
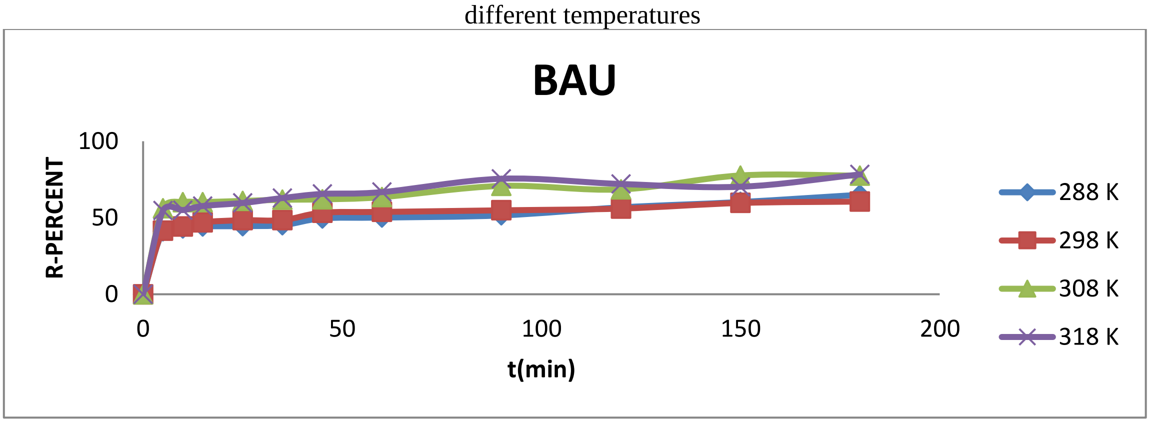


Fig. (4) Effect of contact time on the removal of Janus green by bauxite surfaces (BAU, BAU/CMC-AC) at different temperatures



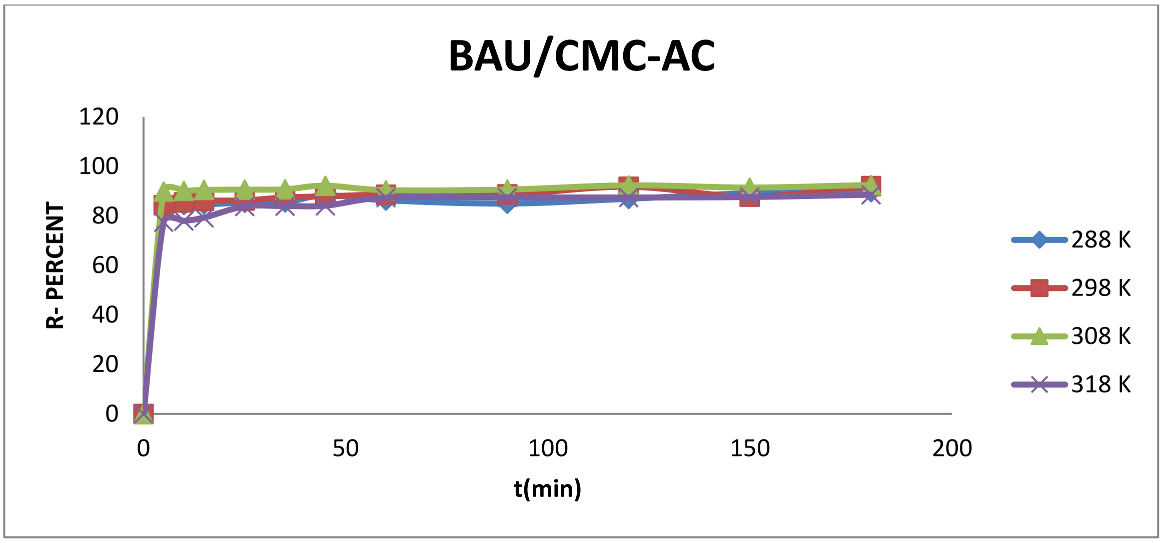


Fig. (5) Effect of contact time on the percentage removal of Janus green by bauxite surfaces (BAU, BAU/CMC-AC) at different temperatures

3.3 Kinetic study of adsorption

Kinetic of adsorption describes the solute uptake rate, which in turn governs the residence time of adsorption reaction. Batch experiment were conducted to study the rate of (JG) (45 mg/L) adsorption by bauxite surfaces (BAU, BAU/CMC-AC) (0.04g) at pH 7 .

Pseudo- first order model

The pseudo first order model was described by lagergren[16],The linear form is :-

$$\ln(q_e - q_t) = ln\, q_e - (K_1)t \qquad (3)$$

Where q_e and q_t are the amount of (JG) dye adsorbed mg /g at equilibrium and at any time t respectively and k_1 (min^{-1}) is the equilibrium rate constant of pseudo first order adsorption . The plot of ln (q_e- q_t) vs. t should give linear relationship from which the value of k_1 , equilibrium adsorption q_e and correlation coefficient R^2 were calculated . The pseudo first order kinetic model for adsorption of (JG) dye on bauxite surfaces (BAU, BAU/CMC-AC) are not applicable due to the low average correlation coefficients($R^2 < 0.76$) and ($R^2 < 0.51$) respectively at different temperatures Table (1), Figure (6) .

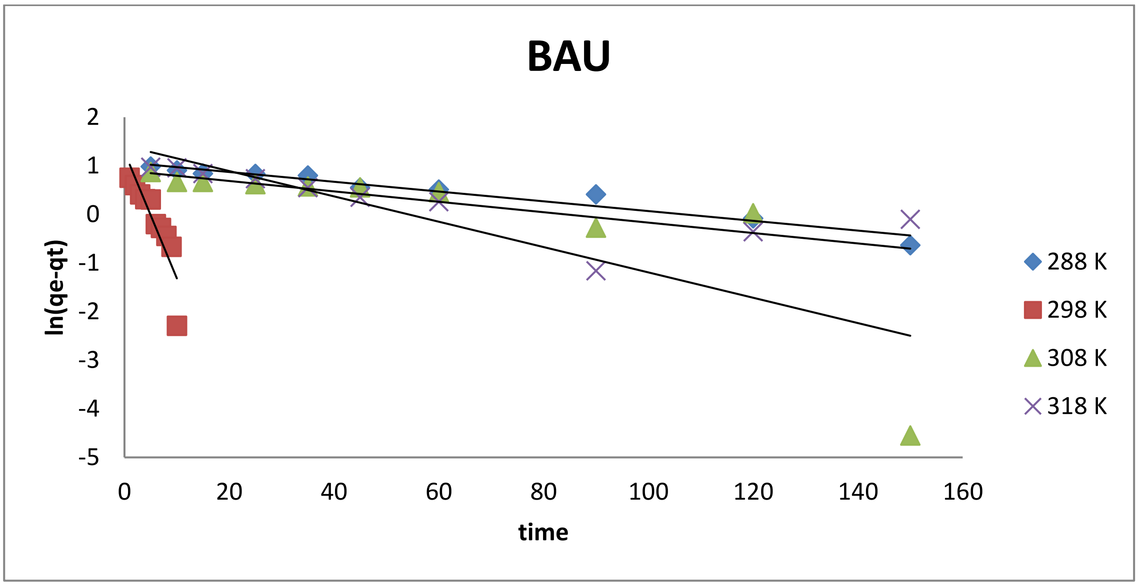
Pseudo -second order model

The pseudo-second order model is represented by the The linear form equation [18]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}(t) \qquad (4)$$

Where k_2 is the equilibrium rate constant of pseudo- second order adsorption (g/ mg.min)

The slope and intercept of plot t/q_t versus t were used to calculate the second order rate constant k_2 .The correlation coefficients was found (R^2 >0.98) for both adsobent different temperatures ,and the calculated q_e values agree very well with experimental data (table 2,figure 7,figure 4). This model confirms that the adsorption of (JG) dye on bauxite surfaces (BAU, BAU/CMC-AC) follows the pseudo second order model .



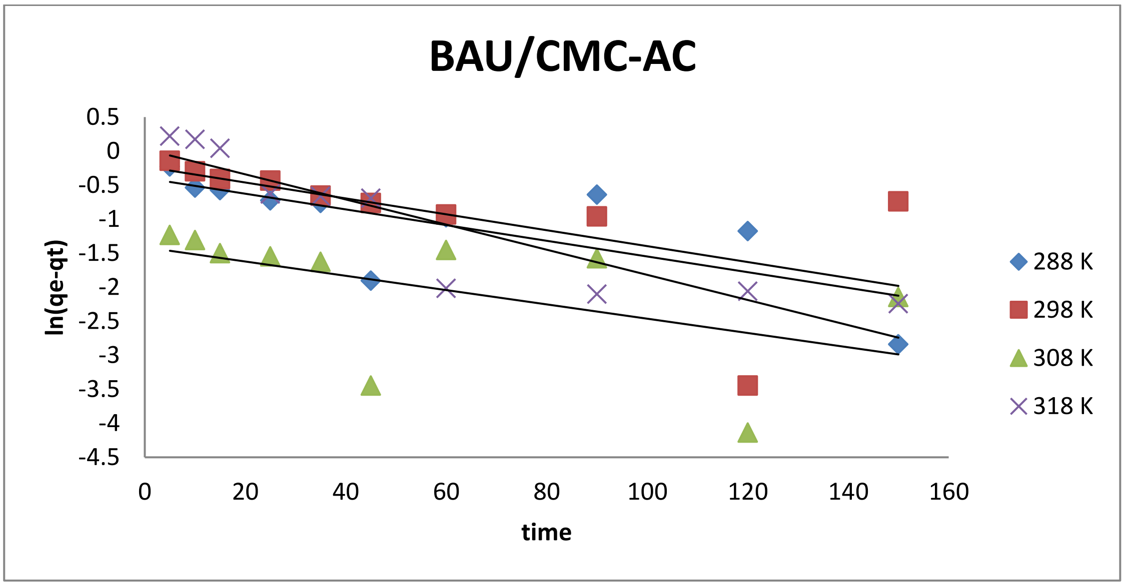
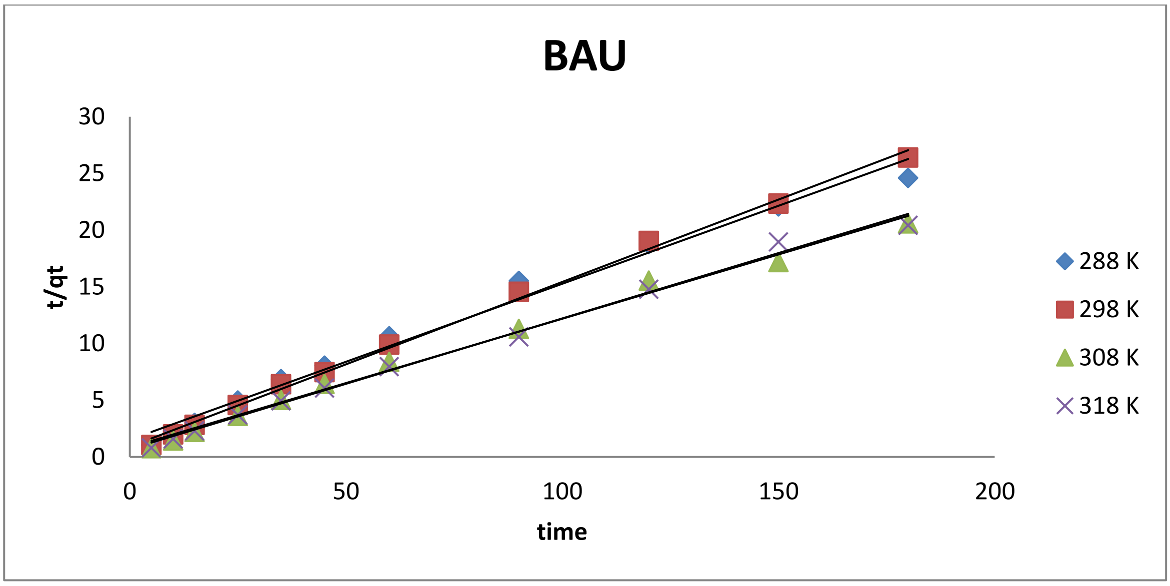


Fig. (6): The applicability of the first order kinetic model to Janus green by bauxite surfaces (BAU, BAU/CMC-AC) at different temperatures



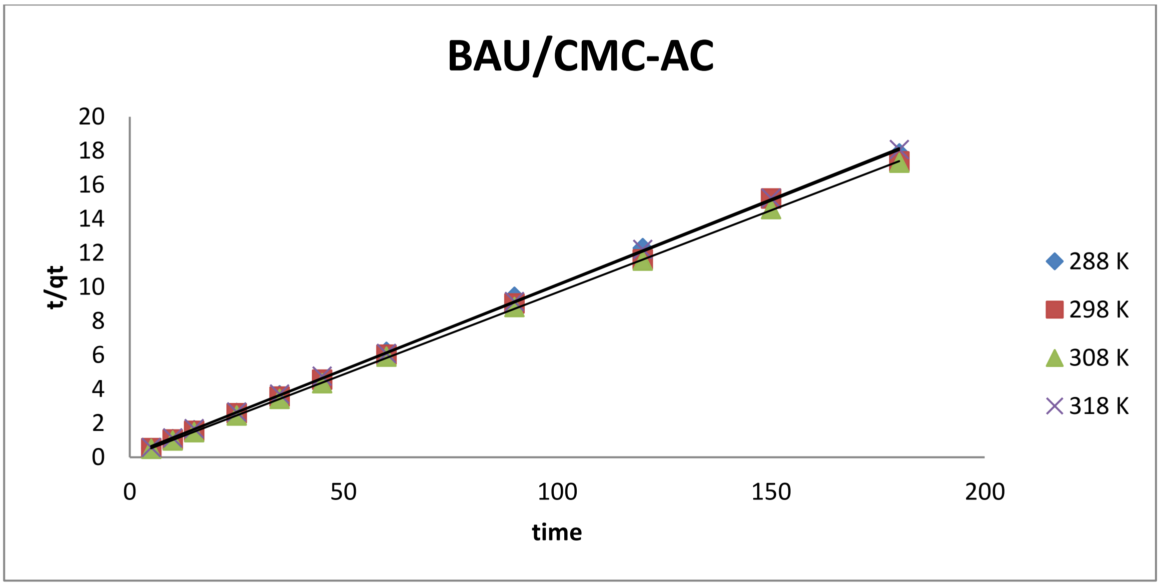


Fig. (7): The applicability of the second order kinetic model of Janus green by bauxite surfaces (BAU, BAU/CMC-AC) at different temperatures

Table (1): kinetics parameters of pseudo-first order for janus green adsorption by bauxite surfaces (BAU, BAU/CMC-AC)

Bauxite surfaces	288 K			298 K		
	Pseudo-first order			*Pseudo-first order*		
	$k_1(min^{-1})$	$q_e(mg/g)$	R^2	$k_1(min^{-1})$	$q_e(mg/g)$	R^2
BAU	0.0100	2.9244	0.945	0.0169	2.2081	0.887
BAU/CMC-AC	0.0115	0.6734	0.535	0.0117	0.7966	0.377
Bauxite surfaces	308 K			318 K		
	Pseudo-first order			*Pseudo-first order*		
	$k_1(min^{-1})$	$q_e(mg/g)$	R^2	$k_1(min^{-1})$	$q_e(mg/g)$	R^2
BAU	0.0261	4.1109	0.632	0.0107	2.4645	0.607
BAU/CMC-AC	0.0105	0.2436	0.276	1.0285	0.0185	0.816

Table (2): kinetics parameters of pseudo-second order for janus green adsorption by bauxite surfaces (BAU, BAU/CMC-AC)

Bauxite surfaces	288 K			298 K		
	Pseudo-second order			*Pseudo-second order*		
	$k_2\,(g.\ mg^{-1}\ .min^{-1})$	$q_e(mg/g)$	R^2	$k_2\,(g.\ mg^{-1}\ .min\ ^{1})$	$q_e(mg/g)$	R^2
BAU	0.0125	7.2701	0.986	0.0232	6.8846	0.997
BAU/CMC-AC	0.0753	10.0450	0.999	0.0804	10.2465	0.999
Bauxite surfaces	308 K			318 K		
	Pseudo-second order			*Pseudo-second order*		
	$k_2(g.\ mg^{-1}\ .min^{-1})$	$q_e(mg/g)$	R^2	$k_2\,(g.\ mg^{-1}\ .min^{-1})$	$q_e(mg/g)$	R^2
BAU	0.0151	8.8195	0.992	0.0192	8.6774	0.994
BAU/CMC-AC	10.3763	0.2044	1.000	0.0622	10.0032	1.000

4. Conclusion

We conclude from this work and the diagnostic tools (XRD and FT-IR) that the process of modification and activation of bauxite clay with carboxy methyl cellulose polymer (CMC) particles has occurred and improved its adsorption properties to remove the green Janus (JG) dye from its aqueous solutions .Where the adsorption percentage was equal to (78%, 88.5%) for both (BAU and BAU/CMC-AC) surfaces respectively, and the process is of an endothermic nature and follows the kinetic model of the second order.

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