Kinetic Study of Methyl Green Dye Adsorption from Aqueous Solution by Bauxite Clay at Different Temperatures

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Abstract

Kinetic experiments were performed to induce of the green methyl dye adsorption from aqueous solution on the bauxite clay. This study includes determination of the adsorption capacity of bauxite clay to methyl green dye adsorption and study the effect of some parameters (temperature , time) on the kinetic of the adsorption process of the dye were studied. Quantity of dye adsorbed was increased when the temperature increases from 298 to 318K which indicates that methyl green adsorption processes are endothermic nature. In order to describe the kinetic data and the rate adsorption constants of the pseudo-first-order and second-order kinetics were used. The kinetics data were applied well with the second-order kinetic model. From activation energy value (E_a) for methyl green dye are energetically favorable and the dye adsorption includes physical and chemical adsorption types.

Key words: Adsorption; Bauxite; Methyl green; Kinetics; Activation energy**.**

Introduction

The process of discharge of wastewater containing different amounts of dyes in the rivers, seas and oceans causes environmental problems because of the difficulty of disposing of them because of their non-biodegradable nature. As a result, their survival has harmful health effects on humans such as carcinogenicity, respiratory poisoning and fertility reduction [1].

Depending on their chemical composition, dyes can be classified into anionic and positive dyes [2]. Due to the presence of sulfonate groups of anionic dyes in its aqueous solution, it can show negative charge while due to the presence of amino or sulpher containing groups of the cationic dyes in aqueous solution which show a positive charge [3].

We treat waste water in our daily life and water polluted with organic pollutants by several physical and chemical methods including precipitation, coagulation and adsorption, filtration with coagulation, reverse osmosis, ozone, ion exchange, and advanced oxidation processes, which have been used. These methods are limited because they are expensive in terms of money and effort. Therefore, the best effective methods for treating and removing organic pollutants in a medium wastewater treatment is the adsorption method [4].

The good adsorbent used in water purification is clay materials, depending on its properties, including its mechanical and chemical stability, high surface area, layered structure and large cation exchange capacity [5].

In this study, emphasis was placed on the kinetic study because it provides data on the period required to reach equilibrium and determine the efficiency of the solvent surface for adsorption of liquid adsorbent materials, as well as the possibility of understanding. The kinetic data is a value for determining the period required to reach equilibrium and the absorption performance evaluation. These data also help to understand the adsorption mechanism which is necessary to improve and develop the efficiency of these processes. [6 & 7].

In one study, the fluorine adsorption process included polluted water by bauxite. The adsorption process was achieved in both batch and continuous experiments. In continuous experiments, the effects of primary concentration of fluoride, flow rate to contact time and adsorption efficiency were studied. As for the batch experiments, the data were described with the Freundleich formula and showed a good application. The results obtained indicate that this bauxite can be used effectively to remove pollutants from drinking water. [8]

In another study, an attempt was made to activate the surface of the adsorbent (pomegranate husks) by a specific acid in order to enhance the adsorption ability of this surface for adsorption of methyl green dye. Several tests were carried in a batch system to examine the effect of system variables, ie pH solution, ionic strength, temperature and time of contact on absorptive capacity. The process data were analyzed by applying the isotherm of equilibrium such as Langmuir, Freundleich, Tamkeen, and Dobinin - Isotherm Radoshkiewicz equations. These data showed that the Langmuir Isotherm was well applied and either the kinetics study of adsorption inetics were applied to follow the pseudo-second rate-rate kinetic rate. Thermal functions have also been calculated and revealed that the dye adsorption is spontaneous endothermic process. [9]

The aim of this paper is to study the kinetics of adsorption of green dye using bauxite clay as adsorbents.

Experimental

Chemicals and materials

Methyl Green is a divalent cationic dye (named basic blue 20) that is chosen in this study as an adsorbate.

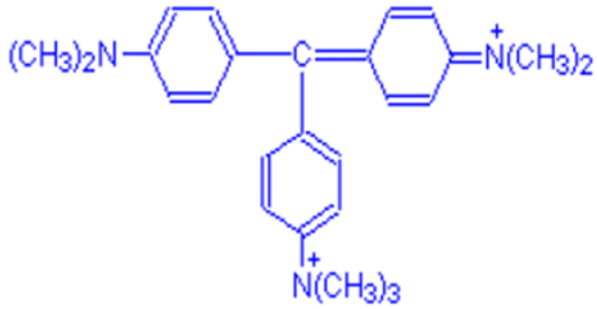

Figure (1): Chemical structure of Methyl Green dye.

Its molecular formula is $C_{26}H_{33}N_3Cl_2$, BDH company, molecular weight 458.5 g/mol, as shown in figure (1). The stock solution of 100 mg/L of methyl green dye was prepared and λ_{max} was recorded by UV-visible spectrophotometer (Double beam, Shimadzu. 1800, Japan) it was found to be 618 nm.

Bauxite clay preparation

The powder of bauxite clay was obtained from (Akkashatt) area in the western desert of Iraq. Bauxite clay was washed with an excessive amounts of deionized water in order to remove the soluble materials, dried for (6 hours) at (120°C) (Daihan Labtech Oven LDO- 060E) then left to coal at room temperature, and kept in air light containers.
The clay was crushed and sieved by using the sieve of nominal size of (≤75µm) which used in all experiments throughout this work, Analysis of bauxite has shown several compounds given in table (1) and expressed as oxides:

Table (1): The chemical analysis of bauxite.

Compound	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	L.O.I	Total
Wt%	15.7	64.2	0.9	1.3	1.5	0.1	0.3	16	100

Batch kinetic studies

Solution of methyl green dye was prepared in concentration (100 mg/l), The tests were carried out with 0.01 g of bauxite adsorbent dose for dye concentration of 16 mg/l. The mixture was excited using a thermostatic shaker water bath (Labtech. Korea) (120 rpm) at temperature range of 25^0C – 45^oC. after the final of the test the sample was left to stalize for 5 min and the supernatant sample was measured for its methyl green concentration using UV-visible spectrophotometer (Double beam, Shimadzu. 1800, Japan) it was found to be 618 nm. The amount of methyl green dye adsorbed was calculated due to the following equation [10]:

$$q_t = \frac{V(C_\circ - C_t)}{m} \text{..... .....} (1)$$

Where:
q_t = Amount adsorbed (mg/g) at time (min)
V = Volume of mehyj green dye solution (L)
C_o= Orginal concentration of mehyj green dye (mg/L)
C_t= Mehyj green dye concentration (mg/L) at time (min)
m = Weight of bauxite adsorbent (g)

Results and discussion:

Effect of contact time

A set of contact time experiments for the methyl green dye has been implemented with constant initial dye concentration of 16mg/l at temperature 298K Figure (2). Figure (2) shows adsorption process including two stages, the one stage was very rapid (high increasing of qt) through the first (5) min for bauxite clay, and the two stage was increased slowly (relative increasing of q_t) with time until reaching equilibrium at this time (contact time =60 min) the amount adsorbed of methyl green dye on bauxite clay was reached to saturation . At this time represented case of dynamic equilibrium between the quantity of dye being adsorbed by bauxite clay with the quantity of the dye desorbing from the bauxite clay. At the equilibrium the quantity of dye adsorbed indicates the maximum adsorption capacity of the bauxite clay under study [11 &12].

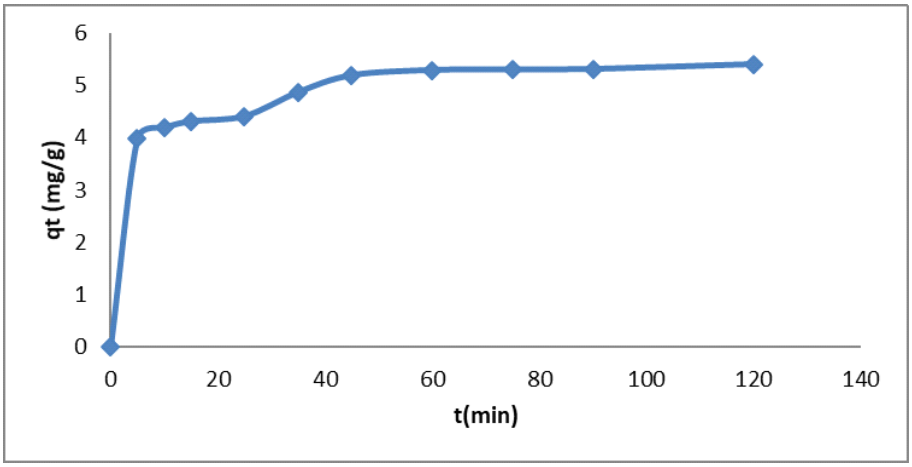

Figure (2): Effect of contact time on methyl green dye adsorption by bauxite clay at temperature (298 K)

Effect of temperature

We studied the methyl green dye adsorption by bauxite through the temperature range of (298,308,318) K at initial dye concentration 16mg/l and pH 7 used in fixation for methyl green dye figure (3).
Figures (3) shows that the adsorption of methyl green dye on bauxite increases with raising the temperature up to 318K indicating that the dye adsorption onto bauxite favored a high temperature [13].
The increase in temperature activates the dye ions which increase their movement. As a result, the pores and the internal structure of the bauxite clay are swelling. This facilitates the entry and occupancy of a larger number of dye ions on the surface and inside pores of the bauxite clay [14 & 15]. This may also be due to an increase in the movement of the dye molecule with an increase in kinetic energy, and the more speed of intraparticle proliferation of dye with

high temperature. It is shown that the adsorption of methyl green dye on bauxite clay is a heat-absorbent process [16].

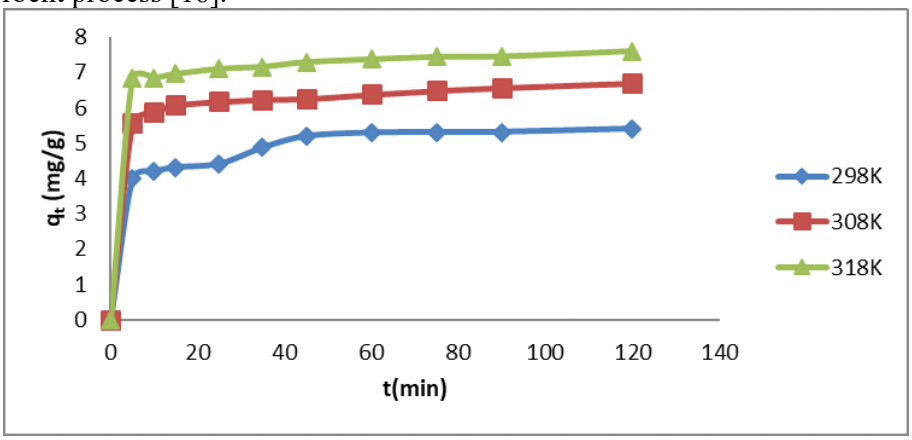

Figure (3): Effect of temperature on methyl green dye adsorption by bauxite clay at different times

Kinetics of methyl green dye adsorption

Kinetic experiment of methyl green dye adsorption on bauxite clay was applied under the conditions (C_0=16 mg/L, pH= 7, T=298,308,318 K). The experimental data were treated with realation to two kinetic models which pseudo-first order (17) and pseudo-second order (18). the linear forms of the pseudo-first order and pseudo-second order kinetics were represented in equations (2 ,3) respectively.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 . q_e^2} + \frac{t}{q_e} \qquad (3)$$

where, q_e (mg/g) is quantity adsorbed of methyl green dye at equilibrium , q_t (mg/g) is quantity adsorbed of methyl green dye at time (t) , k_1 (min^{-1}) is rate constant adsorption of the pseudo-first order figure (4), k_2 (g/min.mg) is rate constant adsorption pseudo-second order figure (5) explain pseudo-first order and pseudo-second order figures for the experimental values. (k_2, k_1) rate adsorption constants determination from the intercepts and slopes which recorded with correlation coefficients (R^2) in tables (1) and (2)

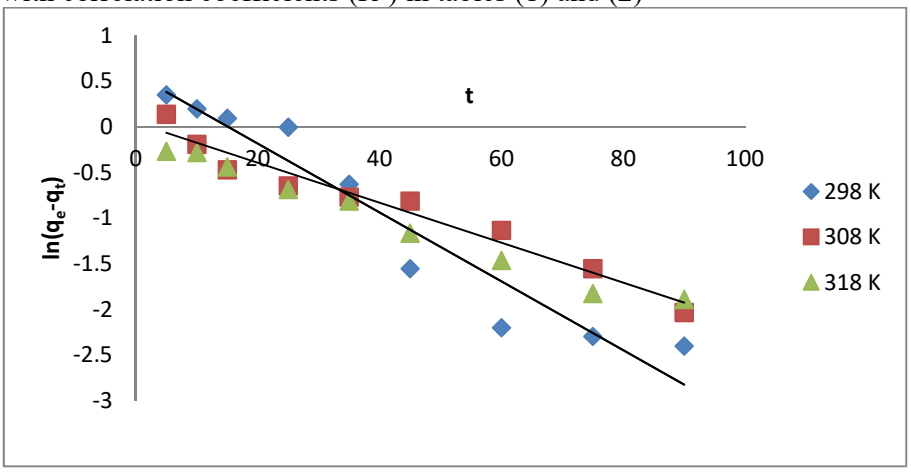

Figure (4): Pseudo-first-order-kinetic model for methyl green dye adsorption onto bauxite clay

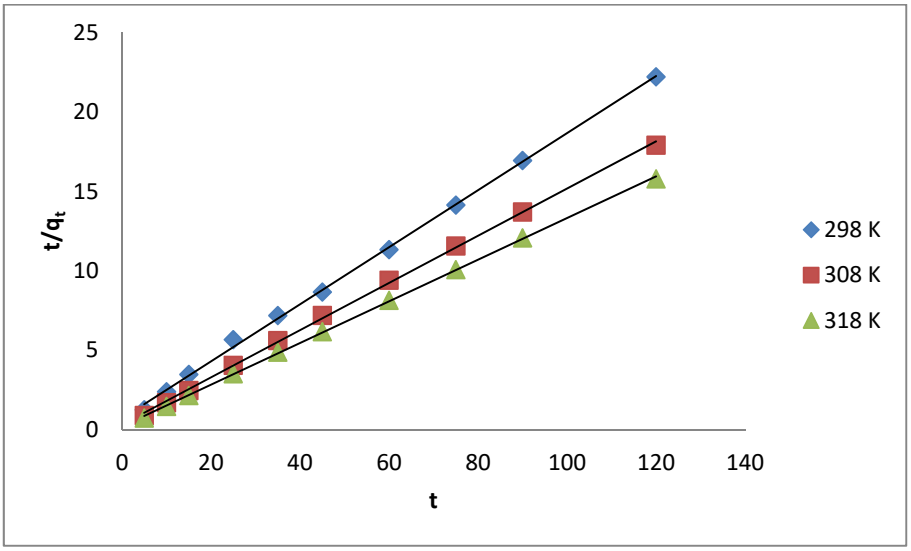

Figure (5): Pseudo-second-order-kinetic model for methyl green dye adsorption onto bauxite clay

Table (2): pseudo-first-order-kinetic parameters for the methyl green dye adsorption onto bauxite clay at various temperatures

Adaorbent	298K			308K			318K		
	k_1	$q_{e,cal}$ (mg/g)	R^2	k_1	$q_{e,cal}$ (mg/g)	R^2	k_1	$q_{e,cal}$ (mg/g)	R^2
Bauxite	0.037	1.764	0.9287	0.021	1.0437	0.9587	0.021	1.1529	0.9839

Table (3): pseudo-second-order-kinetic parameters for the methyl green dye adsorption onto bauxite clay at various temperatures

Adaorbent	298K			308K			318K		
	k_1	$q_{e,cal}$ (mg/g)	R^2	k_1	$q_{e,cal}$ (mg/g)	R^2	k_1	$q_{e,cal}$ (mg/g)	R^2
Bauxite	0.045	5.568	0.9989	0.068	6.7340	0.9994	0.0825	7.6336	0.9997

From tables (2) and (3) and figures (4) and (5) they show the kinetic data that were applied by the pseudo-first and pseudo-second order kinetic models respectively. From table (2) it was observed low correlation between of the equilibrium data with the pseudo-first order kinetic model.

We found high correlation (R^2) between the kinetic data and the pseudo-second order equation. From table (3) the results explained that the kinetic data were good applied by the pseudo-second order ($R^2 \geq 0.9989$) indicating chemical adsorption that had taken place on the bauxite lay surface which might be the rate limiting step that controlled the adsorption process.

From tables (2) and (3) the calculated or theoretical value of adsorption capacity ($q_{e,cal}$) from the plot in Fig. 5 was found in agreement with the experimentally ($q_{e,exp}$) determined value than that calculated from Fig 4. on the other hand the rate constant (k_2) of The pseudo-second order higher than the rate constant (k_1) of the pseudo-first order at all temperatures under study, These indicate that the pseudo-second order model acts the kinetic data high accurately[18].

Generally, the adsorption mechanism for dye adsorption using an adsorbent material can be assumed as contained three stages in which bulk diffusion is considered to be instantaneous [19]:

1. Dye molcules diffusion through the boundary layer to the surface of the adsorbent.
2. Dye molcules transfer from the exterior surface of the adsorbent to the interior pores of particle through intraparticle diffusion mechanism.
3. Adsorption of dye in an active site on the surface of adsorbent.

Based on the above we use the rate constant (k_2) of the pseudo-second- order model to determination the activation energy of the methyl green adsorption process using the Arrhenius equation [20]:

$$\ln k_2 = \ln A - (E_a/RT) \quad \textbf{(4)}$$

where k_2 =the rate constant of the second-order model (g/mg min), A =the frequency factor, E_a = activation energy of adsorption process (kJ/mol), R = the universal gas constant (8.314 J/mol K) and T= the temperature (K), respectively. From the slope of the plot of ln (k_2) versus 1/ T as figure (6) the activation energy could be calculated. The activation energy of the adsorption of methyl green dye onto bauxite was 23.3 kJ/mol, this activation energy leads to the conclusion: the adsorption process of methyl green dye onto bauxite clay a physical adsorption involved chemical process [21].

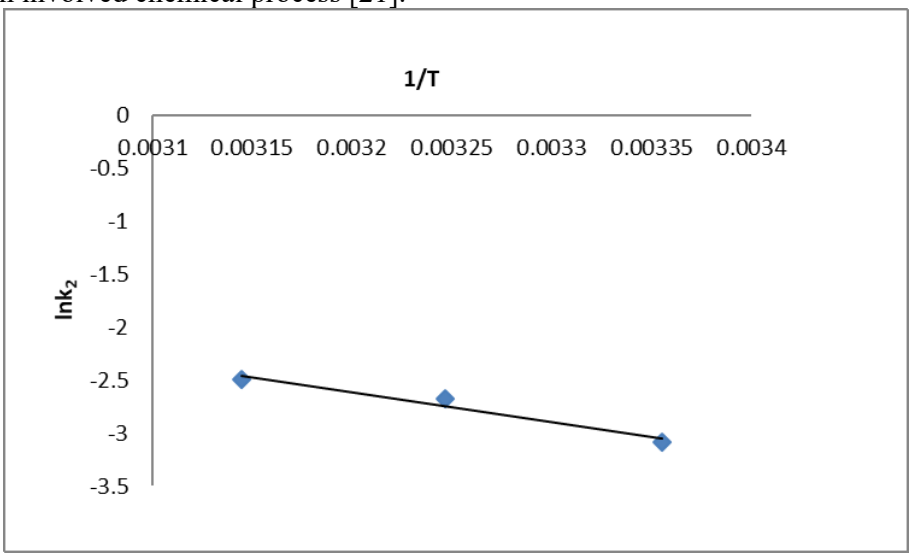

Figure (6): Presents a graph of the linearized Arrhenius equation

Conclusion

This paper investigated the adsorption of methyl green from aqueous solutions using bauxite absorbent .The results indicate that the pseudo-second order kinetic equation show the best application to adsorption of methyl green dye on bauxite clay, due to good fit with pseudo-second order and activation energy value, these indicate forming molecular interaction between methyl green dye and bauxite clay surface and is the rate of limiting step and physical sorption involved the chemical process.

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References

[1] S. Srivastava; S. Rangana; D. Roy,.Toxicological effects of Malachite Green. Aquat. Toxicol., 66 319–329. 2004

[2] T. Robinson; G. McMullan; R. Marchant and P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresource Technology, 77 247 – 255. 2001

[3] S. Netpradit ; P. Thiravetyan ; S. Towprayoon , Adsorption of three azo reactive dyes by metal hydroxide sludge; effect of temperature, pH and electrolytes, Journal of Colloid and Interface Science, 270 255 – 261. 2004

[4] G. Crini. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, Progress in Polymer Science. 30, 38–70. 2005

[5] G.K Sarma; S.S. Gupta; K.G Bhattacharyya, Methylene Blue adsorption on natural and modified clays. Separation Science and Technology., 46 1602–1614. 2011

[6] B. Armağan;M. Turan;M.S. Celik, Equilibrium studies on the adsorption of reactive azo dyes into zeolite, Desalination, 170 33-39. 2004

[7] A.A. Abia ;J.C. Igwe , Sorption kinetics and intraparticulate diffusivities of Cd, Pd and Zn ions on maize cob , African Journal of Biotechnology, 4, 6509-512. 2005

[8]R. Lavecchia ;F. Medici; L. Piga; G. Rinaldi and A. Zuorro , Fluoride Removal from Water by Adsorption on a High Alumina Content Bauxite, Chemical Engineering Transactions. 26 225-230. 2012

[9] M. A. Shouman; S. A. A. Khedr, Removal of Cationic Dye from Aqueous Solutions by Modified Acid - Treated Pomegranate Peels (PUNICA GRANATUM): Equilibrium and Kinetic Studies, Asian Journal of Applied Sciences. 3 574-588. 2015

[10] N. Kannan; T. Veemaraj, (2009): Removal of Lead (II) ions by adsorption onto bamboo dust and commercial activated carbons-A comparative study. E-Journal of Chemistry, 6 247-256. 2009

[11] J. X. Lin;S. L. Zhan; M. H. Fang; X. Q. Qian, J. Porous. Mater., 12449-455. 2007

[12] R. Katal, M. S. Baei, H. T. Rahmati, H. Esfandian, Journal of Industrial and Engineering Chemistry., 18 295-302. 2012

[13] S. Ali .; T. Hussain; R. Nawaz ; Optimization of alkaline extraction of natural dye from Henna leaves and its dyeing on cotton by exhaust method. Journal of Cleaner Production, 17 61–66.2009.

[14] H. Yoshida ; A. Okamoto ; T. Kataoka , Adsorption of acid dye on crosslinked chitosan fibers-equilibria, Chemical Engineering Science., 48 2267–2272. 1993

[15] S.M Venkat , D.M Indra , C.S. Vimal , Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution, Dyes Pigments., 73 269–278 . 2007

[16] Z. Aksu ; A.I Tatli ; O.A. Tunc ,. comparative adsorption/biosorption study of Acid Blue 161: Effect of temperature on equilibrium and kinetic parameters, Chemical Engineering Journal, 142 23–39. 2008

[17] S. Lagergren, Zur Theorie der Sogenannten Adsorption Gelöster Stoffe, Kungliga Svenska Vetenskapsakademiens Handlingar, 24(1898) 1-39.

[18] G. McKay; Y. S. Ho, Pseudo-second order model for sorption processes, Process Biochemistry, 34451-465. 1999

[19] K.A. Guimarães Gusmão, L.V. AlvesGurgel, T.M. Sacramento Melo, L.F. Gil., *Dyes. Pig.,* 92 967-978. 2012

[20] N. Lazaridis; D. Asouhidou ,. Kinetics of sorptive removal of chromium(VI) from aqueous solutions by calcined Mg–Al–CO_3 hydrotalcite. Water Research. 372875–2882. 2003

[21] A. M. Abbas, Y. I. Mohammed, T. A. Himdan, Adsorption of Anionic Dye from Equeous Solution by Modified Synthetic Zeolite, Ibn AL-Haitham Journal For Pure and Applied Science ,28 52-68. 2015