Removal Orange (G) Dye from aqueous solution by adsorption on Bentonite

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Abstract:

The adsorption and removal of commercial Orange (G) dye onto bentonite from aqueous solution, was studied in a batch system with respect to contact time and concentration. UV-Spectrophotometric technique has been applied to study the adsorption isotherms. The pseudo first order and pseudo second order kinetics model were used to describe the kinetic data and the rate constants were evaluated. The results of kinetics studies indicated that the adsorption process can be well described with the pseudo first order kinetic model. The Langmuir and Freundlich adsorption model were applied to describe the equilibrium isotherms and the isotherms constants determine. Thermodynamic parameters such as ΔG, ΔH and ΔS were calculated, The values of the parameters showed that the process were exothermic.

Introduction*:*

Dyes are widely used in industries such as textile, rubber, paper, plastic, cosmetic, etc. Among these various industries, textile rank first in usage of dyes for coloration of fiber. Presently, it was estimated about 10^4 of different commercial dyes and pigments exists and over $7x10^5$ tones are produced annually word wide(1).

Color affects the nature of the water and inhibits sunlight penetration into the stream and reduces photosynthetic action(2). Most of the dyes are stable to biological degradation. Several biological, physical and chemical methods have been used for the treatment of the industrial textile wastewater including microbial biodegradation, membrane, filtration, oxidation and ozonation(3). However, most of these processes are very expansive and cannot effectively be used to treat the wide rang of dyes waste(4). The adsorption process is one of the effective methods for removal dyes from waste influent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removal dyes, even from the diluted solution.

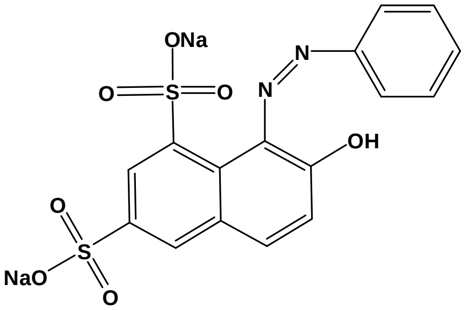
Bentonite is a heterogeneous clay which has the highest absorbent capacity than any of minerals clay. Its advantages over other minerals (especially with regards to its law density and high specific surface) which have been accepted for along time, and they account for most of the current uses of bentonite(5).

The main aim of current study is determine the thermodynamic and kinetics of adsorption Orange (G) on the bentoni

Materials and methods:

dye solution preparation:

For this study, Orange (G) was used and accurate weighted quantity of the dye was dissolved in distilled water to prepared stock solution (500 mg L^{-1}). Experimental solution was obtained by dilutions. Dye concentration was determined by using absorbance values measured before and after the treatment, at 475 nm with Centra 5 UV – Visible spectrophotometer.



Orange (G)
Acid orange 10
$C_{16}H_{10}N_2Na_2O_7S_2$
λ_{max} = 475 nm

Fig. 1: The Orange (G) structure.

Adsorption experiment:

In each adsorption experiment, 50 ml of dye solution of known concentration was added to 0.5 mg of adsorbent (bentonite) in 250 ml round flask at room temperature and mixture stirred on electronically shaker at 120 rpm. The adsorbed amounts of Orange (G) were calculated from the concentrations in solutions before and after adsorption according to the equation:

$$Q_e = \frac{V_{sol.}(C_o - C_e)}{m} \quad \ldots\ldots\ldots\ldots. (1)$$

Where C_o and C_e are the initial and equilibrium liquid phase concentration of dye solution (mg L^{-1}), respectively; Q_e is equilibrium dye concentration on adsorbent (bentonite) (mg g^{-1}). V is the volume of dye solution (L), and m is the mass of the bentonite sample used (g).

Result and Discussion:

Effect of contact time :

A plot of percentage adsorption versus adsorption time is shown in Fig. 2. It is evident from the figure that the equilibrium time is dependant on the adsorbate concentration. All the curves obtained were smooth indicating formation of monolayer on the surface of the adsorbent.

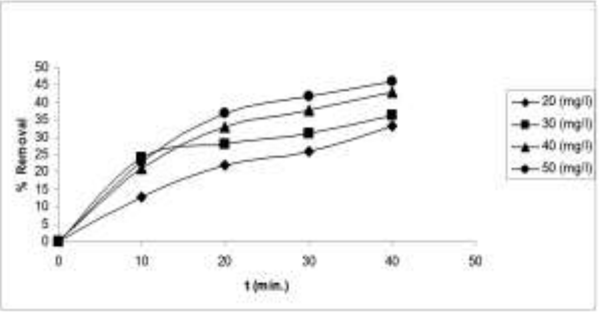


Fig 2: Effect of contact time on removal dyes from aqueous solution.

Effect of temperature:

Temperature has an important effect on the process of adsorption. The percentage of Orange (G) adsorption was studied as a function of temperature in the range of 303 – 313 K. the results obtained are presented in Fig.3. The decrease in percentage of adsorption with the increase in temperature may be due to the desorption caused by an increase in the available thermal energy. Higher temperature induces higher mobility of the adsorbate causing desorption. Then the quantity of adsorption was found to increase as the temperature decreased (exothermic process).

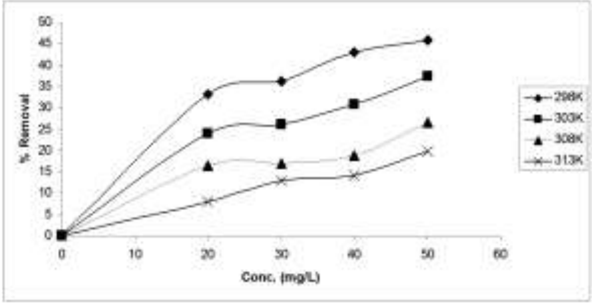


Fig.3: Effect of contact time on adsorption OG on bentonite.

Adsorption isotherms:

The purpose of the adsorption isotherms is to relate the adsorbed concentration in the bulk and adsorbed amount at the interface$^{(6)}$. The analysis of isotherm data is important to develop an equation which accurately represents the results and which could be used for design purpose$^{(7)}$. Several isotherm equations are available, Two of them have been selected in this study: Langmuir and Frendlich isotherms the linear form of Langmuir equation can be written in the following form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K} + \frac{C_e}{Q_m} \quad \text{………… (2)}$$

Where Q_m is the monolayer capacity of the adsorbent (mg/g) and K is the adsorption constant (L mg^{-1}). The plot of C_e/Q_e versus C_e should be a straight line with a slope $1/Q_e$ and intercept $1/Q_mK$ when adsorption follows the Langmuir equation$^{(8)}$.

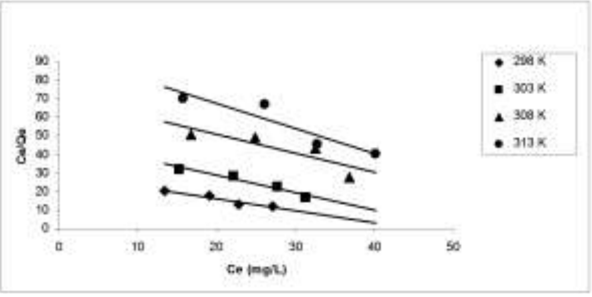


Fig.4: Langmuir istherms for adsorption OG on bentonite.

Freundlich equation in logarithmic form can be written as follows:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{……….. (3)}$$

The plot of $\ln Q_e$ against $\ln C_e$ will give a straight line, of slope 1/n and intercept $\ln K_F^{(9)}$. The value of Q_m, K, n and K_F are summarized in table (1).

Table (1): The value of Q_m, K_L, n and K_F are summarized in.

Temperature (K)	K_L	Q_m	R^2	K_F	N	R^2
298	67.75	0.011	0.8824	5.93	0.197	0.9832
303	69.84	0.014	0.7399	6.20	0.173	0.9625
308	51.27	0.021	0.9457	5.05	0.174	0.9122
313	45.06	0.034	0.9514	6.12	0.149	0.9843

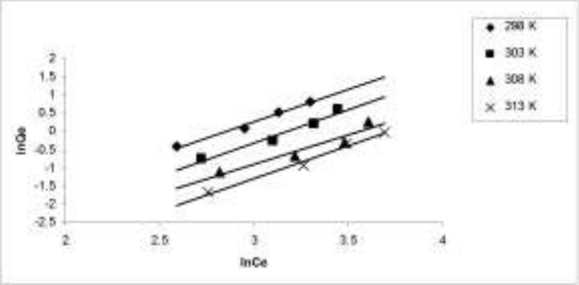


Fig.5: Frendlich isotherms for adsorption OG on bentonite.

Adsorption thermodynamic parameter:

In order to qualify the present adsorption process, thermodynamic factor including the Gibbs free energy, the enthalpy change of adsorption and the entropy change of adsorption were calculated using the following equation:

$$X_m = \frac{q_e}{C_e} \quad \text{………. (4)}$$

$$\ln X_m = -\frac{\Delta H}{RT} + conc. \text{……… (5)}$$

$$\Delta G = -RT \ln X_m \quad \text{………… (6)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{…………. (7)}$$

Where X_m is the adsorption distribution coefficient, R is the gas constant (8.314 KJ/mol.K) and T is the absolute temperature (K).

The ΔH value was obtained from the slope of $\ln K_d$ against 1/T as shown in Fig (6) and table (2).

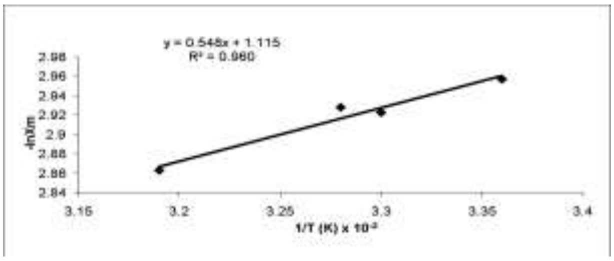


Fig. 6: Arrhenius equation

Table (2): The thermodynamic parameter.

Temperature (K)	ΔG KJ.mol^{-1}	ΔH KJ.mol^{-1}	ΔS J.mol^{-1}
298	-7.32618	-4.56355	9.271
303	-7.36244	-4.56355	9.237
308	-7.49776	-4.56355	9.527
313	-7.45033	-4.56355	9.223

Adsorption Kinetics study :

For evaluating the adsorption kinetics of Orange (G), lagergren first – order and second order models were used to fit the experimental data. The first order equation:

$$\ln(q_e - q) = \ln q_e - K_{ad} t \quad \ldots\ldots\ldots\ldots (8)$$

Where q_e is the amount of solute adsorbed at equilibrium per unit mass (mg.g^{-1}), q is the amount of solute adsorbed at any time t and K is the rate constant.

The plot of $\ln(q_e-q)$ versus t gave a straight line of slope K_{ad} (time^{-1}) were K_{ad} is the rate constant of first order reaction.

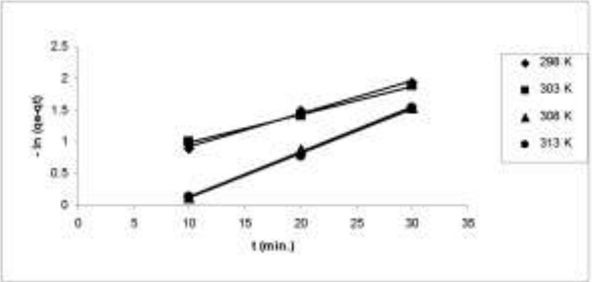


Fig. 7: lagergren first order reaction.

Table (3): rate constant of first order reaction.

Temperature (K)	k (min.$^{-1}$)	R^2
298	0.052	0.9944
303	0.0546	0.9982
308	0.0535	0.9985
313	0.0571	0.9975

A pseudo second order reaction model(10) may also be applicable to kinetics of adsorption and the equation is :

$$\frac{t}{q} = \frac{1}{K_2 . q_e^{2}} + \frac{t}{q_e} \quad \ldots\ldots\ldots\ldots\ldots (9)$$

Where K_2 is the rate constant of second order model (g/mg. min.). the plot of t/q against t should give a linear relationship Fig. . from which K_2 can be determine from the slope of the plot, the result are given in table .

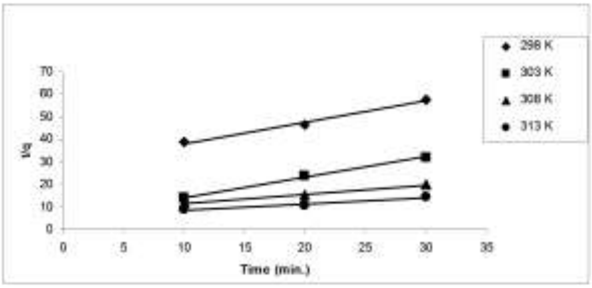


Fig. 8: second order reaction.

Table (4): rate constant of second order reaction.

Temperature (K)	K (g/mg min.)	R^2
298	0.9475	0.9891
303	0.9135	0.9978
308	0.399	0.9922
313	0.282	0.9787

From table (4), it can be concluded that the process of adsorption Orange (G) on the bentonite is best fitted to pseudo (First Order) kinetics since the R^2 value matched very well.

Mass transfer model :

The intra – particle diffusion varies with square root of time(11) as shown below:

$$q_t = K_{id} t^{0.5} \quad \ldots\ldots\ldots\ldots (10)$$

Where q_t is the amount of adsorbed at time t (mg/g), t the time (min.) and K_{id} is the intra – particle diffusion coefficient (mg/g. min$^{0.5}$).

The K_{id} value was determined from the slope of linear plot between q_t versus $t^{0.5}$ Fig. And it found to be 7.9995 (mg/g. min.$^{0.5}$).

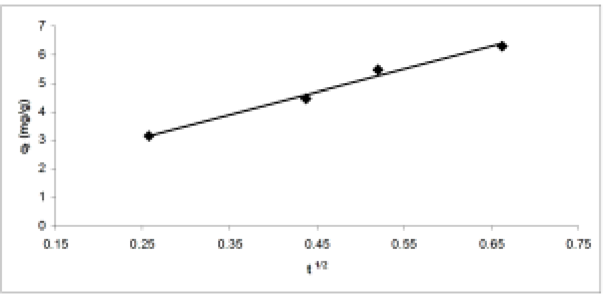


Fig. 9: Mass transfer model.

Conclusion:

From the presented study, it may be concluded that the removal of Orange (G) from aqueous solutions by adsorption on bentonite has been found to be useful for controlling the water pollution due to dye. The adsorption data fitted well to the Freundlich adsorption isotherm and the result of the kinetic studies show that the adsorption of Orange (G) onto bentonite can be obey with the pseudo first order kinetic model. The decrease in percentage of adsorption with increase in temperature indicates that the process is exothermic in nature and so low temperature favor the adsorption process.

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ازالة الصبغة البرتقالية من المحاليل المائية بواسطة امتزازها على البنتونايت

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الملخص

تم دراسة امتزاز الصبغة البرتقالية من المحاليل المائية على سطح طبقة البنتونايت بطريقة الوجبة مع الاخذ بعين الاعتبار زمن التماس والتركيز واستخدمت مطيافية الأشعة المرئية/فوق البنفسجية في تعيين كميات الامتزاز. كما تم استخدام معادلة المرتبة الاولى ومعادلة المرتبة الثانية لوصف حركية التفاعل وحساب قيمة ثابت سرعة التفاعل. اوضحت النتائج ان التفاعل يخضع لمعادلة المرتبة الاولى. استخدمت معادلتي لانكماير وفريندليش لوصف ايزوثيرمات الامتزاز وتعيين ثوابت لانكماير وفريندليش. تم حساب المتغيرات الثرموديناميكية مثل ΔG و ΔH و ΔS وقد اوضحت قيم ΔG و ΔH ان العملية باعثة للحرارة.