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A kinetic & Thermodynamic study of carthmus tinctorious & nigrocine dyes from aqueous solution by modified montmorilonite

دراسه حركيه وثرموديناميكيه لازالة صبغتي الكارثموس تكتوريوس والنكروسين من محاليلها المائيه باستعمال المونتموريلونايت المعدل

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Abstract:

The results of this work included the study of the adsorption of carthmus tinctorious & nigrocine dyes from its water solutions on the modified montmorilonite surface using UV spectroscopy. The results showed that the isotherms of dyes are similar to the Giles classification type (S1,L3) also study of the temperature change within the experimental range (303-333K) in the process of adsorption of dyes on the surface of the clay, and carried out the study of adsorption of the dye (carthmus tinctorious) it decreased by increasing the temperature while the dye (nigrocine) increase by increasing the temperature, and study the effect of acidity on the capacity Adsorption and the thermodynamic functions were calculated to process of adsorption, containing Gypsum free energy and Entropy and Enthalpy

الخلاصه :

تضمن موضوع البحث دراسة ايزوثيرمات الامتزاز لصبغتي (carthmus tinctorious & nigrocine) من محاليلها المائيه على سطح المونتموريلونايت المعدل باستعمال مطياف الاشعه المرئيه-فوق البنفسجيه ، وضحت النتائج ان ايزوثيرمات الصبغات مشابهه لايزوثيرمات فرندلش من نوع (S1,L3)وفق تصنيف جيلز ، كما درس تاثير تغير درجة الحراره ضمن المدى التجريبي (K333-303) في عملية امتزاز الصبغات على سطح الطين ، واجري دراسة امتزاز صبغة(carthmus tinctorious) انها تقل بزيادة درجة الحراره بينما صبغة (nigrocine) تزداد بزيادة درجة الحراره ، كما تمت دراسة تاثير الداله الحامضيه على سعة الامتزاز وتم حساب الدوال الثرموديناميكيه لعملية الامتزاز والمتضمنه طاقة جبس الحره والانتروبي والانثالبي .

Introduction:

Adsorption can be defined as a process that collects molecules, atoms or ions of a substance called adsorbent substance on the surface of a solid or liquid substance called the adsorbent surface. In 1918, Langmuir proposed an equation to explain the phenomenon of adsorption based on the assumptions of the theory that adsorption is of one layer, excluding interactions between the adsorbed particles and the surface are excluded. The amount of adsorbent is increased rapidly at the beginning of adsorption and then gradually stabilized due to thermal irritation leading to what is known as adsorption , This is the opposite process of adsorption.

When the speed of adsorption is equal to the speed of absorption R_d, the process is in equilibrium, and if encode the covered part of the surface with the particles of the adsorbent matter relative to the total surface of the substance adsorbed by (Θ), the uncoated part at any time shall be (1-Θ), thus the speed of adsorption depends either on pressure P in the case of adsorption of gases on solid materials or on the concentration of solution at equilibrium (Ce) in the case of adsorption of solution on solid materials and on the number of active sites not covered by N (1-Θ). N is the total number of active sites. If K_a is the constant speed of adsorption and K_d is the constant velocity of absorption[1,2],

$R_a = K_a$ PN (1-Θ) .... (1)

$R_d = K_d$ N .... (2)

K_d PN (1-Θ) = K_d N .... (3)

$\Theta = \frac{a\,P}{1+a\,P}$ …………(4)

$a = \frac{Ka}{Kd}$…………(5)

Equation (4) is called Langmuir equation for adsorption of gases on surfaces of solid materials and because the amount adsorbed by the ratio of the unit area or the mass of the adsorbent material corresponds to the covered part of the surface, [1]

$Y = K\Theta = \frac{KaP}{1+aP} = \frac{KP}{1+aP}$ ……….(6)

K = Ka…………(7)

Where (a, K) is the Langmuir constants.

Equation (6) can be written for adsorption of solution as follows[2]:

$Qe = \frac{K\,Ce}{1+a\,Ce}$ …………(8)

(Qe) represents the amount of adsorbent and in order of equation (6) we obtain:

$\frac{Ce}{Qe} = \frac{1}{K} + \frac{a}{K}$ Ce …………(9)

It graph ($\frac{Ce}{Qe}$) versus (Ce) obtained for the slop of straight line ($\frac{a}{K}$) and ($\frac{1}{K}$) and the slope and intersection values can be calculated for the Langmuir constants (a, K).

The Frundlich equation is the most important equations used in the case of adsorption of the solution, as the change in the amount of adsorbed in the unit area or mass of the adsorb substance with the concentration of equilibrium[2]:

$Qe = K_f\,Ce^{1/n}$ ……………(10)

(n, K_f) is experimental Frundlich constants , these parameters are based on the nature of the adsorbed substance, the surface adsorbed and the temperature, and can be calculated by taking logarithm equation (8): -

Log Qe = Log K_f + $\frac{1}{n}$ Log Ce ……..(11)

And graph(Log Qe) versus (Log Ce) are obtained in a straight line and his slop ($\frac{1}{n}$), which is a measure of adsorption intensity, and the(log K_f) is a measure of adsorption capacity.

The adsorption process is automatic with a decrease in the degree of freedom of the adsorbed substance expressed thermodynamically by the decrease of the entropy (ΔS) This process took place under the conditions of Isomeric and according to the relationship thermodynamic thermal[3]: -

$\Delta G = \Delta H - T\Delta S$ .... (12)

The slope of the linear relationship below can be calculated from the value (ΔH) of the graph (log Xm) versus the inverse temperature and based on the equation of the Vant Hoff-Errhenius[3] :

$\text{Log } X_m = \frac{-\Delta H}{2.303\,RT} + C$…………(13)

Here: -

Log Xm: The largest logarithmic mass adsorbent (mg / g).

Con: Van Hoof equation constant.

T: Temperature.

R: The general constant of gases.

It is also possible to obtain the value of free energy from the relationship [1]: -

$\Delta G = -RT\ Lin(\frac{Qe}{Ce})$…………(14)

where

Ce: Concentration at equilibrium (mg / L).

Qe: Amount of adsorbent substance (mg / g).

The aim of this study was to remove the dyes used from their aqueous solutions on the modified montmorilonite surface using optical absorption technology.

Experimental part :-

Used apparatuses and chemicals: -

1 - U.V. visible recording spectrophotometer type shimadzu (U.V., 700), Japan.
2. Furnace memmert , W.Germany
3. Electronic Balance Sartorius , W.Germany
4- Electric Heater with Megnetic stirrer, Hof plate, LMS-100, Korea
5. pH-meter Instrument, Portugal
6 - Water bath equipped with electric vibrator and temperature controlled Shaking inductor, GCA , precision scientific Chicago, USA.

All the chemicals used in this research were of a high degree of purity.

Procedures: -

Bentonite is an one of the samples that used as raw materials in the industry, The main metal component in bentonite and is the most important sources for the obtaining of mineral materials and the importance of this clay to its chemical composition and one of the basic components of soil
With a total of other silica species. The chemical analysis of the clay showed that it was a mixture of various hexane oxides. It was also found contain a high percentage of silica (56%), alumina (15%) and other oxides, as in Table [2]

Table (1) Percentage of bentonite clay components used

constituent	wt %
SiO_2	56.77
Al_2O_3	15.67
Fe_2O_3	5.12
CaO	4.48
MgO	3.42
Na_2O_3	1.11
K_2O	0.6
P_2O_5	0.65
SO_3	0.59
Cl	0.57
C	0.56
Loss on Igination	0.49

Modification of montormonite clay: Modified clay by wash with a few times with distilled water to remove it from the impurities, then dry in oven (50-100) °C for (24 hours), then crush to a fine powder and then sieve with a particle size (75μm).

The natural montmorilonite clay was added (1wt %) to distilled water (100 ml) using a magnetic mixer (350 rpm) and temperature (60 °C) for (15 min) and then gradually added to the bentonite, Obtained a homogeneous solution in the form of thin, high-viscous clay, where PVA is adsorbed on the surface of the particles to improve the binding. The material was then dried and crushed and seived with a particle size (75 µm) to be used in the current research experiments[2].

Preparation of dyes:

Preparation of Carthmus tinctorious dye:

The process of grinding the flowers of the plant using an electric mixer was then homogenized with deionized water by 1 g: 5 ml (leaves - distilled water) using the electric vibrator for (15 min) and then leave the mixture for (24 hours). Then filtered by sterile medical , the centrifugal filtration process was carried out at a speed of (3000 rpm) for 15 min, The leachate was taken and distributed in sterile glass bottles, which was placed in an electric oven (40 °C) to dry the extract, The material was then weighed from the drying process to prepare six concentrations (5-30) mg/L for this study, and the following figure(1) shows the chemical composition of this dye [3].

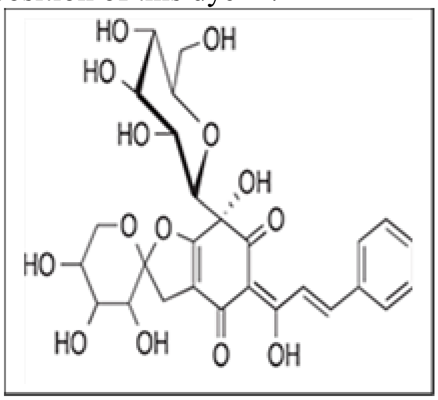


Fig (1) Chemical structure of carthmus tinctorious

Preparation of nigrocine dye:

Prepare of (10 ml) of six different concentrations (5,10,15,20,25,30 mg / l) were mixed with (0.1 g) from clay used and temperature constant in the water bath device for (60 min) and the following figure(2) Shows the chemical composition of this dye.

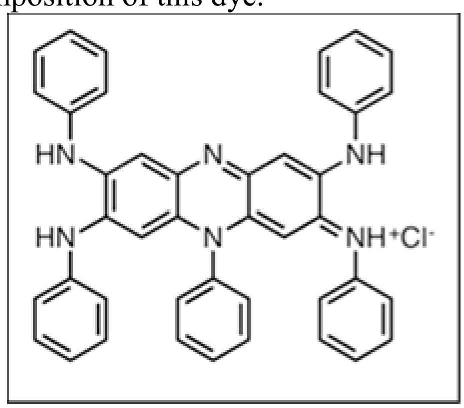


Fig (2) Chemical structure of nigrocine

Contact time : To determine the time required for the equilibrium between the solvent surface and the adsorbent material, prepared of ten flasks were added (0.1 g) of bentonite (surface) and (20 mg/L) of the dye solution,and these flasks were put in a water bath with vibrating and temperature control at (303 K) ,and the analyzed at different time intervals to determine the change in concentration over time. The found that the best time for equilibrium is 30 min ,this result was agreement with results in references [4].

Determination of Isotherm Adsorption:

In order to find the of isotherm adsorption, several concentrates (5-30) ppm were prepared for each dye and placed in contact with (0.1 g) of montmorilonite in a conical flask equipped with a tight seal and placed in a water bath with a temperature control at (303 K), The material was then cooled and placed in a test tube then enter in a centrifuge to separate the surface from the dye, The amount of the absorbent substance dyes was calculated as follows[5]:

Where:

$$Qe = \frac{(C_o - Ce)Vsol}{M} \quad ....(15)$$

Where

Qe: Amount of adsorbent substance (mg / g).

C: Primary concentration of the adsorbent substance (mg / L).

Ce: Concentration at equilibrium for solution of adsorbent substance (mg / L).

Vsol: The total volume of the solution of the adsorbent substance (L).

M: weight of the adsorbent substance (g).

Effect of temperature in adsorption process : A study was conducted showing the effect of temperature in adsorption of carthmus tinctorious and negrosine on the modified montmorilonite surface in the experimental thermal range (303-333 K) and showed the forms of the adsorption isotherm of these degrees [6].

Effect of pH: On adsorption process ,the effect of the acidic function on adsorption of the used dyes on the modified montmorilonite surface was evaluated at different pH values (pH at ranges = 3,7,10), [7].

Results and discussion :

As shown in Figure (3), the adsorption of the two dyes of their aqueous solutions on the surface of the montmorilonite mortar at (303 K), according to the Giles classification and compared to the general form of isotherm of adsorption, was found to be of the type (S1, L3),also this isotherm due to interpreter adsorbent substance with the surface of the adsorption is made through the types of forces depend on the substance adsorbent and the material adsorbent as the particles are in clusters or rows of vertical on the surface and this is confirmed by the form of increasing isotherm increase concentration of equilibrium.

The Frundlich adsorption isotherm of the dyes used on the surface of the clay, the values of (K_f ,n) were calculated from plote. The table (2) shows that the value of (Log K_f ,n) for the dye of nigrocine and carthmus ,this indicates an increase in the adsorption capacity and the carthmus dye of the surface over the second dye [8].

The effect of temperature in the process of adsorption of dyes on the surface of the montmorilonite clay was that found adsorption is increased at high temperature of the dye of nigrocine, that the process of heat absorption (Endothermic) and this gives an indication of the existence absorption of particles adsorbed inside the pores and increase the speed of spread with increase of temperature ,thus in carthmus dye that adsorption process is (Exothermic), which increases the temperature of the dsorption to decrease of absorbtion, because the particles adsorbed on the surface less rapidly spread, resulting in a decrease in the mutual interaction between the dye and the surface and in figure (5) and (6) .

Figure 7 explains the time required for the equilibrium of carthmus and nigrocine. The times required for the equilibrium of nigrocine and carthmus (70min) and (40min) respectively , The decrease in the equilibrium time is due to the lack of active sites prepared for dye binding In addition to a change in the capacity of the return pores of clay.

The effect of the pH in the adsorption of dyes and the observed effect of the acidic effect was different on the dyes. Hydrogen ion affects on the ionization of the dye and the surface of the adsorbent and the figure (8) and (9) shows the isotherm of adsorption and showed the increase of the quantity of the adsorbent substance with Acid-resistant for dyes in the following order [9]

Carthmus dye , pH = 7 > 3 > 10

Nigrocine dyes , pH = 10 > 3 > 7

This is due to increased adsorption of the basic medium to increase the efficiency of the acidic groups on surface, while the effectiveness of the basic groups decreases and the chances of electrostatic interference increase, In the acid medium, the tendency of the dye to attach to the surface is greater than that of the solvent molecules.

The linear relationship was obtained as in Fig. 8 and its value ΔH was obtained from equation (12) and entropy value from equation (10) and the table(3) express the value of (ΔH,ΔS,ΔG) at(303 K) [10].

Conclusions:

1 - The figure of isotherms obtained from the adsorption of dyes studied on the surface of the montmorilonite is followed by Frundlich and Langmuir equivalent of the type (S1, L3) according to Giles classification for carthmus and nigrocine respectively.

2 - The study showed the effect of temperature in the dyes for some of them are adsorbed by heat absorption (adsorption and absorption) and some heat emitter depending on the quality of the dye, while the value of ΔG negative study indicated that adsorption occurs automatically on the surface.

3- The study showed the effect of the pH in adsorption of the dyes on the surface. The carthmus dye had a adsorption capacity in pH = 7while nigrocine was adsorbed in pH = 10

Table (2) Frundlich constants for absorbtion

Dyes	Frundlich constants	
	n	Log K
Nigrosine	0.4203	0.61
Carthmus	0.4302	0.72

Table (3) Thermo values for dyes at (303 K)

Dyes	ΔH ($K.J.mol^{-1}$)	ΔG ($K.J.mol^{-1}$)	ΔS ($J.mol^{-1}$)
Nigrosine	+1.8	-8.2	+63.7
Carthmus	+2.595	-11.3	+27.9

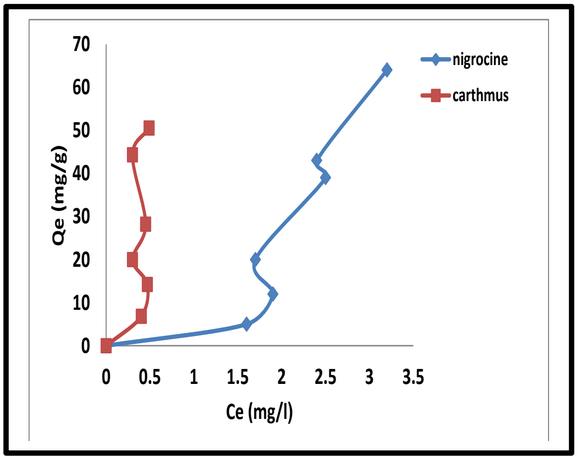
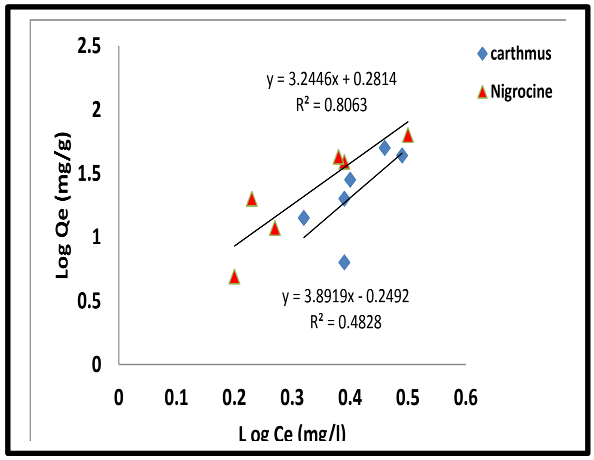
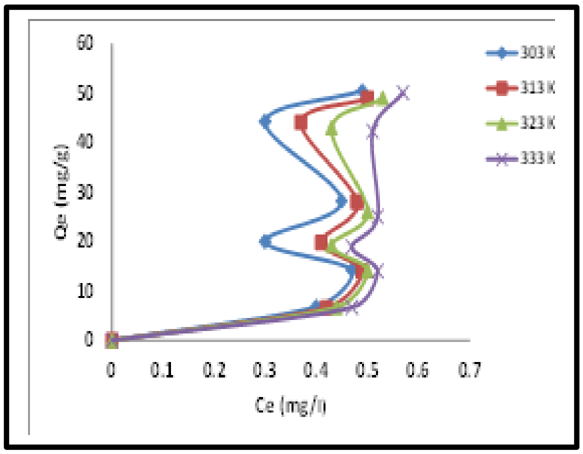


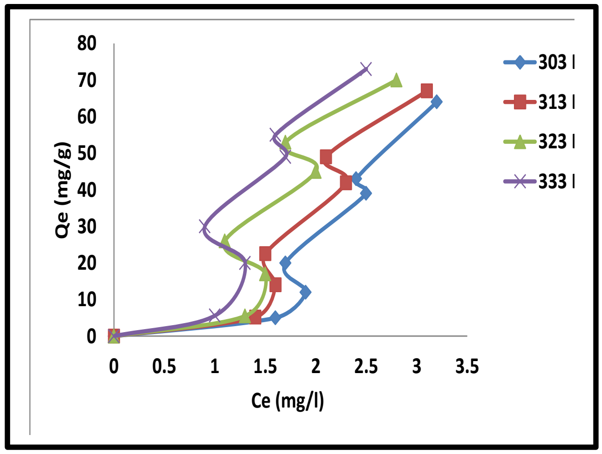
Fig (3) Adsorbtion isotherm of dyes with modified montmorilonite clay



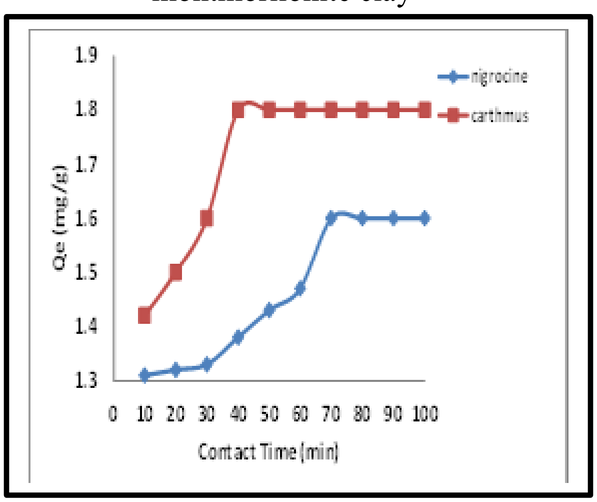
Fig(4)Frindlish adsorbtion isotherm of dyes with modified montmorilonite clay



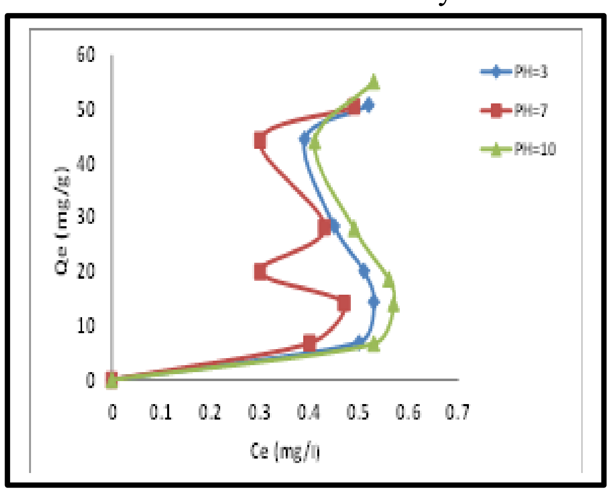
Fig(5) Effect of temperature on the adsorption capacity of carthmus dye with modified montmorilonite clay



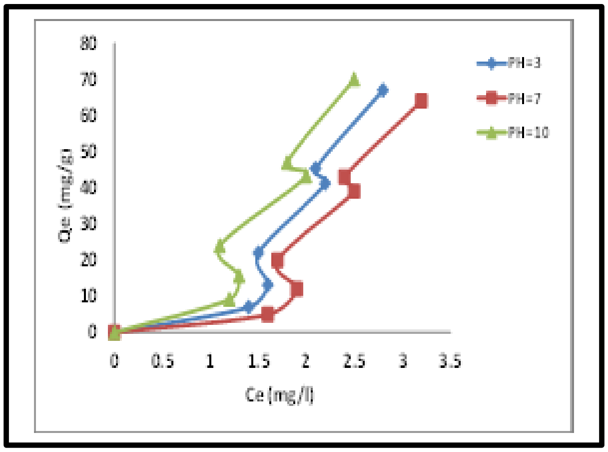
Fig(6) Effect of temperature on the adsorption capacity of nigrosine dye with modified montmorilonite clay



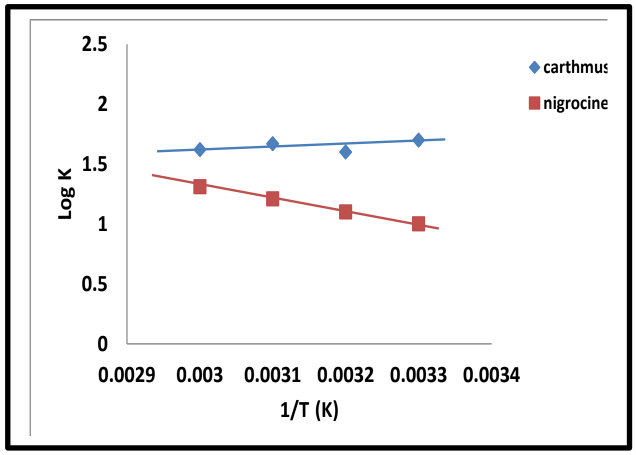
Fig(7)Adsorption capacity against contact time of dyes with modified montmorilonite clay



Fig(8)Effect of PH on the adsorption of carthmus dye with modified montmorilonite



Fig(9) Effect of PH on the adsorption of nigrocine dye with modified montmorilonite clay



Fig(10)Temperature dependence of the adsorption of dyes with modified montmorilonite clay

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