

Removal of Leshman's stain from aqueous solution By adsorption on modified kaolin and kaolin clays in Batch Techniques

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Abstract:-

Kaolin clay and Modified clay (Polymer of kaolin- poly vinyl Alcohol) as an adsorbent for the removal of textile dye from aqueous solution .

The aim of this study was to search for selective active surface in adsorption of Leshman's stain .The adsorption of dye on clays were found to be dependent contact time, dye concentration, initial pH , and amount of adsorbent. The removal data of Modified clay were fitted on Freundilch and Langmuir adsorption isotherm equations., While adsorption isotherm on Kaolin clay was fitted on Freundilch isotherm only .The adsorption of Leshman's stain on Modified clay was much higher than that on Kaolin clay . The adsorption isotherm data will employ to Calculate the thermodynamic parameters like (ΔG) Gibb s free,(ΔH)change in enthalpy and (ΔS) entropy .The values of percent removal and K_D for dye by modified clay and Kaolin clay were also calculated at temperatures ranging from (298-328 K)

Key words:- Modified clay, polymer , Kaolin clay ,dye ,Adsorption isotherms. Thermodynamics of adsorption

Introduction:-

Many industries like plastics ,paper, textile and cosmetics use dyes in their products .these dyes are common water pollutants and they may be frequently found in trace quantities in industrial wastewater .In addition , many dyes were difficult to degrade due to their complex aromatic structure and they tend to persist in the environment and creating serious water quality and public health problems .Several physical and chemical techniques including coagulation, precipitation, filtration, Oxidation, membranes ,reverse osmosis have been used for the treatment of dye^(1,2),but all of these methods suffer from one or other limitations ,and none of them were successful for completely removing the color from wastewater .These dyes can be partially or totally purified by adsorption process .Among the adsorbents normally used in this process ,clay has been an important material due to its good sorption capacity such as Kaolin clay⁽³⁾, modified clay with Urea –Formaldehyde polymer ⁽⁴⁾, natural zeolite ⁽⁵⁾ and clay fixed on polymers ⁽⁶⁾ , red mud⁽⁷⁾were successfully employ for removal of dyes from aqueous solutions . The most important clay mineral is kaolinite [$A_1_2O_3, 2 SiO_2, 2H_2O$] which is the main composed of kaolinite clay⁽⁸⁾.Table .1.

Although kaolinite exhibits the least exchangeability among clay minerals , several studies have confirmed the potential of natural kaolinite for the adsorption of metal ions from solution^(9,10) .

Polymer of kaolin- poly vinyl Alcohol is the commercial name of modified clay⁽¹¹⁾, is an amorphous synthetic on of kaolin and poly vinyl Alcohol produced under carefully controlled conditions in order to achieve specific adsorbing properties, modified clays are odorless tasteless, free flowing grayish white powders practically, insoluble in water, organic solvents mineral acids and solutions of alkali hydroxides.

In this work , the use of modified and unmodified Kaolin clays as adsorbent agents was studied .the removal of certain water- Soluble dye, namely Eosin methylen blue (Leshman's stain)as an organic pollutant was the main goal of the study .

Table/ 1.The Chemical analysis of Duekhla kaolinite

| Oxides | % | Oxides | % |
|--------------------------------|-------|-------------------|-------|
| SiO ₂ | 52.35 | MgO | 1.11 |
| Al ₂ O ₃ | 43.02 | SO ₃ | 1.05 |
| FeO ₃ | 1.31 | Na ₂ O | - |
| TiO ₃ | 0.12 | K ₂ O | - |
| CaO | 1.04 | L.O.I | 12.54 |

Materials and Methods

Materials and Apparatus:-

Adsorbates: dye were used as adsorbates:

Eiosn methylen blue (Leshman's stain) it was used as commercial salts without purification and were supplied by B.D.H .Adsorbents: Kaolinite was obtained from the general Company for Geological survey and mining, Duekhla, Iraq, poly vinyl alcohol was supplied by, AG,CH-9470 Fluka Apparatus: shimadzu UV-Vis 1700 digital double beam recording spectrophotometer using (1) cm glass cells.

-A digital pH meter. 720 WTW 82362 was used.

Thermic treatment of the clay

Kaolinite sample (50 Mm) was washed with an excess amount of distilled water. It was treated in an oven with temperatures varying from (50 to 100 c°) for 24 hours, and at 100 c° at the heating time 7 hours ground then sieved by 50 Mm sieve. The particles under 50 Mm are used in further experiment.

Modified clay Manufacturing

Poly vinyl Alcohol solution⁽¹²⁾ were mixed with (100 ml) of distilled water in container with magnetic stirrer at 85c° for 30 min.

It was sopened in Hcl solution of pH=5. then it was mixed with clay and heated at nominal softening temperatures of 200c° for two hours in an oven, sieved by 50 Mm sieve, the ratio mass of clay/ polymer was (2/3).

General Procedure

The adsorption isotherms have been determined by mixing of dyes solution (20 ml) of known initial concentration (5-60 p.pm) and varied amounts of adsorbents (0.05-0.2gm) were placed into volumetric flasks. Analytical determinations of dye in solution after reached equilibrium (30 min at 25c°) were performed by means of ashimadzu

TRUV 754 spectro photometer. Optical densities were determined at (516 nm) Fig.1 for Leshman's stain, which corresponds to the maximum absorption peak of dyes. The adsorption capacity Q_e was calculated from the difference between the initial and equilibrium adsorbate (dye) concentration which as follows:

$$Q_e = \frac{(C_o - C_e) V_{sol}}{M} \dots\dots\dots (1)$$

Where: Q_e is the adsorption capacity ($mg.g^{-1}$), C_o and C_e are the initial and equilibrium Concentration ($mg. L^{-1}$) respectively, M is the adsorbent dosage (g) and V is the solution Volume (L). A plot of equilibrium dye loading Q_e , against the residual concentration of dyes remaining in the solution C_e is shown in figure (2). It is evident that dyes can generally be easily removed from the solution by modified clay and unmodified Kaolin clays particles and reducing the particle size will increase Q_e for high values of initial dye Concentration C_o .

The adsorption Capacity was determined with the effects of contact time, initial concentration of dye solution and pH, adsorbent dosage, temperature, The equilibrium concentration, adsorption capacity at equilibrium were determined to fit in the adsorption isotherms.

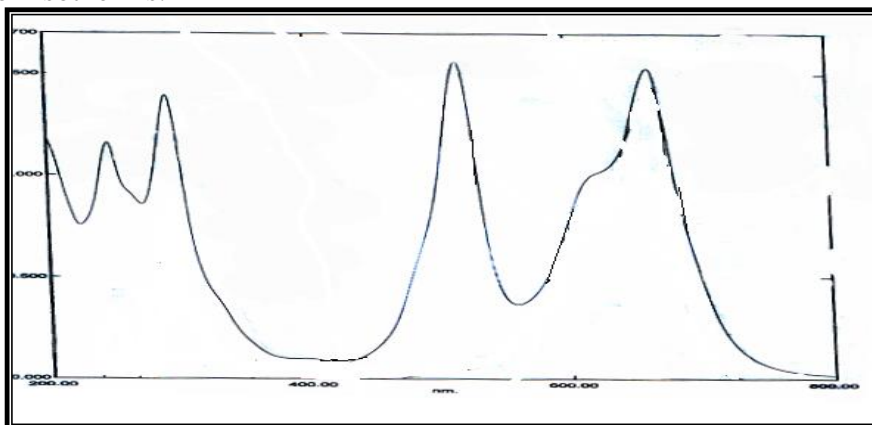


Fig:1-Spectrum of Leshman's stain

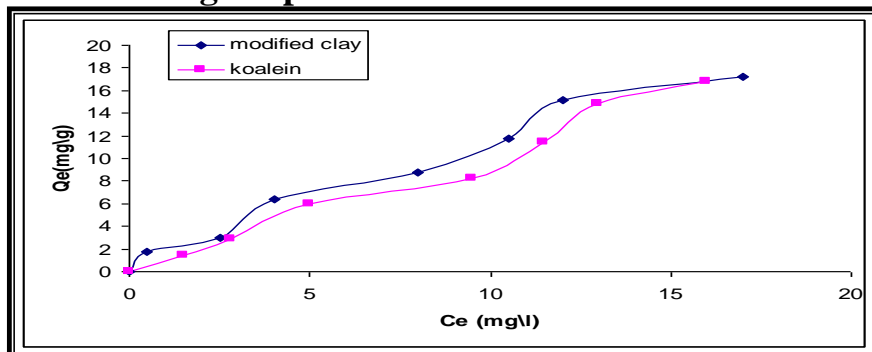


Fig: 2-Adsorption isotherm of Leshman's stain by modified and Unmodified Kaolin clays at pH(7)

Contact time

For the determination of effect of time for the adsorption of Leshman's stain on modified and unmodified Kaolin clays ,the optimum amount of adsorbent (0.05g)was added in flasks with 20ml of optimum concentration(30p.p.m) of dye solution for different intervals of time . was conducted through batch experiments to achieve the equilibrium as shown in Fig.3 The mechanism of colour removal Can be described in migration of the dye molecule from the solution to the adsorbents particle and diffusion through the surface. The results showed that the equilibrium time was reached with in 30 min of operation for modified and unmodified Kaolin clays. The adsorption capacity was constant there after for case of all dyes observed.

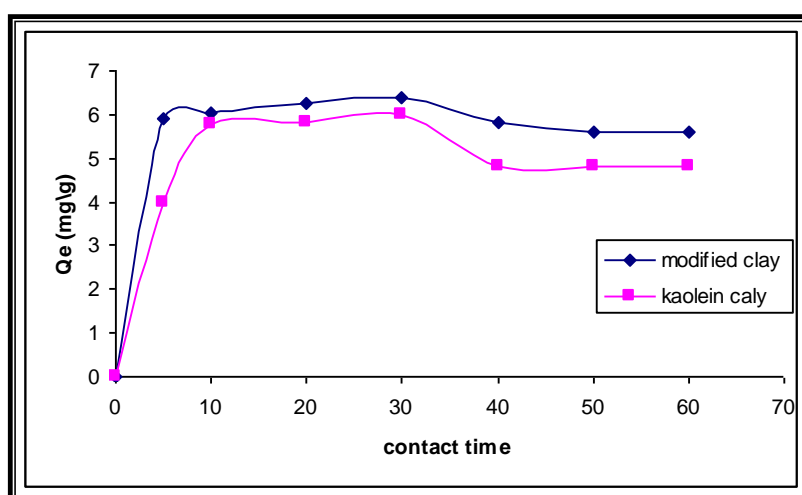


Fig:3 Adsorption capacity against contact time of Leshman's stain with modified and unmodified Kaolin clays at pH(7) .

Results and Discussion

Adsorption isotherm

Many theories of adsorption were put forward to explain the phenomena of adsorption . Langmuir and Freundlich adsorption isotherm are some of them . The well known Langmuir equation(2) is ⁽¹³⁾ given below :

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{a}{C_e} \dots\dots (2)$$

Where (a) represents a practical Limiting adsorption Capacity when the surface is fully Covered with a monolayer of adsorbate. The constant (b) is the equilibrium adsorption constant which related to the affinity of the binding sites Table (2) Fig (4).

The applicability of these equations on the adsorbent- adsorbate (solute) system assume of the formation of one layer of adsorbate molecules on the surface while the Freundlich adsorption isotherm (equation) consider heterogeneity of the surface and the formation of more than one layer is probable.

The linear form of Freundlich isotherm is:

$$\text{Log } Q_e = \text{Log } K_f + \frac{1}{n} \text{Log } C_e \dots (2)$$

Where K_f and n are Freundlich Constants characteristics of the system, including the adsorption capacity and the adsorption intensity, respectively⁽¹⁴⁻¹⁵⁾, Table.2. Fig.5. The values showed that the equilibrium data in modified clay fitted well to both the Freundlich and Langmuir isotherm in the studied concentration ranges .As seen that the Langmuir model is better than the Freundlich model in simulation of the adsorption isotherm. Based on the correlation coefficients (R^2), While adsorption isotherm on Kaolin clay was fitted on Freundilch isotherm only Table.2. many outhers have used these isotherms to evaluated the adsorption capacity by different dyes^(16,17). The adsorption constants evaluated from the isotherms with correlation coefficient are shown in Table (2) very high regression coefficients (0.996-0.964) were found for dye. The percent adsorption (%) and distribution ratio (kd) of dye by adsorbents were calculated Table.3. For Leshman's stain as adsorbate ,the maximum and minimum adsorption values were obtained at concentrations of 5 p.p.m and 60 p.p.m respectively. While the maximum values for unmodified Kaolin clays 20 p.p.m and minimum values at 30 p.p.m at 298 K. The difference in % adsorption of this dye on the surface of Modified clay may be due to the presence of more or less irregular and defective edges. These play significant role on the adsorption phenomenon . These edges strike the unsaturated part of the dyes and accelerate the removal of dye molecules ⁽¹⁸⁾ These types of observations were also observed for the adsorption of Fast green on the surface of Azodiracht indicia leaf powder⁽¹⁹⁾ .

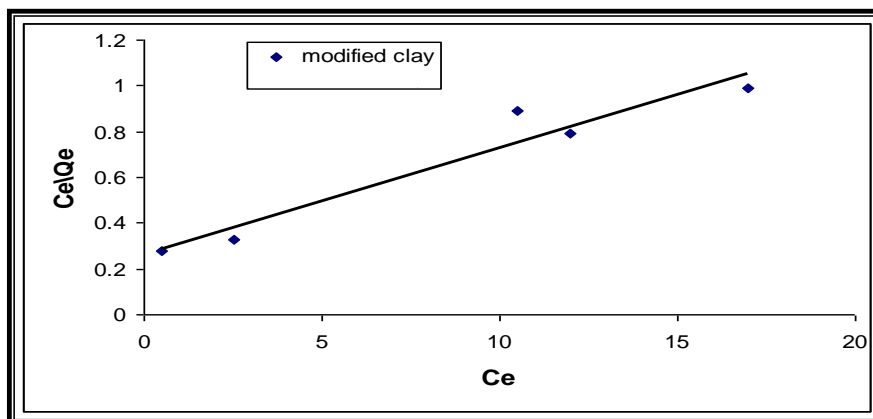


Fig :4 Langmuir adsorption isotherm of Leshman's stain with modified Kaolin clay at pH(7)

Table/2- Langmuir and Freundlich constants for dyes in aqueous solution using modified and unmodified Kaolin clays

| Adsorbent | Leshman's stain | | | | | |
|---------------|-----------------|-------|-------|----------------|------|-----|
| | Freundlich con. | | | Langmuir con. | | |
| | R ² | n | Kf | R ² | a | b |
| Modified Clay | 0.986 | 1.564 | 2.705 | 0.938 | 3.84 | 5.6 |
| Kaolin clay | 0.983 | 0.999 | 0.997 | - | - | - |

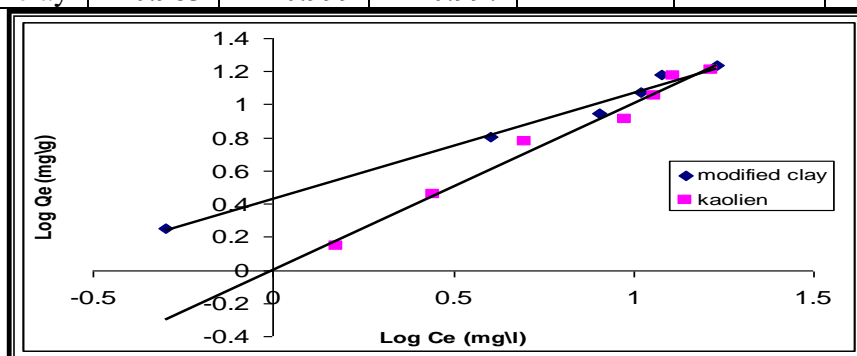


Fig :5 -Freundlich adsorption isotherm of Leshman's stain with modified and unmodified Kaolin clays at pH(7).

Table/3-Kd values and % adsorption of dyes in aqueous solution using modified and unmodified Kaolin clays

| dyes conc. p.p.m | modified Kaolin clay | | | | | unmodified Kaolin clay | | | | |
|------------------|----------------------|-------|-------|------|-----|------------------------|-------|-------|------|-----|
| | Removal (%) | | | | Kd | Removal (%) | | | | Kd |
| | K 298 | 308 K | 318 K | 328K | | K 298 | 308 K | 318 K | 328K | |
| 5 | 90 | 80 | 60 | 50 | 144 | 70 | 60 | 40 | 30 | 112 |
| 10 | 75 | 70 | 60 | 50 | 120 | 72 | 70 | 50 | 40 | 115 |
| 20 | 80 | 75 | 64 | 55 | 128 | 75 | 71 | 60 | 55 | 120 |
| 30 | 73 | 70 | 66 | 58 | 117 | 68 | 66 | 60 | 56 | 109 |
| 40 | 74 | 72.5 | 68 | 66 | 117 | 71 | 70 | 68 | 65 | 114 |
| 50 | 76 | 73 | 72 | 68 | 122 | 74 | 72 | 68 | 65 | 118 |
| 60 | 72 | 70 | 66 | 65 | 115 | 73 | 66 | 65 | 61 | 112 |

Effect of pH

The influence of the initial pH of the solution on the adsorption Capacity of adsorbates by clays appears to be much more efficient at lower pH is shown in Fig. 6. It may be related to the presence of excess H^+ ions competing with protonate amine groups of dye molecules to form groups $-NH_3^+$, It is also possible that the surface properties of clays are depended on pH of the solution . A similar trend was observed by Kaolinite⁽²⁰⁾ adsorbent .

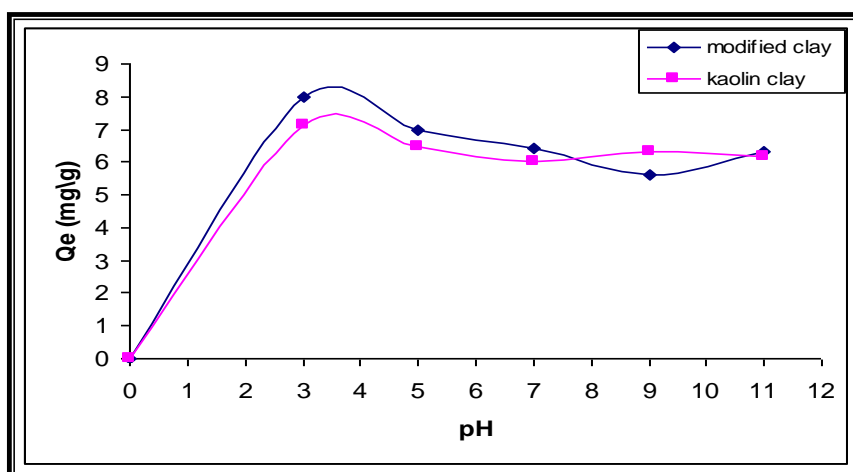


Fig: 6-Removal of colour from aqueous solution of Leshman's stain with pH of solution.

Effect of temperature

In order to fully understand the nature of adsorption ,the thermodynamic studies play an important role. removal of Leshman's stain using modified and unmodified Kaolin clays has been studied at 298to 328K. determine the adsorption isotherms and thermodynamic parameters, which is presented in Fig. .8.9. thermodynamic parameters, i.e free energy (ΔG) enthalpy (ΔH) and entropy (ΔS). changes were also calculated using Eqs. (4-6)⁽²²⁾ and are given in Table (4) .

$$\Delta G = -RT \ln K \dots\dots\dots (4)$$

$$\text{Log} X_m = \frac{\Delta H}{2.303RT} + \text{Con.} \dots\dots\dots (5)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \dots\dots\dots (6)$$

According to equation (5),the mean value of the enthalpy change due do the adsorption of Leshman's stain by modified and unmodified Kaolin clays over temperature range studied can be determined graphically by the linear plotting of Log X_m against $1/T$ Fig.7.

The negative values of ΔG indicate the feasibility and spontaneous nature for dye adsorption on modified and unmodified Kaolin clays. While the values of (ΔH) was found to be negative (Table.4). The negative values confirm the exothermic nature of adsorption^(24,25), many variable such as the molecular volume of the dye its planarity and its ability to bind to the adsorbent, among others, Can effect the degree of adsorption.

The adsorption capacity on modified clay is higher than on unmodified Kaolin clay. This difference most be related to higher affinity of Leshman's stain for the modified clay than Kaolin clay. Also this may be due to a tendency for the dye molecule to escape from the solid phase of adsorbent surface to the liquid phase of dye with an increase in temperature of solution^(26,27).

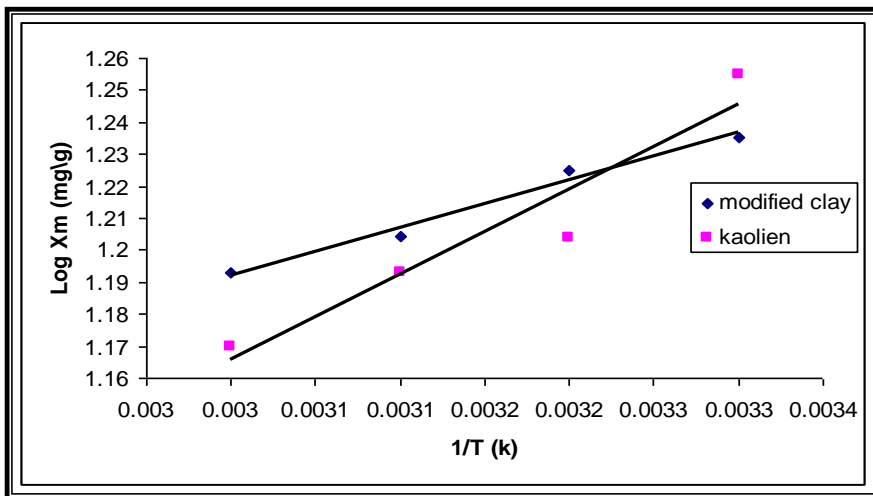


Fig 7-Relationship between the Log Xm and 1/Tof dye with modified and unmodified Kaolin clays as an adsorb .

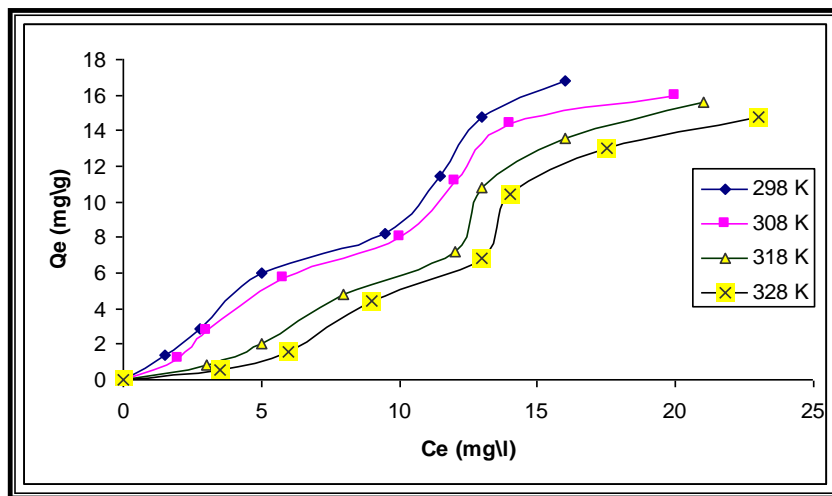


Fig: 8-Effect of temperature on the adsorption capacity of Leshman's stain with modified Kaolin clay at pH=7.

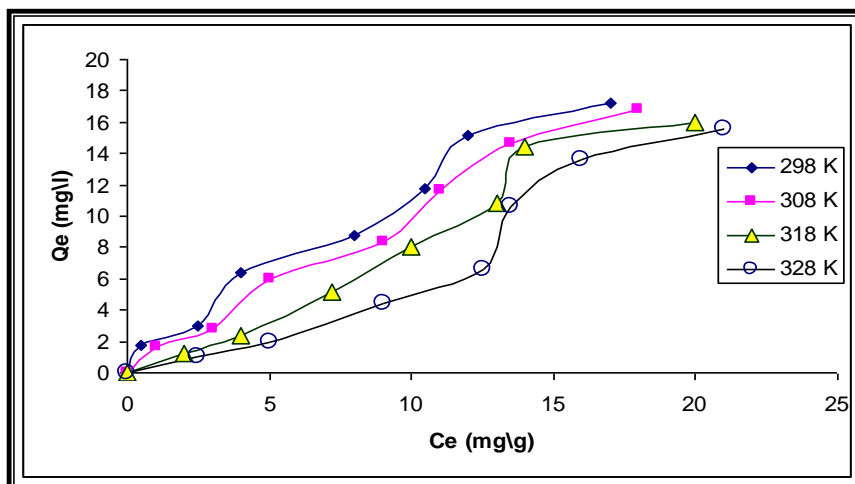


Fig: 9-Effect of temperature on the adsorption capacity of Leshman's stain with unmodified Kaolin clay at pH=7.

Table/4-Thermodynamic values of dyes in aqueous solution using modified and unmodified Kaolin clay as an adsorbents .

| Adsorbent | ΔH KJ.mol ⁻¹ | ΔG KJ. mol ⁻¹ | ΔS J.mol ⁻¹ .k ⁻¹ | Cos. |
|------------------------|---------------------------------|----------------------------------|---|------|
| modified Kaolin clay | -2.83 | 0.028 | -9.4 | 0.74 |
| unmodified Kaolin clay | -5.08 | -5.78 | 2.33 | 0.36 |

Conclusion

To produce modified clay as a sorbent for removing dyes and other toxicants from low quality water, Unusual treatments depend on thermal transformation and acid activation to increase the exchangeability properties of kaolinite. The Obtained results showed that the porous of collapsed crystalline structure of this modified kaolinite can adsorb a large amount of pollutants dyes such as Leshman's stain from wastewater. A comparison of relative removing values revealed that the removing on modified kaolinite is more favored than kaolin clay. Some advantage in using the pellets of P.V.A- clay with regard to the original adsorbent were noted. Such as sedimentation and separation in static process happened quickly and easily, without need of flocculent addition and/or use of centrifugation.

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ازالة صبغة لشمان من المحاليل المائية بواسطة امتزازها على السطوح اطيان
الكاولين المعالج والكاولين بطريقة الدفعات

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الخلاصة:-

الدراسة الحالية تعنى بدراسة قابلية بعض من سطوح الأطيان المختارة مثل الطين المعالج(بوليمر الكاؤولين- فاينيل الكحول) وطين الكاؤولين في امتزاز صبغة ليشمان في محاليلها المائية للبحث عن سطوح انتقائية ذات فعالية في امتزاز الاصبغ. اعتمدت امتزاز الصبغة في البحث على مختلف المتغيرات مثل زمن الأتزان ، الدالة الهيدروجينية، التركيز الابتدائي للصبغة وكذلك كمية المادة المازة. بينت نتائج الدراسة أن معلومات الاتزان للصبغة على سطح الطين المعالج كان الانطباق لها يشتمل على ايزوثيرمات فرندلش ولانكماير. بينما على سطح طين الكاؤولين هو ايزوثيرم فرندلش فقط. أظهرت نتائج الدراسة بأن كمية الأمتزاز سطح الطين المعالج اكثر كمية من طين الكاؤولين. كما تم حساب القيمة الترموديناميكية مثل ΔG و ΔH وكذلك ΔS . كما تم حساب النسبة المئوية (K_D و%) للامتزاز الصبغة على سطوح الأطيان في المدى الحراري التجريبي (298-328 K).