

A thermodynamic Study of adsorption of two Dyes on Iraqi Bentonite Modified clay

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Abstract:-

In this study, the adsorption of certain water-soluble cationic and anionic two dyes, (Fast Green and Crystal violet) from aqueous solutions on to Bentonite clay (Polymer of Bentonite clay - poly vinyl Alcohol) as an adsorbent.

A series of experiments were undertaken in a batch adsorption technique to access the effect of the process variables i.e. initial dye concentration, contact time, initial pH, adsorbent dose, temperature and agitation rate. The adsorption capacity of basic dyes was higher (3.1, 7.1 mg.g⁻¹) with the Lower value of the temperature (293 K), adsorbent dosage (0.1, 0.05 gm) higher values of initial pH (7.0) and agitation rate (100 rpm) for (F.G) and (C.V) respectively. The equilibrium in the solution was observed within (30 min) which indicated by UV-Visible absorption spectroscopy technique.

The equilibrium data for adsorption were fitted to the Freundlich and Langmuir. The temperature thermodynamic parameters like ΔG , ΔH , and ΔS have been calculated. The values of percent removal and K_D for two dyes by modified Bentonite clay were calculated.

Key words:- Modified clay, polymer, cationic dye, anionic dye, Adsorption isotherms.

الخلاصة:-

يتناول موضوع البحث دراسة الامتزاز لصبغتي البلورات البنفسجية الموجبة و الفاست الخضراء السالبة الذائبتين في المحاليل المائية على سطح طين البنتونايت المعالج (فانيل الكحول-البنتونايت). كما أجريت سلسلة من التجارب في تقنية الامتزاز لبيان تأثير مختلف المتغيرات مثل التركيز الابتدائي للصبغة، زمن الاتزان، الدالة الهيدروجينية، كمية المادة المازة، درجة الحرارة وكذلك سرعة الرج. بينت النتائج ان سعة الامتزاز للصبغتين تكون بحدود (3.1، 7.12 mg.g⁻¹) على التوالي في درجة الحرارة المثلى (293 K) وكمية السطح الماز (0.1، 0.05 gm) على التوالي وقيمة الدالة الهيدروجينية (7) وسرعة الرج (100 rpm). وجد أن زمن الاتزان لعملية الامتزاز هي (30min) والتي حددت باستخدام تقنية مطيافية امتصاص الأشعة المرئية- فوق البنفسجية. كذلك أوضحت النتائج أن معلومات الاتزان كان الانطباق لها يشتمل على ايزوثيرمات فرنشل ولانكماير. وتم حساب القيمة الترموديناميكية مثل ΔG و ΔH وكذلك ΔS . كما تم حساب النسبة المئوية (K_D %) لامتزاز الصبغتين على سطح الطين المعالج.

Introduction:-

The Cleaning of waste and waste water is one of most serious environmental problems of the present day.

Discoloration in drinking water may be due to the presence of coloured organic substances or highly coloured industrial wastes, of which pulp, paper and textile wastes are common.

Many physical and chemical methods including coagulation, precipitation, filtration, Oxidation, membranes have been used for the treatment of dye^(1,2), However these processes are costly and cannot effectively be used to treat the wide range of dye waste waters.

There is growing interest in using low cost, commercially available materials for the adsorption of dyes.

A wide variety of materials such as activated carbon and metals oxides⁽³⁻⁵⁾, phenolic resins⁽⁶⁾, cotton stalks⁽⁷⁾, rice husk⁽⁸⁾, Kaolin clay⁽⁹⁾ are being used as a viable and low cost to remove dyes from industrial coloured effluents. Bentonite is the rock composed essentially of clay minerals of the smectite (montmorillonite group). The theoretical formula for the structure given above is $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20n}(\text{interlayer})\text{H}_2\text{O}$.⁽¹⁰⁾

Polymer of Bentoniet clay - poly vinyl Alcohol is the commercial name of modified clay⁽¹¹⁾, is an amorphous synthetic from 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 study, the adsorption of certain water- Soluble dyes, namely basic violet 3 (Crystal violet) and food green 3 (Fast green), were investigated by using synthetic modified Bentoniet clay. . These water- soluble dyes resemble the large molecular dyes found in waste water , and they are toxic and carcinogenic.

Table/ 1. some properties of the dyes.

Name	Chemical formula	molar mass g.mol^{-1}	$\lambda_{\text{max}}/\text{nm}$
Fast green		765.89	638
Crystal violet		407.99	585

Materials and Methods

Materials and Apparatus:-

Adsorbates: Two dyes were used as adsorbates: Basic violet3 (Crystal violet) and Food green3 (Fast green) they were used as commercial salts without purification and were supplied by B.D.H and Fluka.

Adsorbents: Bentoniet Iraque was obtained from the general Company for Geological survey and mining, Doghla, 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

Bentoniet Powder sample (50 Mm) was washed with an excess amount of distilled water. The it was treated in an oven with temperatures 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 magnetic stirrer at 90c° for 30 min.

It was sopended in HCl solution of pH=5. then it was mixed with clay and heated at nominal softening temperatures of 200c° for tow hours in an oven, ground then sieved by 50 Mm sieve, the ratio mass of clay/ polymer was (0.5%).

General Procedure

The adsorption isotherms have been determined by mixing of dyes solution (20 ml) of known initial concentration (3-21 p.pm) and varied amounts of adsorbents (0.05-0.1 gm) were placed into volumetric flasks. Analytical determinations of dyes in solution after equilibration (30 min at 20c°) were performed by means of ashimadzu TRUV 754 spectro photometer. Optical densities were determined at (638, 585 nm) for fast green (F.G) and crystal violet (G.V) respectively, 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).

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

Results and Discussion

Adsorption isotherm

Analysis of isotherm data is important in order to develop an equation which both accurately represents the experimental results and could be used for design purposes.

A plot of equilibrium dye loading Q_e , against the residual concentration of dyes remaining in the solution C_e is shown in figure (1). It is evident that dyes can generally be easily removed from the solution by Bentoniet clay modified particles and reducing the particle size will increase Q_e for high values of initial dye Concentration C_o .

The adsorption isotherms determined experimentally were analyzed according to Langmuir isotherm, Equation(2). The Linear form of the Langmuir equation can be represented⁽¹³⁾ as:

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

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⁽¹³⁾ Table (1) Fig (2).

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⁾, Tabl.1. Fsig.3.

The Linearized Freundlich and Langmuir adsorption isotherm initial two dyes concentration and pH, 21 p.p.m mg.L⁻¹ and pH 7 respectively, temperature 20°C, Calculate the adsorption capacity of modified clay for (F.G) and (G.V), the adsorption constants evaluated from the isotherms with correlation coefficients are shown in Table.1.

The values showed that the equilibrium data for fast green (F.G) and crystal violet (G.V) fitted well to both the Freundlich and Langmuir isotherm in the studied concentration ranges. Based on the correlation coefficients (R^2), the equilibrium data was fitted in the Langmuir isotherm and Freundlich equation table.2. many others have used these isotherms to evaluate the adsorption capacity by different dyes^(16,17). The adsorption constants evaluated from the isotherms with correlation coefficient are shown in Table (1) very high regression coefficients (0.996-0.964) were found for dyes.

The higher regression values showed that the equilibrium data for dye fitted well to both isotherms in the studied concentration range.

The percent adsorption (%) and distribution ratio (K_d) of two dyes by modified clay were calculated Table.2. For Fast green as adsorbent, the maximum and minimum adsorption values were obtained at concentrations of 3 p.p.m and 12 p.p.m respectively. While the maximum values for Crystal violet at 6 p.p.m and minimum values at 12 p.p.m.

The difference in % adsorption of these dyes on the surface of Bentonite 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 dyes molecules⁽¹⁸⁾ These types of observations were also observed for the adsorption of organic acids on the surface of finely divided charcoal⁽¹⁹⁾.

Effect of pH

The pH of the dyes solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The variation of fast green and crystal violet adsorption on modified clay over a broad range of pH is shown in fig .4. As shown, the adsorption of crystal violet is lower at pH <7 then is increased to higher values at pH >7^(20,21). Crystal violet is a basic dye. In water, it produces cation (C^+) and reduced ion (CH^+). In addition, the basic dye will become protonated in the

acidic medium and positive charge density would be located more on the dye molecules at Low pH. Resulting the lower up taking. While Fast green is lower at pH>7 then is increased to higher values at pH<7. if the solution pH is above the zero point of charge the negative charge density on the surface of Bentoniet modified clay increases which surface the sorption of dyes⁽²¹⁾.

Contact time

The influence of the contact time on the adsorption capacity of two dyes by modified clay was conducted through batch experiments to achieve the equilibrium as shown in Fig. 5. 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 Bentoniet modified clay. The adsorption capacity was constant there after for case of both adsorbate observed.

Effect of temperature

The removal of fast green and crystal violet using modified Bentoniet clay has been studied at 293 to 333 K. determine the adsorption isotherms and thermodynamic parameters, which is presented in Fig. .6.7. 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 (3).

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

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

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

The negative values of ΔG indicate the feasibility and spontaneous nature for both adsorbates adsorption on modified clay. The change in enthalpy (ΔH) for crystal violet was found to be positive (Table.3). The positive values confirm the endothermic nature of adsorption⁽²³⁾ while. The uptake of fast green decreased with an increased in temperature up to 50c°. the results indicate that the adsorption process is exothermic in nature^(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 of crystal violet is much higher than of fast green. This difference must be related to higher affinity of crystal violet for the adsorbent surface than Fast green. Also this may be due to a tendency for the dye molecule to escape from the solid phase of Bentoniet modified clay to the liquid phase of dye with an increase in temperature of solution^(26,27).

Conclusion

Thermal treatment increased the adsorption of clay. Manufactured powder presented a homogeneous fixation on the clay surface. It was abserved that layer thickness was reduced around 50% after the adsorption- dessorption process. Some advantage in using the pellets of P.V.A- Bentoniet 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.

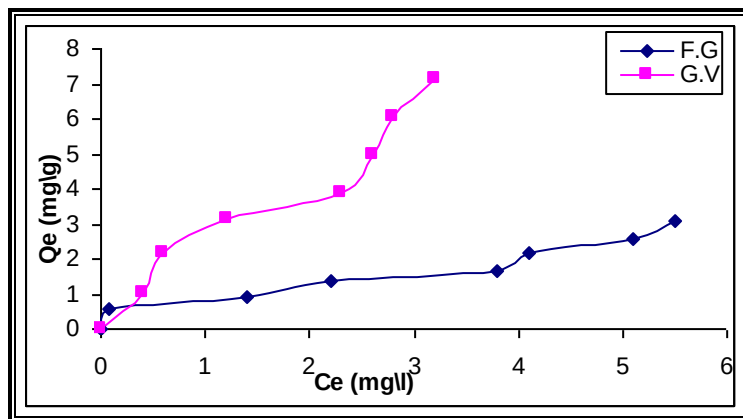


Fig: 1-Adsorption isotherm of Crystal Violet and Fast Green by modified Bentoniet clay and at pH(7)

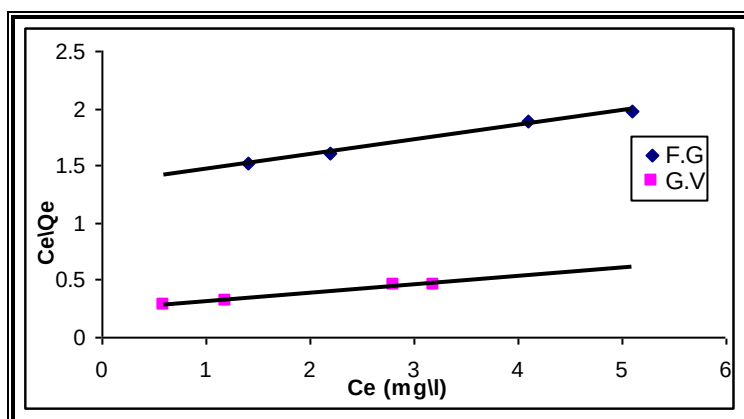


Fig :2- Langmuir adsorption isotherm of Crystal Violet and Fast Green with modified Bentoniet clay at pH(7)

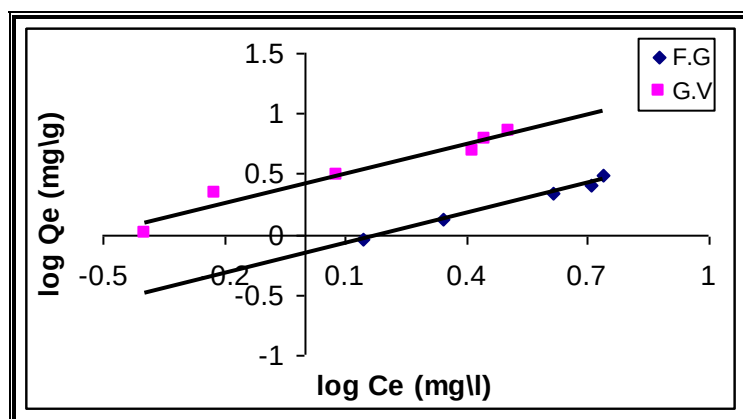


Fig :3- Freundlich adsorption isotherm of Crystal Violet and Fast Green with modified Bentoniet clay at pH(7).

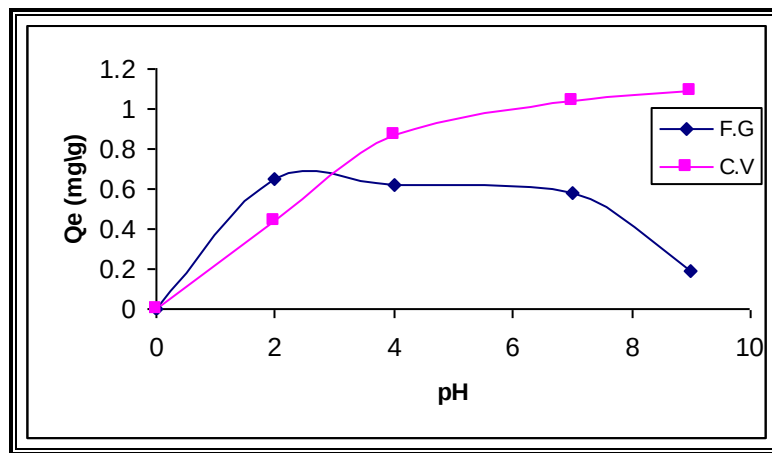


Fig: 4-Removal of colour from aqueous solution of Crystal Violet and Fast Green with pH of solution.

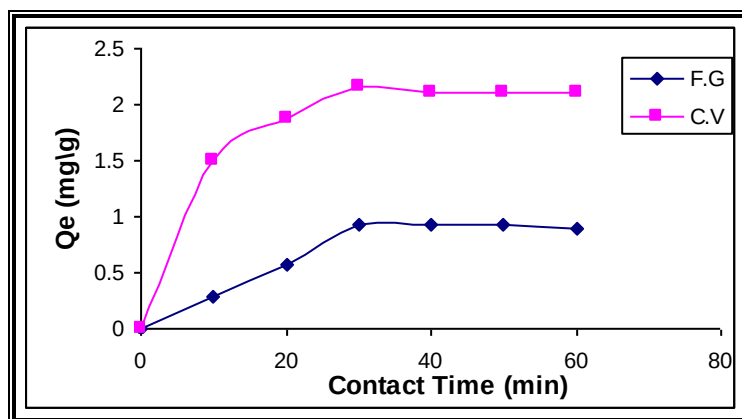


Fig:5- Adsorption capacity against contact time of Crystal Violet and Fast Green with modified Bentonite clay.

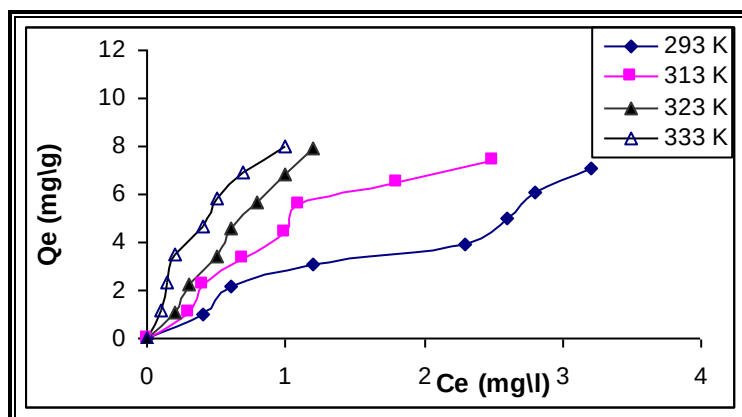


Fig: 6-Effect of temperature on the adsorption capacity of Crystal Violet with modified Bentonite clay at pH=7.

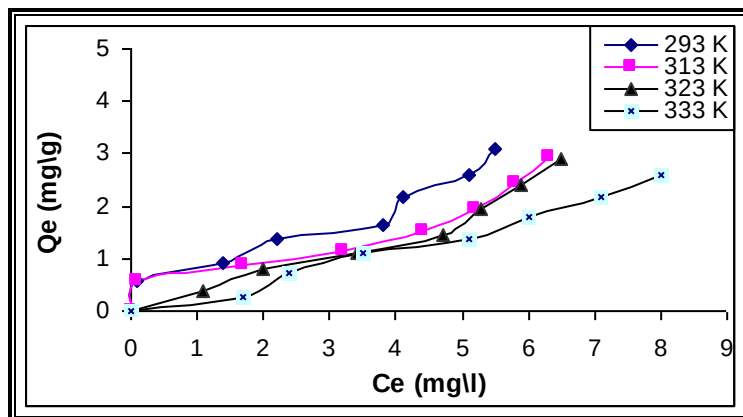


Fig: 7-Effect of temperature on the adsorption capacity of Fast Green with modified Bentonite clay at pH=7.

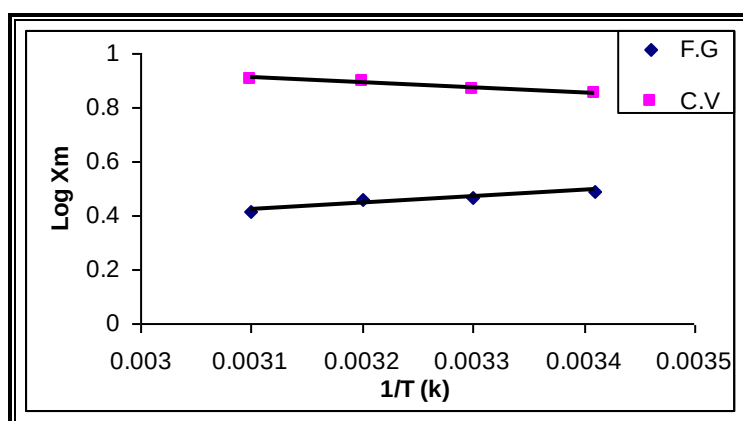


Fig 8:-Relationship between the Log Xm and 1/T of dyes with modified Bentonite clay as an adsorb .

Table/1- Langmuir and Freundlich constants for dyes in aqueous solution using modified Bentonite clay.

Adsorbent	Modified Bentonite Clay					
	Freundlich con.			Langmuir con.		
	RF	n	Log Kf	RL	a	b
Fast Green	0.99	1.566	0.6208	0.996	0.743	10.67
Crystal Violet	0.96	1.231	0.417	0.994	4.36	3.086

Table/2- Kd values and % adsorption of dyes in aqueous solution using modified Bentoniet clay

dyes conc. p.p.m	Fast Green		Crystal Violet	
	%Adso.	Kd	%Adso.	Kd
3	97	38	87	138
6	77	31	90	144
9	76	30	87	139
12	68	27	81	129
15	73	29	83	132
18	72	29	84	135
21	74	30	85	136

Table/3- Thermodynamic values of dyes in aqueous solution using modified Bentoniet clay as an adsorbents .

Adsorbent	$\Delta H \text{ KJ.mol}^{-1}$	$\Delta G \text{ KJ. mol}^{-1}$	$\Delta S \text{ J.mol}^{-1}.\text{k}^{-1}$	Cos.
Fast Green	-4.35	1.39	-19.6	-0.281
Crystal Violet	3.38	-1.94	-18.17	1.45

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