Removal of water- soluble Fast Green and Crystal violet Days with 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 modified Clay (Polymer of kaoline- 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 (3.1,7.12 $mg.g^{-1}$) with the Lower value of the temperature (293 K), adsorbent dosage (0.1, 0.05 gm) higher values at pH_7 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 Freundilch and Langmuir isotherm, . The thermodynamic parameters ΔG, ΔH, and ΔS have been calculated which the values of percent adsorbed(%) and Distribution ratio(K_D)for two dyes by modified Clay were calculated

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

الخلاصة

تناولت هذه الدراسة امتزاز لصبغتين الموجبة والسالبة الذائبة في المحاليل المائية (البلورات البنفسجية وصبغة الفاست الخضراء) على سطح الطين الكاؤولين المعالج (بوليمر فانييل الكحول –الكاؤولبن) 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 وتبين ان سعة الامتزاز للصبغتين تكون بحدود (3.1،7.12 $mg.g^{-1}$) في درجة الحرارة المثلى (293K) وكمية السطح الماز (0.1،0.05gm) وقيمة الدالة الهيدروجينية (7.0) وسرعة الرج (100rpm) للصبغة البلورات البنفسجية والفاست الخضراء على التوالي وجد أن زمن الاتزان لعملية الامتزاز هي (30) دقيقة والتي حددت باستخدام تقنية مطيافية امتصاص الأشعة المرئية- الفوق البنفسجية. كذلك أوضحت النتائج أن معلومات الاتزان لعملية الأمتزاز كانت في تطابق مع ايزوثيرم فرندلش ولانكماير.وتم حساب قيم الثرموديناميكية ΔG وΔH وكذلكΔS, والتي اعطت قيمة ل ΔG(1.39 , -1.9) وΔH(3.3,-4.35) وΔS(-18.1,- 19.6) لصبغة الفاست الخضراء وللبلورات البنفسجية على التوالي. كما تم حساب النسبة المئوية(%) ونسبة التوزيع(K_D)للامتزاز 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), How ever 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.

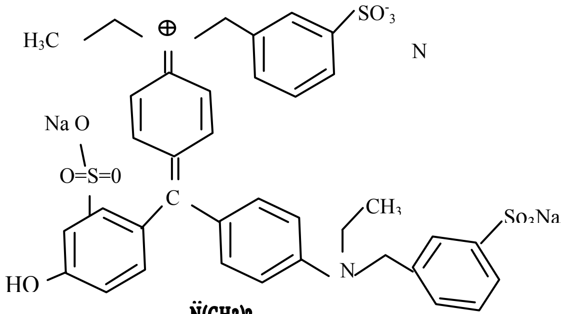
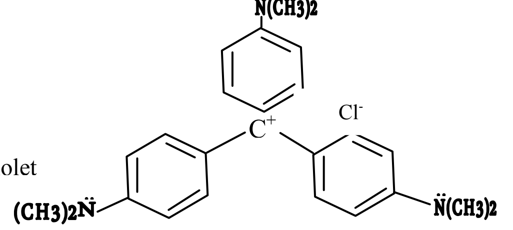
A wide variety of materials such as activated carbon and metals oxides(3-5), phenolic resins(6), cotton stalks(7), rice husk(8), Kaolin clay(9) are being used as a viable and low cost to remove dyes from industrial coloured effluents.

The most important clay mineral is kaolinite [$A1_2O_3$, 2 SiO_2, $2H_2O$] which is the main composed of kaolinite clay(10).

Polymer of kaoline- poly vinyl Alcohol is the commercial name of modified clay(11), is an amorphous synthetic from 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 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}	λmax/nm
Fast green		765.89	638
Crystal violet		407.99	585

Materials and Methods

Materials and Apparatus:-

Adsorbates: Two dyes were used as adsorbates:

(Crystal violet) and (Fast green)dyes they were used as commercial salts without purification and were supplied by B.D.H and Fluka.

Adsorbents: Kaolinite 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

Kaolinite sample (50mm) was washed with an excess amount of distilled water. Then 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 50mm sieve. The particles above 50mm are used in further experiment.

Modified clay Manufacturing

Poly vinyl Alcohol solution(12) was mixed with (100 ml) of distilled water in magnetic stirrer at 90°c 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 200°c 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 (20ml) of known initial concentration (3-21 ppm) and varied amounts of adsorbents (0.05-0.1gm) were placed into volumetric flasks. Analytical determinations of dyes in solution after equilibration (30 min at 20°c) were performed by means of ashimadzu TRUV 754 spectrophotometer. Optical densities were determined at (638, 585 nm) for(F.G) and(G.V) respectively, which corresponds to the maximum absorption peak of dyes.

The adsorption capacity Qe was calculated from the difference between the initial and equilibrium adsorbate (dye) concentration which as follows:

$$Qe= \frac{(Co - Ce)\ V_{sol}}{M} \quad \dots (1)$$

Where: Qe is the adsorption capacity ($mg.g.^{-1}$), Co and Ce 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 which determined was affected by contact time, initial concentration of dye solution and pH, adsorbent dosage, temperature and agitation rate.

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 is the seam Qe, against residual concentration of dyes remaining in the solution Ce is shown in figure (1). It is evident that dyes can generally be easily removed from the solution by modified clay particles and reducing the particle size will increase Qe for high values of initial dye Concentration Co.

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

$$\frac{Ce}{Qe} = \frac{1}{ab} + \frac{a}{Ce} \quad \dots. (2)$$

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:

$$\text{Log Qe} = \text{Log } K_f + \frac{1}{n} \text{ Log Ce} \;\ldots\ldots (2)$$

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. Fig.3.

The Lienarized Freundlich and Langmuir adsorption isotherm two dyes concentration initia21 ppm mg.L^{-1} l pH 7and temperature 20°c respectively, 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 (F.G) and (G.V) dyes fitted well to both the Freundlich and Longmuir isotherm in the studied concentration ranges.

From the higher regression values based on the correlation coefficients (R^2), the equilibrium data was fitted in the Langmuir and Freundlich isotherm equation 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 (1) very high regression coefficients (0.996-0.964) were found for dyes.

The percent adsorption (%) and distribution ratio (Kd) of two dyes by modified clay were calculated Table.2.For(F.G) dye as adsorbent ,the maximum and minimum adsorption values were obtained at concentrations of 3ppm and 12 ppm respectively. While the maximum values for(C.V)dye at 6 ppm and minimum values at 12 ppm .

The difference in % adsorption of this dyes 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 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 (F.G)and (C.V) dyes adsorption on modified Clay over abroad rang of pH is shown in fig .4. The adsorption(C.V) is lower at pH <7 then is increased to higher values at pH>7(20,21). (C.V)dye 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 change density would be located more on the dye molecules at Low pH. Resulting the lower up taking. While(F.G) is lower at pH>7 then is increased to higher values at pH<7. 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 (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 modified clay. The adsorption capacity was constant there after for case of both adsorbate observed.

The dyes is consisting of polar and non – polar portions . The sulphonic acid group is susceptible to electrostatic interactions with the adsorbent surface , whereas , non polar portions play an important role in hydrophobic interactions (Van der Waals bonds).

Due to the positively charged characteristics of modified Clay in aqueous media , the cationic dye should be adsorbed more rapidly than anionic dye .The results obtained here indicate the effect of coulombic interactions between the adsorbent and dye

Effect of temperature

The removal of(F.G) and(C.V)dyes using modified clay has been studied at 293 to 333 K. determine the adsorption isotherms and thermodynamic parameters, which is presented in Fig 6&7. free energy (ΔG) enthalpy (ΔH) and entropy (ΔS). changes were also calculated using Eqs. (4-6)(22) and are given in Table (3)at293K .

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

$$\mathrm{Log}X_m = \frac{\Delta H}{2.303RT} + \mathrm{Con.} \;\ldots\; (5)$$

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

The negative values of ΔG indicate the feasibility and spontaneous nature for both adsorbates adsorption on modified clay. The change in enthalpy (ΔH) for (C.V)dye was found to be positive (Table.3). The positive values confirm the endothermic nature of adsorption(23) while the uptake of (F.G)dye decreased with an increased in temperature up to 50°c. 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(C.V)dye is much higher than of(F.G). This difference most be related to higher affinity of(C.V)dye for the adsorbent surface than(F.G)dye. Also this may be due to a tendency for the dye molecule to escape from the solid phase of 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 observed that layer thickness was reduced around 50% after the adsorption- desorption process. 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.

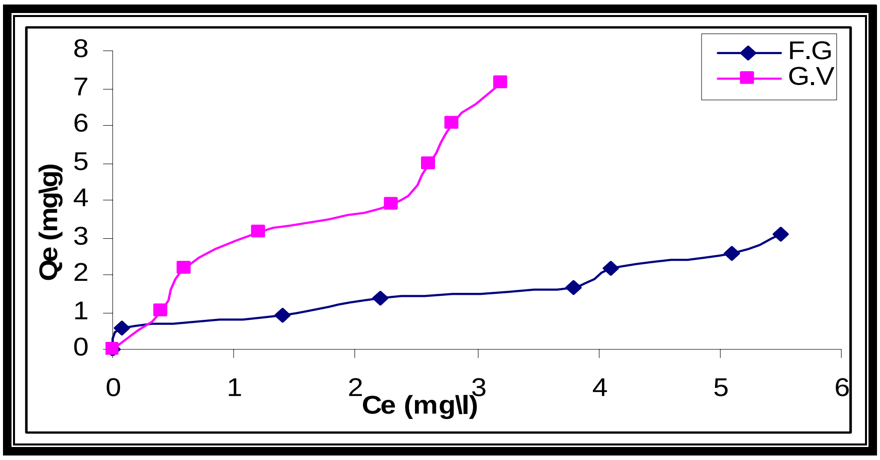


Fig: 1-Adsorption isotherm of(C.V) and (F.G)dyes by modified Clay at pH(7)

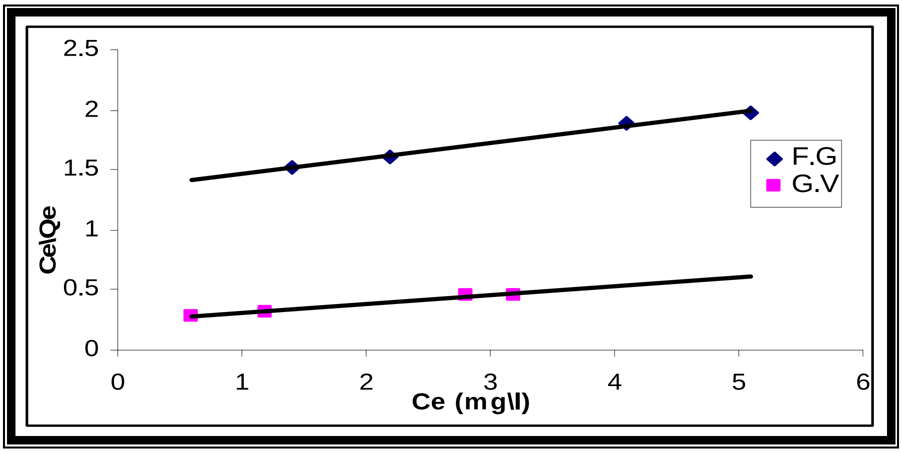


Fig :2- Langmuir adsorption isotherm of (C.V) and (F.G)dyes with modified Clay at pH(7)

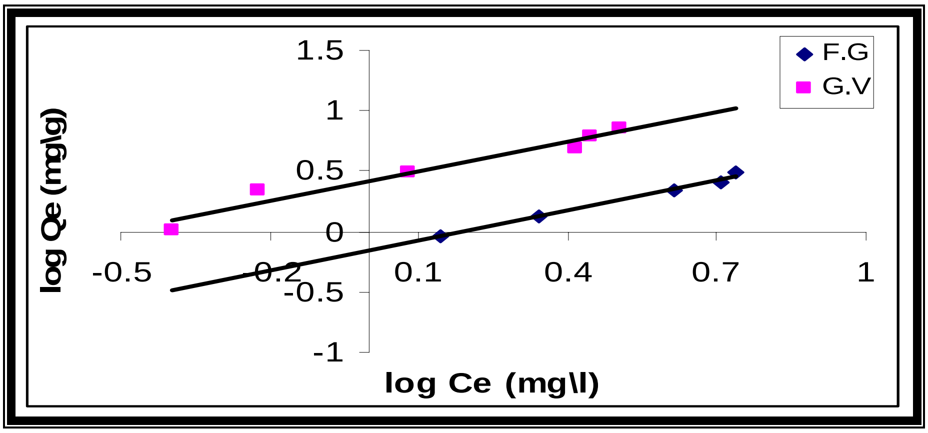


Fig :3- Freundlich adsorption isotherm of (C.V) and (F.G)dyes with Modified Clay at pH(7).

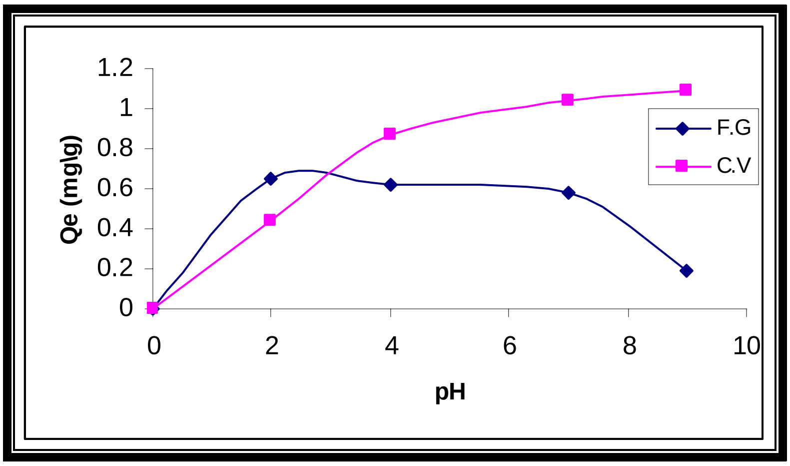
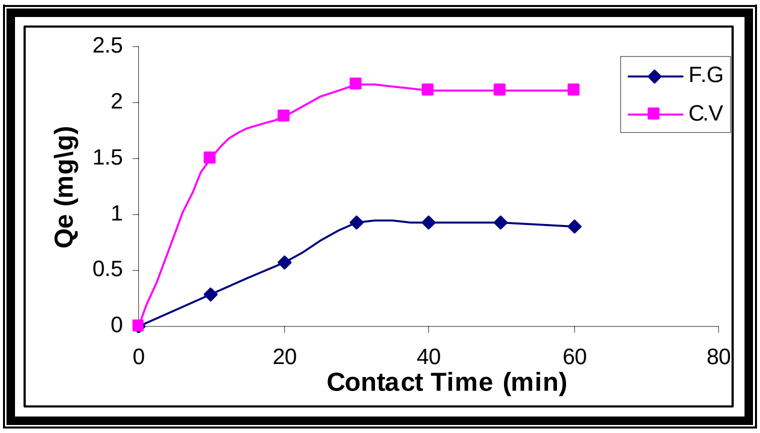


Fig: 4-Removal of colour from aqueous solution of(C.V) and(F.G)dyes with pH of solution.



F ig:5- Adsorption capacity against contact time of (C.V) and (F.G)dyes with modified Clay

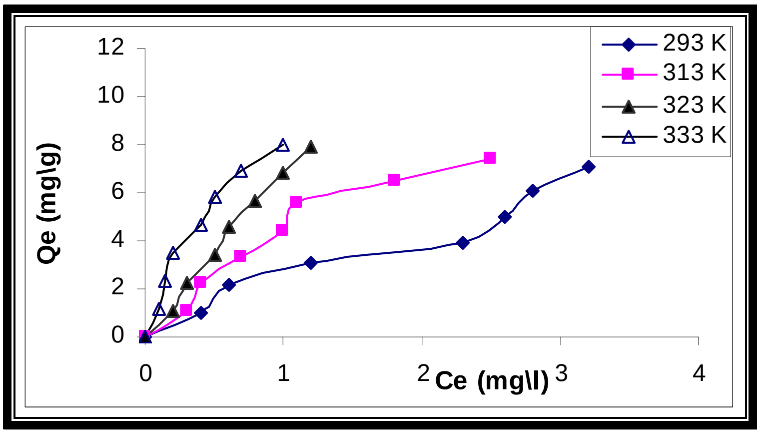


Fig: 6-Effect of temperature on the adsorption capacity of(C.V)dye with modified Clay at pH=7.

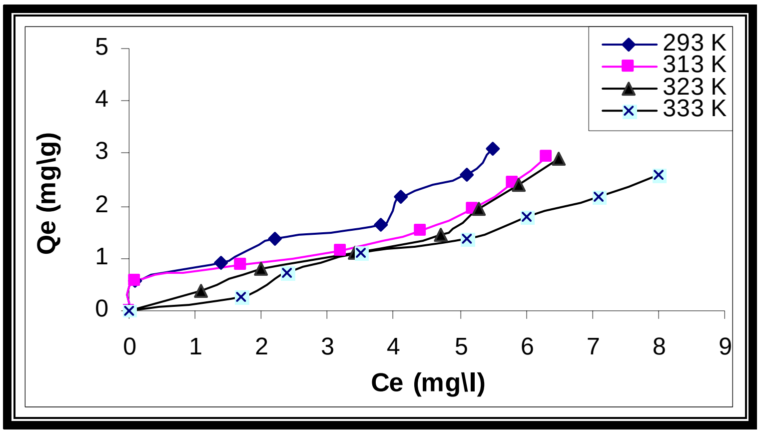


Fig: 7-Effect of temperature on the adsorption capacity of (F.G)dye with modified Clay at pH=7.

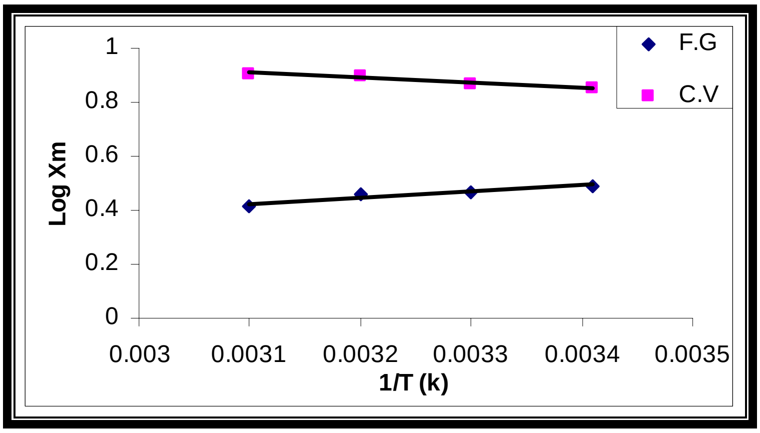


Fig 8:-Relationship between the Log Xm and 1/Tof dyes with modified Clay as an adsorb .

Table/1- Langmuir and Freundlich constants for dyes in aqueous solution using modified 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/2- Distribution ratio Kd values and percent adsorbed % adsorption of dyes in aqueous solution using modified Clay

Adsorbent	Modified 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	0.964	4.36	3.086

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

Adsorbent	ΔH KJ.mol^{-1}	ΔG KJ. mol^{-1}	ΔSJ.mol^{-1}.k^{-1}	Cos.
Fast Green	- 4.35	1.39	-19.6	-0.28
Crystal Violet	3.38	-1.94	-18.17	1.45

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