Study the Adsorption of Yellow (W6GS) dye from Aqueous Solutions by using Attapulgite Clay

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Abstract

The study is concerned with the adsorption of terasil yellow (W-6GS) dye from aqueous solution by using attapulgite clay , where the effects of initial concentration of dye, pH and the equilibrium contact time, were investigated, also studies the effect of acid, base and salt concentrations on the adsorption process. Isotherm of it's adsorption was measured.

الخلاصة

في هذه الدراسة تم استخدام طين الاتابلكايت كمادة مازة لصبغة terasil yello(W-6GS) المنتشرة من محاليلها المائية حيث تضمن البحث تعيين زمن الاتزان ودراسة تأثير كل من الدالة الحامضية وكذلك تأثير تركيز ونوع الحامض والقاعدة والاملاح على عملية الامتزاز ، كما تم قياس ايزوثيرم الامتزاز .

Keywords:- *adsorption, attapulgite clay, isotherm.*

Introduction

Adsorption process can be defined as the attachment of particles to a surface[1], or is the collection of a substance on to the surface of adsorbent solids [2] .

The textile industry has a major impact in the economy but also on the environmental quality of life in many communities. Textile industry requires the use of vast amounts of water and chemicals, and the effluents have important effects on environmental quality in textile manufacturing regions [3].The color removal from textile effluents has been the subject of great attention in the last few years, not only because of its toxicity but also mainly due to its visibility [4].

The widespread application of dyes in textiles, printing, dyeing, and food plants has produced a large amount of dye waste water because some dyes and their degradation products may be carcinogens and toxic, the removal of dyes from waste water becomes an important issue in the environmental protection. This urges an intensive search for the best available technology for the removal of dyes. Some physico- chemical methods (such as advanced oxidation and biological process, coagulants, oxidizing agents, membrane, electrochemical, and adsorption techniques) have been proposed to satisfy the above requirements(5-7).

Attapulgite clay is a kind of natural minerals with large specific surface area and porous structure. It has been applied widely at abroad for its many special behaviors(8-10). Attapulgite structure is commonly called a chain layer. It is unique mineral structure that manifests ribbons of alumino–silicate layers to be joined at their edges. Attapulgite crystals are needles shaped (circular) rather than flat or flake – like, which have high surface area (11). Attapulgite is superior kaolinite, because it is an open structure enclosing channels into which organic compound (12). It has smaller trimorphic unit, intermediate between di – and tri octahedral in character. These minerals have been considered to belong to the category of (chain –lattice silicates). However; since they bear a closer relationship to the phyllosilicates than to the chain silicates (13).

The aim of this work was to investigate the possibility of attapulgite clay
for the absorptive removal of yellow(W-6GS) dye from aqueous solution.

Experiment

Materials

The adsorbent is attapulgite clay has a composition of $[(OH_2)_4(Mg,Al,Fe)_5(OH)_2Si_8O_{20}].4H_2O$ (14). It was obtained from the general company for geological survey and mining, Baghdad, Iraq, from Akashatt area in Iraqi western desert. It was collected from an opened mine. It was a buffer material, yellow-light orange powder and is practically insoluble in water, organic and inorganic acids and in solutions of the alkali hydroxides. The chemical analysis of Attapulgite is listed in table (1) (15).

Table 1: The chemical analysis of attapulgite

chemical	Wt %
SiO_2	44.66
Al_2O_3	13.36
CaO	13.71
Fe_2O_3	4.2
MgO	3.2
SO_3	0.23
Loss on ignition	17.97
Total	97.33

Terasil yellow (W6GS) dye obtained from textile industry of Hilla, the structural form of this dye is given in Figure 1.

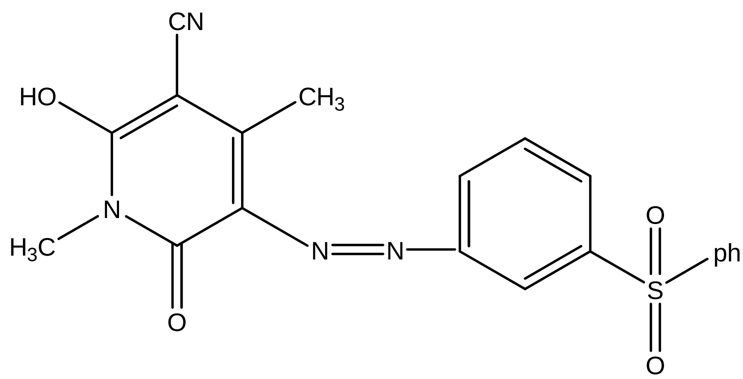

Figure (1) Structure of terasil yellow (W–6GS) dye

The wave length of this dye was (487nm) and it's measured spectrophotometrically with the use of a double beam, Shimadzo uv-1650 pc.

Instruments

The following instruments were used in this study:
Digital balance, Sartoris ,BL 210S (Germany), Uv-Visible Spectrophotometer, Single Beam, Apel PD-303uv (Japan), Digital pH-Meter, knick (Germany), Shaker, Memmert Water Bath, WNB 22, Oven, Blue M, Aunit of General Signal, Shaker, orbit VRN-480 (Taiwan), Uv- Visible Spectrophotometer, double Beam, Shimadzo uv-1650 PC (Japan) and Centrifuge machine, PLC series (Taiwan).

Preparation of Clay powder :-

Attapulgite clay was supplied in the powder form. It was suspended in HCl solution with (1×10^{-3})N to remove carbonate and it was washed several time with distilled water to remove the soluble materials. Finally the sample was filtered, dried in an oven at 115C^{o}, sieved by 200 mesh sieves the maximum particle size optained was 75 µm [16] and stored in closed containers for further test.

Procedure :

Adsorption experiment: In each adsorption experiment, 25 mL of dye solution of (8ppm) concentration was added to (0.5gm) of attapulgite clay in a tightly closed flask and the mixture was stirred on a rotary orbital shaker for a priod time (5-l00 min), until the adsorption of day solution on the clay reaching equilibrium at certain pH and temperature. The sample was withdrawn from the shaker at the predetermined time intervals and absorbents were separated from the solution by centrifugation at 3000 rpm for 5 min. The absorbance of the supernatant solution was estimated to determine the residue of dye concentration spectrophotometrically at λ_{max} .

Also the adsorption of day on clay was carried out during different pH solusion, concentrations of dye and different temperatures.

Result and Discussion

A. Calibration curve of dye.

Solutions of different concentrations were prepared by serial dilutions of dye. Absorbence values of these solutions were measured at the specified λ_{max} value (487nm) and plotted versus the concentration range from 10-100 ppm, that fell in the region applicability of Beer- Lambert's law were then used in subsequent quantitative estimation. Figure (2) show the Calibration curve of dye.

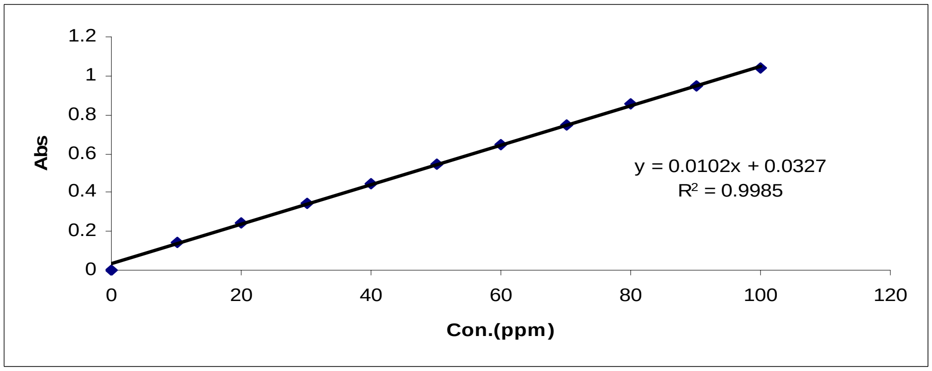

Figure (2) calibration curve of dye

B. Equilibrium contact time

The equilibrium contact time required for adsorption of dye on the surface of attapulgite clay were almost (30 min) as shown in Figure (3).

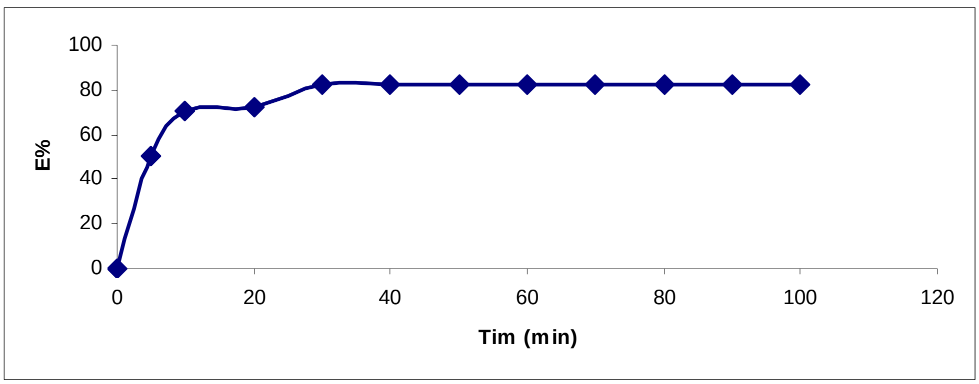

Figure (3) equilibrium contact time of adsorption

C. Effect pH on adsorption

Studied the adsorption of dye on the surface of clay with rang pH from (2-10), and show the maximum amount of adsorption of yellow (W6GS) dye at pH=2 .This shown in figure (4), and the change pH does not effected on the λ_{max} of dye solution. The E% value decrease in pH=10 may be due to the competing of high concentration of OH on the sites of attapulgite clay .

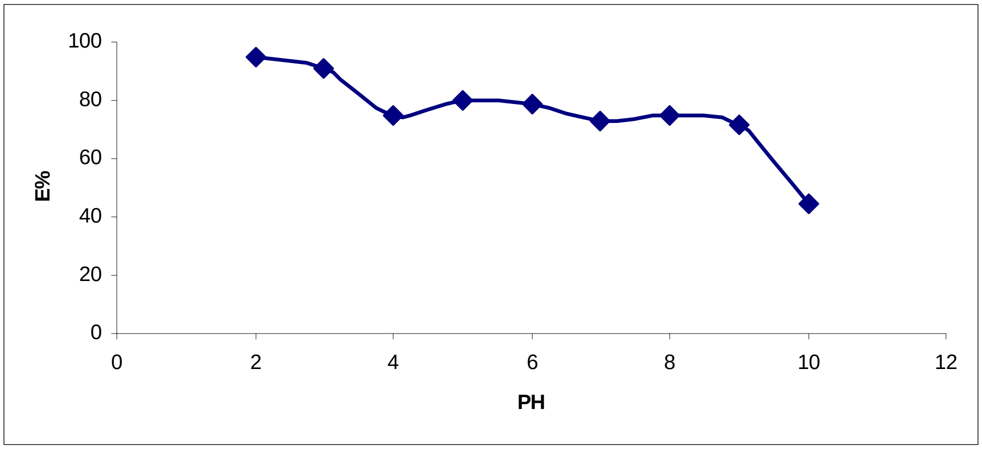

Figure (4) effect PH value on adsorption of dye

D. Adsorption isotherm

Adsorption isotherm experiments were carried out in 250 ml conical flasks which 0.5g of natural attapulgite and 25 ml of appropriate concentration of test dyes were added, i.e., 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, mg/L. Then the samples were respectively shaken at 150 rpm for 30 mins At the end of the adsorption period, the solution was centrifuged for 5 min at 3000 rpm and then the concentrations of the residual dye, *Ce*, were determined with the aid of an UV-vis spectrophotometer at absorbance. The measurements were made at maximum wavelength of dye. The final concentrations can be calculated with their absorbance standards curve, respectively. The adsorption capacity of dyes (mg/g), (*qt*), on natural attapulgite was calculated from the mass balance equation as follows [17].

$$Q_e = \frac{(C_0 - C_e)\,V}{m} \quad \text{......} (1)$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye solution (mg/L), respectively; V the volume of dye solution (L); and m the mass of attapulgite sample used (g). Figure (5) show the adsorption isotherm of dye.

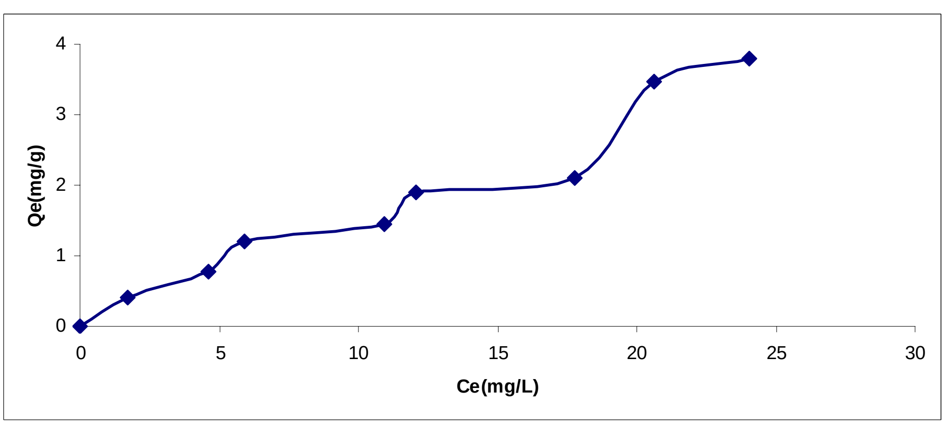

Figure (5) adsorption isotherm of dye.

This figure showed the adsorption isotherm agrees S_4 type of Gilles classification.

The adsorption curves were applied to the Langmuir and Freundlich isotherms equation, the Langmuir equation is the mathematical function most commonly used to describe this process[18]. The Langmuir isotherm can be expressed as

$$Q_e = \frac{X_m\, kC_e}{1 + kC_e} \quad \ldots\ldots (2)$$

where Q_e amount of dye adsorbed per unit weight of adsorbent (mgg−1), C_e is concentration of dye remaining in solution at equilibrium (mgL−1), X_m is amount of dye adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface(mgg−1) and k = a constant related to the energy or net enthalpy (k). The linear form of the Langmuir isotherm equation is represented in equation (2).

$$\frac{C_e}{Q_e} = \frac{1}{kX_m} + \frac{C_e}{X_m} \quad \ldots\ldots (3)$$

Straight lines were obtained by plotting ***C e / Q e*** against **Ce** for the adsorption of dye on to attapulgite illustrated in Figure 6 .

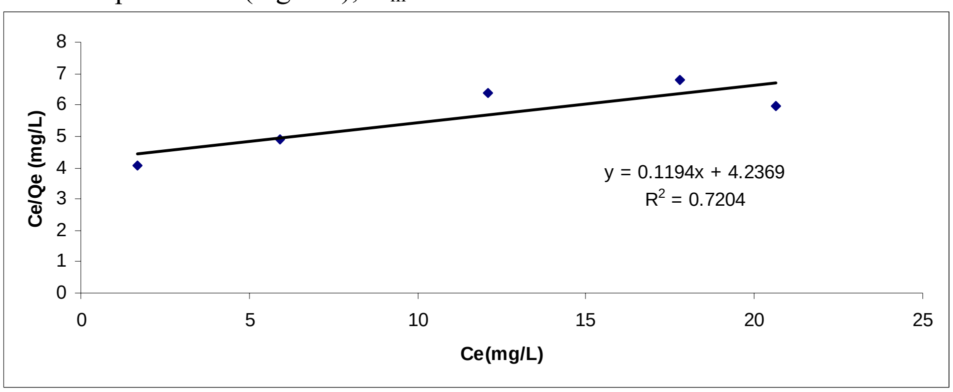

Figure 6: Langmuir plots attapulgite / yellow (W6GS) dye at PH=7

The values of X_m and k_L calculated from the slopes and intercepts of the Langmuir plots and correlation coefficients R. As it can be seen most of the adsorption isotherms obeyed the Langmuir equation with correlation coefficients $0.96<R^2>0.83$. Many experimental isotherms conforming to a Langmuir isotherm involve monolayer coverage [18].

The adsorption curves were also applied to Freundlich equation. The Freundlich isotherm is given as [18].

$$Q_e = K_f C_e^{1/n} \quad \ldots\ldots\ldots (4)$$

where K_f is roughly an indicator of the adsorption capacity and (1/n) of the adsorption intensity all data are illustrated in Figure 7.

Values n > 1 represent a favorable adsorption condition K_f and 1/n can be determined from the linear plot of $\ln(Q_e)$ vs. $\ln(C_e)$. The Freundlich isotherm fits quite well with the experimental data (correlation coefficient $0.854<R^2> 0.987$.

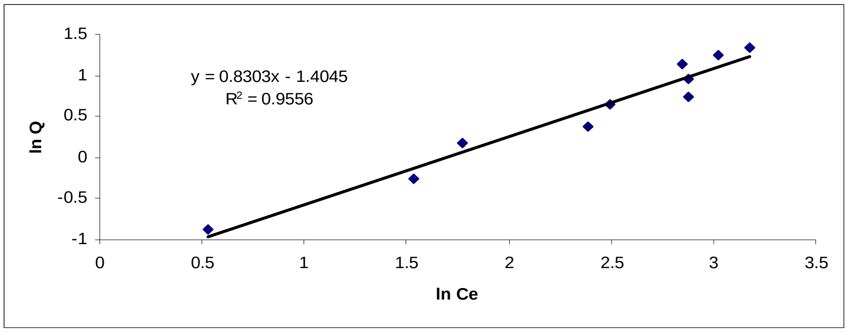

Figure 7: Freundlich plots attapulgite / yellow (W6GS) dye at pH = 7

E. Effect of Acids concentrations.

Effect of different concentrations of (0.5-2.5) M acids solutions (HCl, HNO_3 and H_2SO_4) on the percentage of adsorption of given dye by used the attapulgite clay shown in Figure (8).It was appear slight increase the percentage of adsorption with increase of the concentration of acids.

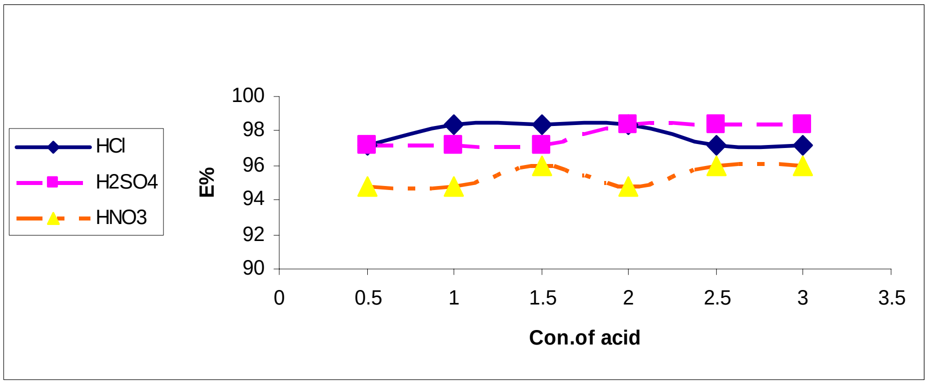

Figure (8) effect the concentration and type of acids on the percentage of adsorption

F. Effect of Bases concentrations.

When used a different concentrations of bases such as (NaOH, KOH), it was notice decrease in concentration of dye, because this dye was sensative to the alkali medium and it precipitate in such mediums[19].

G. effect of salts concentrations.

Effect of different concentrations of (0.1-2.5) M salt solutions such as (NaCl, $CaCl_2$ and KCl) on the percentage of adsorption of given dye by used the attapulgite clay shown in Figure (9).It was appear increase the percentage of adsorption with increase the concentration of salt, due to the ionic force of adsorption solution was high may be effect on the adsorption of dye on the attapulgite surface.

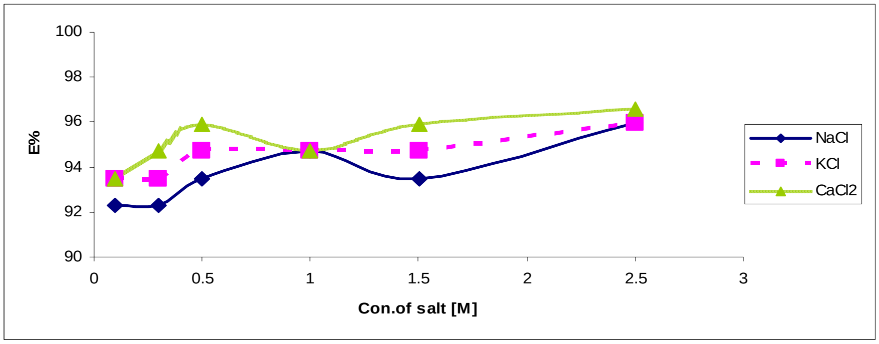

Figure (9) effect the concentration and ty pe of salt on the percentage of adsorption

H. effect of ethanol solvent.

Effect of different concentrations of (5-25) % of absolute ethanol on the percentage of adsorption of given dye by used the attapulgite clay shown in Figure (10).It was appear decrease the percentage of adsorption with increase the concentration of ethanol. and show the maximum amount of adsorption of yellow (W6GS) dye at 5% ethanol.

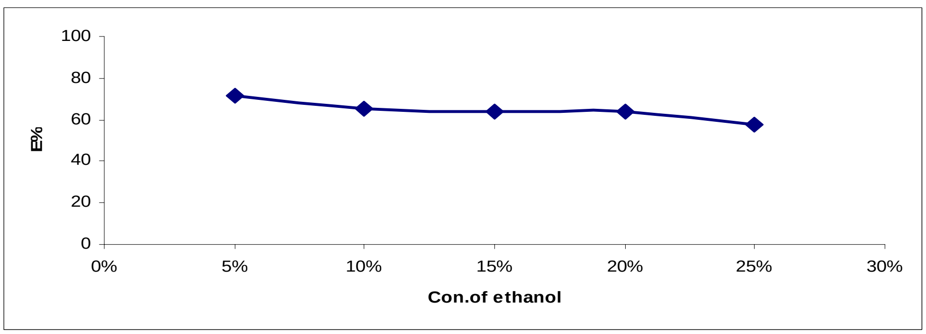

Figure (10) effect the concentration of ethanol on the percentage of adsorption

The high concentration of absolute ethanol large than 5% cause a low adsorption of dye on the clay, due to the competing of ethanol on the active sites of clay with day .

Thermodynamic parameters:

The thermodynamic parameters for the adsorption of yellow (W6GS) dye by attapulgite such as the enthalpy change (ΔH^o), the Gibbs free energy change (ΔG^o) and the entropy change (ΔS^o) can be calculated from the variation of maximum adsorption with temperature (T) using the following basic thermodynamic relations [20].

$$\log K_d = -\frac{\Delta H^o}{2.303\,RT} + \text{constant} \quad \ldots (5)$$

$$\Delta G^o = -RT \ln K_d \quad \ldots\ldots (6)$$

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \quad \ldots.. (7)$$

According to equation 5, the mean value of the enthalpy change due do the adsorption of dye by attapulgite over the temperature range studied can be determined graphically by the linear plotting of log k_d against 1/T using the least squares analysis shown in Figure 11. The mean enthalpy change can be determined from the slope of the straight line. The variation of Gibbs free energy and entropy change with temperature can be calculated using equations 6 and7, respectively [21].

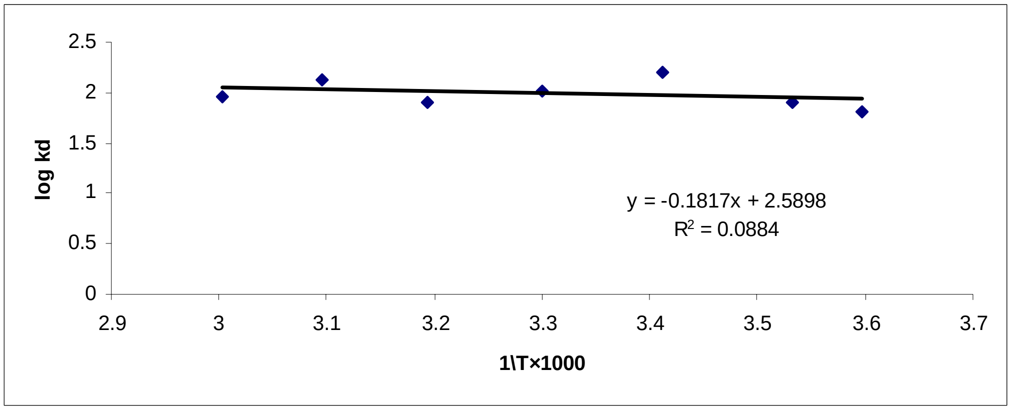

Figure 11. Van't Hoff equation for adsorption of dye on attapulgite surfac

T/K	**Δ*H***(KJ/mole)	**ΔG(KJ/mole)**	**Δ*S*(J/mole.K)**
283	-21.538	-12.294	-32.661
293	-	-12.364	-31.308
303	-	-11.725	-32.386
313	-	-11.416	-32.336

The thermodynamic parameters for the adsorption of dye on the Attapulgite

Conclusions

Attapulgite clay as an adsorbent has a considerable potential for removing terasil yellow (W6GS) dye because of it's higher surface area.
The adsorption curves were applied to the Freundlich equation mor than Langmuir equation.
The adsorption of terasil yellow (W6GS) dye on the attapulgite clay was exothermic.

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