RESEARCH ARTICLE

Use of Iraqi Attapulgite (ATP) and Surfactant-modified Iraqi attapulgite for Adsorption of Crystal Violet from Aqueous Solutions

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Abstract

Iraqi attapulgite (ATP) mineral clay was modified using anionic surfactant (Sodium dodecyl sulfate (ATP-SDS)) to improve its adsorption capacity for crystal violet (CV^+) dye. Different techniques were used to characterize the ATP and ATP-SDS such as FTIR spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The adsorption properties of crystal violet (CV^+) from aqueous solutions by ATP and ATP-SDS were further evaluated. Many parameters like adsorbent dosage, contact time, pH and temperatures were investigated and discussed. The adsorption kinetics were described using pseudo-first-order and pseudo-second-order models. The CV^+ dye uptake process obeyed the pseudo-second-order kinetic. The experimental data were examined using Langmuir, Freundlich and Temkin isotherms models. The results showed better fit to Freundlich and Temkin models than Langmuir model. Thermodynamic values (ΔG^o, ΔH^o and ΔS^o) showed that adsorptions of CV^+ onto ATP and ATP-SDS were endothermic, spontaneous and randomness increasing for both sorbents. The results indicate that this natural and modified Iraqi attapulgite could be employed as low-cost alternative for removal of cationic dye CV^+ from wastewater.

Keywords: *Adsorption, attapulgite, Sodium dodecyl sulfate, crystal violet, Thermodynamic parameters.*

Introduction

Cationic dyes are widely used in many industries including texture, leather, paint and varnishes, ink, plastics, pulp and paper, cosmetics, tannery etc. [1, 2]. One of those well-known used dyes is crystal violet (CV^+) is used for various purposes such as a biological stain, a dermatological agent, a veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus etc. It is also extensively used in textile dying and paper printing [3].Generally, industrial effluent contaminated with dyes are believed to be extremely toxic and a hazardous to the environment.

Thus, it is important to remove dyes from industrial discharges [4]. Moreover, many treatment technologies such as adsorption [5, 6], photodegradation [7], coagulation flocculation [3], chemical oxidation [8], electrochemical oxidation [9], biological process [10] are available for the removal of

dye from the wastewater. Attapulgite (ATP) or Palygorskite is a species of hydrated magnesium aluminum, silicate mineral clay [$Si_8Mg_5O_{20}$ (OH) $_2(OH_2)_4.4H_2O$]. ATP was widely used as adsorbent for the removal of many pollutants' heavy metals [12], dyes [13] and phenols [14] from aqueous solutions. In this work, the aim is toward studying the removal of CV^+ onto ATP and ATP-SDS adsorbents. The effects of adsorbent mass, effect of contact time, effect of pH were studied. The obtained experimental data were analyzed using adsorption isotherm models.

Experimental Part

Adsorbent and adsorbate

The ATP was obtained from Akashat area at Al-Anbar governorate/ Iraq. The adsorbent powder was washed with de-ionized water and dried at 100^oC. The chemical composition of attapulgite is given in Table (1).

The anionic surfactant (Sodium dodecyl sulfate (SDS ≥ 98%)) was purchased from Romil Company. The adsorbate, crystal violet (CV$^+$) was obtained from BDH (≥99%).

The chemical structure of (CV$^+$) is shown in Figure (1). A stock solution (1000 mg/L) was prepared by dissolving 1g of CV$^+$ in 1L of deionized water.

Table 1: The chemical analysis of attapulgite clay (ATP)

Al$_2$O$_3$	SiO$_2$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	L.O.I	Total %
10.68	41.08	4.08	17.93	3.93	1.3	20.96	99.96
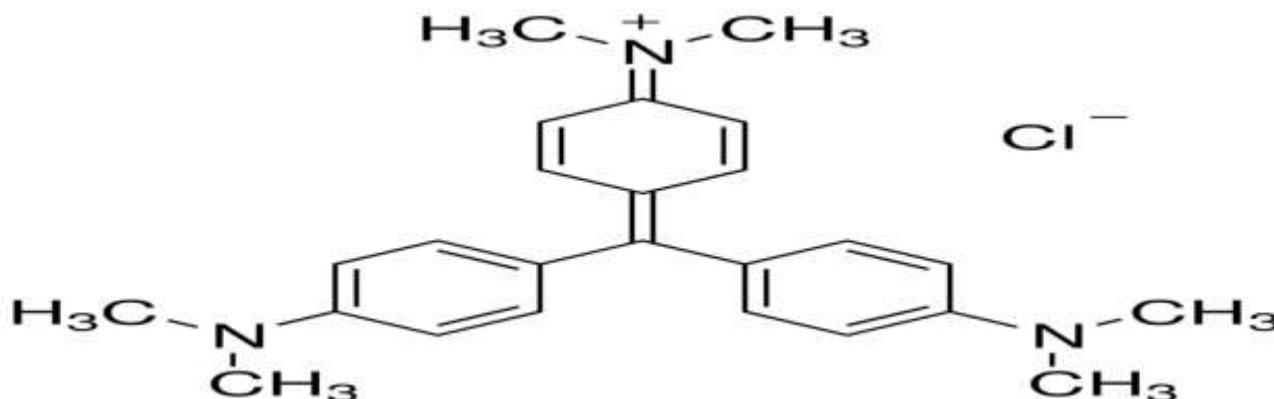
Figure 1: The chemical structure of CV$^+$

Preparation of Surfactant-attapulgite Clay (ATP-SDS)

The clay in powder form was washed several times with excessive amount of deionized water and then was dried at 100°C for six hours, left to cool at room temperature and then was kept in an airtight container. The ATP-SDS was prepared by dissolving 3.5 g of sodium dodecyl sulfate (SDS) in 1L of deionized water and mixed with 50 g of attapulgite and stirred for 24 hours. The suspension was then decanted, washed several times with deionized water and then dried at 100 °C for five hours. The ATP and ATP-SDS in this work were sieved to ≤ 75µm.

Characterization of the Adsorbents

The minerals analysis of ATP and ATP-SDS were characterized using X-ray diffraction (XRD) technique (Shimadzu 6000 powder diffractometer (Japan) using CuKα radiation, λ=1.5418A°at 40kV, 30 mA and 2θ range from 5-60°. The Fourier transforms infrared spectroscopy (FTIR) (Shimadzu 8400, Japan) in the wavenumber range of (4000 to 400 cm-1) was used to identify the modification of ATP. Scanning electron microscope (SEM) type-T-Scan, Vega- 111(Czech) was used to determine the surface morphology of the samples.

Adsorption Isotherm Studies

The adsorption experiments were carried out using 0.2 g for both adsorbents (ATP and ATP-SDS (separately) with 10 mL of CV$^+$ at different initial concentrations (100, 150, 200, 250, 300, 350 and 400 mg/L). The adsorption equilibrium, adsorbent dosage, pH, Ionic strength, kinetics, temperature effect at 25, 35 and 45°C and thermodynamics are described below. The concentration of CV$^+$ was determined by measuring the absorbance using UV-VIS spectrophotometer (T80) at 584 nm. The mass of the adsorbed amount of CV$^+$ (q_e, mg/g) was calculated following equation (1).

$$q_e = (C_o - C_e) V/W \quad (1)$$

Where V is the volume (L), W is the adsorbent mass dosage (g), C_o mg/L is the initial concentration and C_e mg/L the residual concentration at equilibrium.

The percentage of CV$^+$ removal was calculated according to the equation (2).

$$\% \text{ Removal (R \%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Results and Discussion

FTIR Spectra

The FTIR spectra for ATP and ATP-SDS are shown in Figures 2a and 2b, respectively.

The bands in Figure 2a at 3624.2 and 3538.3 cm^{-1} are due to the stretching vibration band of OH group and the band at 1622.1cm^{-1} is assigned to OH deformation. Bands appeared at 1014.5 cm^{-1} due to stretching Si-O group, at 916.1 cm^{-1} due to stretching band of Al-OH group, at 873.7 cm^{-1} due to Stretching band Fe-O group and 796.6 cm^{-1} due to stretching band of Mg-OH group [1, 15].The appearance of bands at 2920 and 2850 cm-1 in modified (ATP) Figure 2b attributed to the symmetric and asymmetric stretching vibrations of CH$_3$ and CH$_2$ groups of the SDS surfactant [16,17].
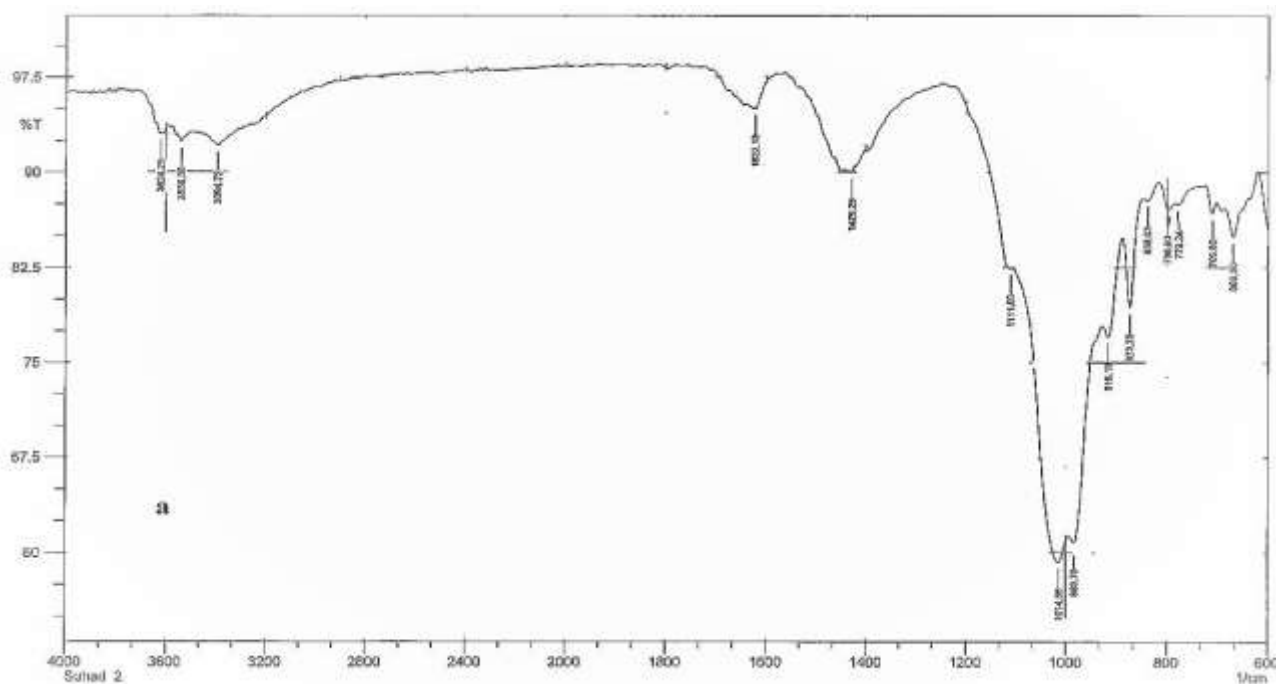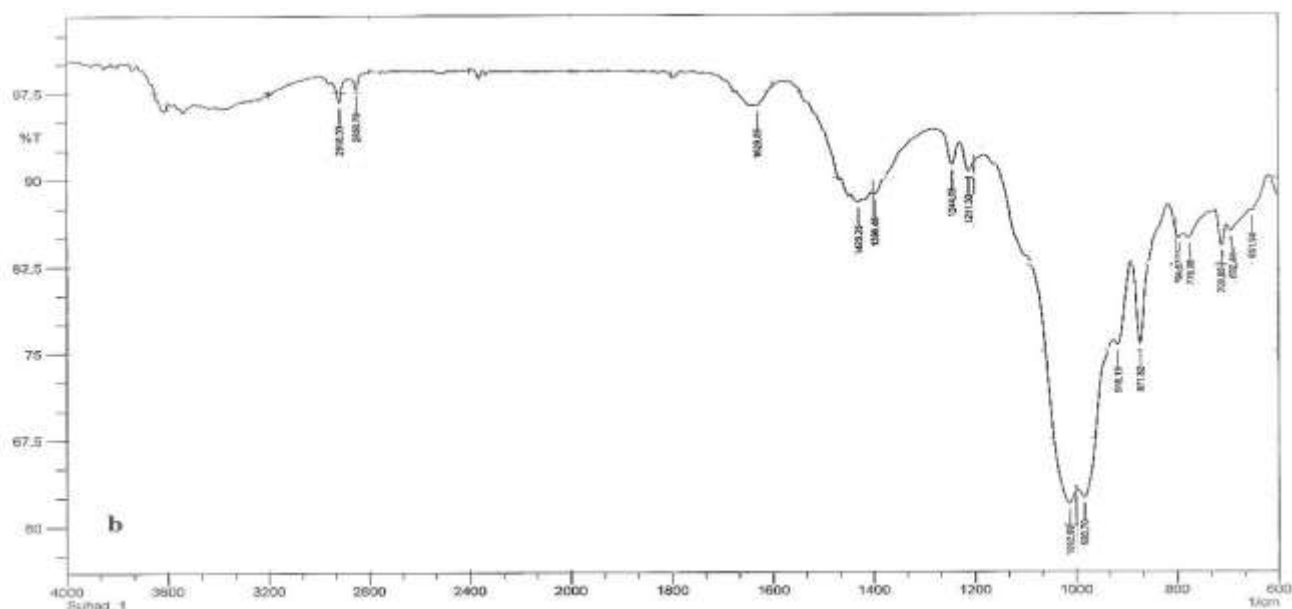

Figure 2a: FTIR spectra of ATP

Figure 2b: FTIR spectra of ATP –SDS

SEM Analysis

The SEM images of attapulgite (ATP) and (ATP-SDS) are shown in Figures 3a and 3b, respectively. Obviously, the agglomerates of attapulgite contain few numbers of particles compared with those of ATP-SDS. Several of the particles in attapulgite and ATP-SDS show laminar crystalline habit characteristic of phyllosilicates. However, these certain particles dominate more in ATP-SDS. Interaction of surfactant molecules in the interlayer space by electrostatic attraction between the positive surface site and anion surfactant (SDS) may also stand behind the domination of comparatively large laminar crystallites and large agglomerates [11, 18]. In this case, intercalation of the anionic

surfactant not only changes the surface properties of clays from hydrophilic to hydrophobic, but also increases the basal spacing of the clay interlayer's [19].
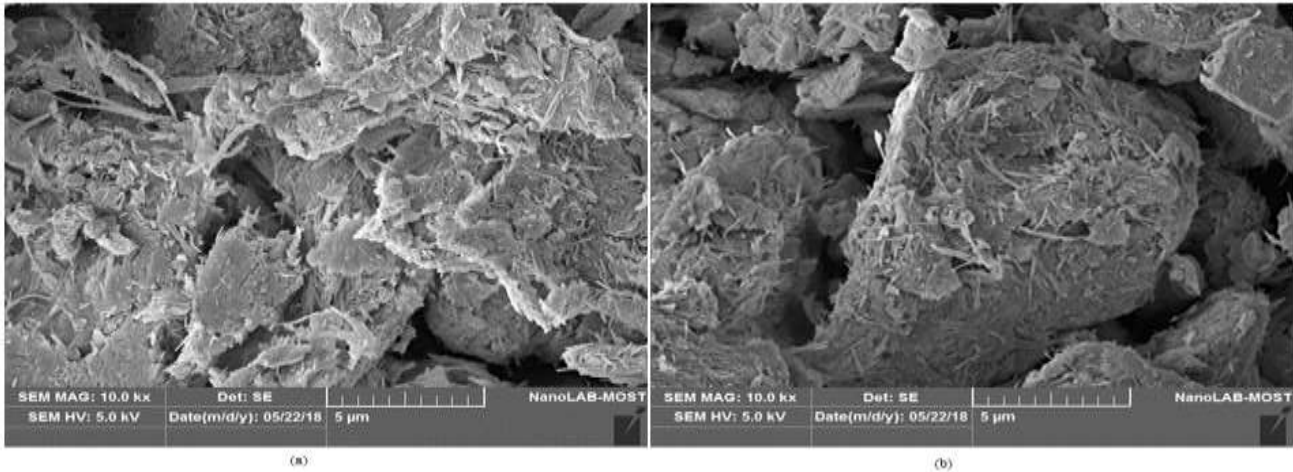

Figure 3: SEM photomicrographs for ATP (a) and ATP-SDS (b)

XRD Analysis of ATP and ATP-SDS

The XRD analyses of ATP and ATP- SDS were shown in Figure (4). Figure 4a showed the typical diffraction peaks at $2\theta = 8.58°$ (110), $19.82°$ (011), and $29.42°$ (100), Figure 4b showed no change in ATP mineral clay after modified with SDS,which proves that SDS did not change original crystal structure of attapulgite[20].
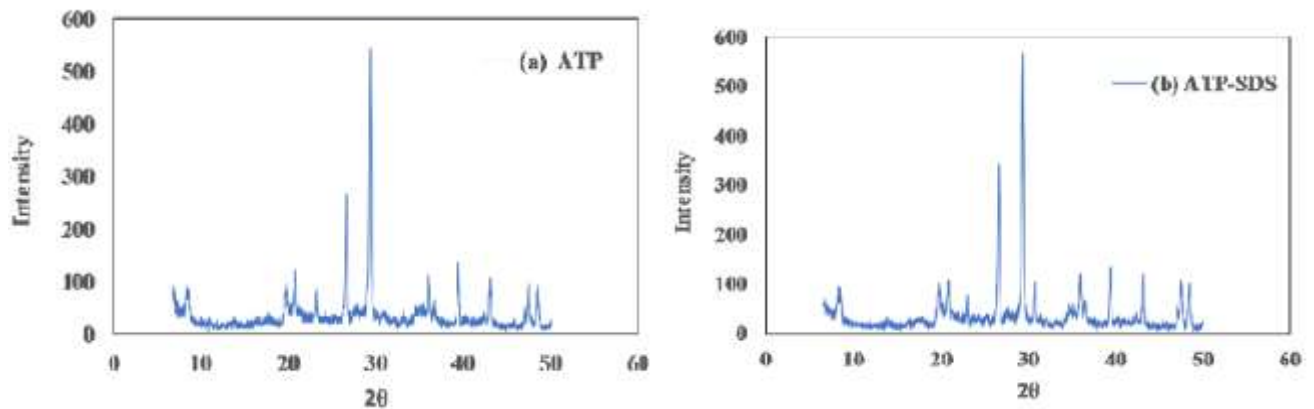

Figure 4: XRD patterns of ATP (a) and ATP-SDS (b)

Effect of Amount of Adsorbent

The effect of ATP and ATP-SDS dosage on removal of CV^+ dye was studied at $25°C$ and initial concentration of 250 mg/L is shown in Figure 5. When the sorbent dosage increased from 0.05 to 0.2 g, the percentage of dye removal (R %) onto ATP and ATP-SDS increased from 97.0518 to 97.0575% and 98.6727 to 99.6828%, respectively. After adsorbent dosage of 0.2g, both surfaces showed no effect on the removal and adsorption are nearly constant (97.0575 and 99.6828% for ATP and ATP-SDS respectively). This increase can be explained due to the abundance of free adsorbent sites and the high concentration gradient between the solution and the solid adsorbent [21].
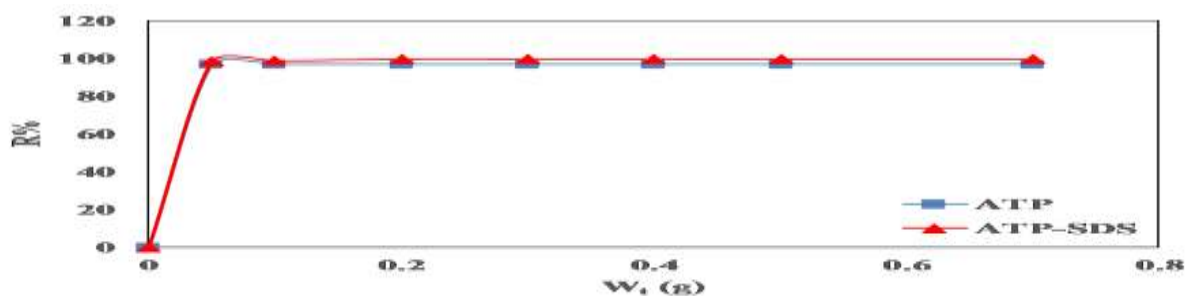

Figure 5: Effect of adsorbent dose on the adsorption of (CV+) dye on ATP and ATP-SDS

Effect of Contact Time

The effect of contact time on the adsorption of CV^+ onto ATP and ATP-SDS at laboratory temperature (25^oC), initial concentration of 250 mg/L and 0.2 g of adsorbents was examined. The adsorption capacity of CV^+ showed rapid increase with time and reached a constant value at a certain time. The equilibrium time required for the adsorption process of CV^+ onto ATP and ATP-SDS was found to be 5 min for ATP and 2 min for ATP-SDS, Figure 6.
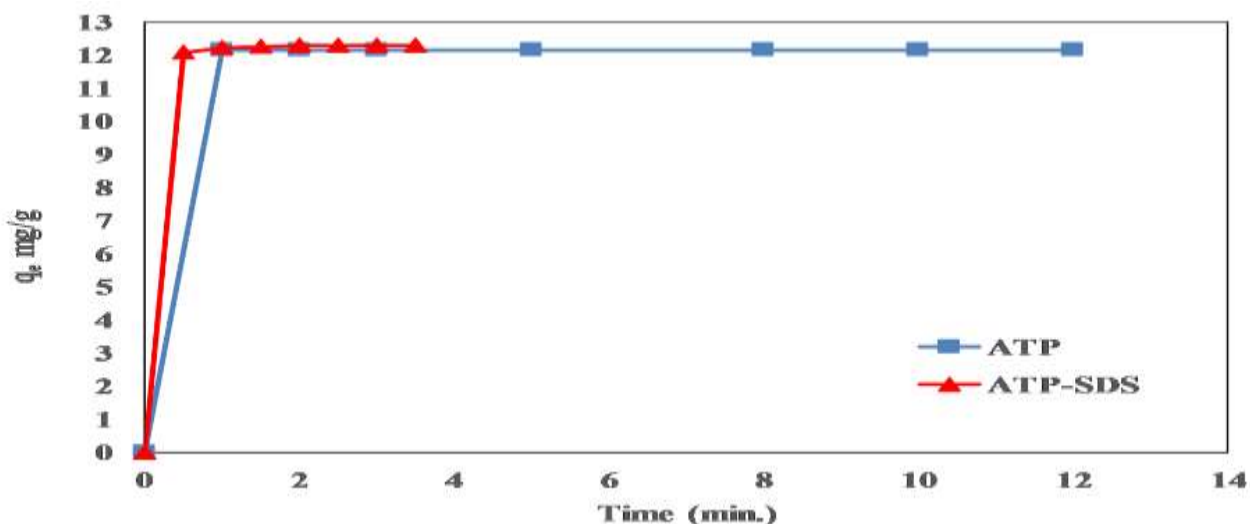

Figure 6: Effect of contact time on adsorption of (CV^+) onto ATP and ATP-SDS at 25 ^oC

Effect of Solution pH

The effect of pH on the adsorption capacity of CV^+ onto ATP and ATP -SDS was investigated at concentration of 250 mg/L, 25^oC and adsorbent dosage of 0.2 g. It was found that there is a linear relation between pH value and the adsorption capacity of CV^+ onto ATP, Figure 7. This may be related to the formation of protonated form of CV^+; while, lower pH, the surface of the adsorbent becomes protonated which results in lower adsorption of the cationic dye [22]. For ATP – SDS surface in alkaline media the adsorption capacity of CV^+ onto ATP-SDS decreases because (electrostatic attraction) between the small ions (OH^-) with the positive part of CV^+ dye faster than the attraction of the cationic dye to the surface [23].

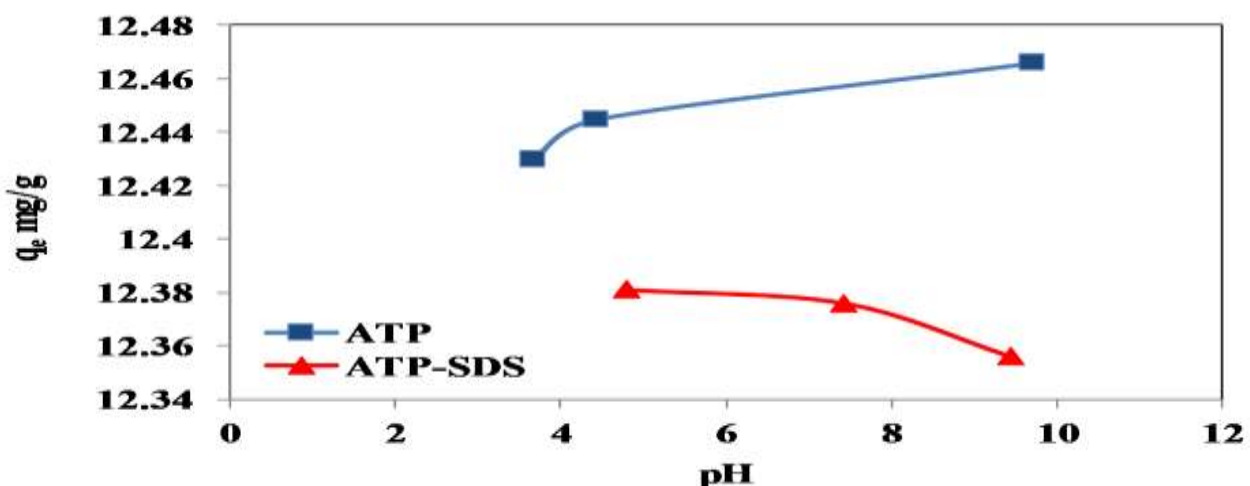Figure 7: Effect of pH on the adsorption of (CV+) dye on ATP and ATP-SDS

Adsorption Isotherms

In current study, three isotherm equilibrium models, namely, Langmuir, Freundlich and Temkin were used to analyzed the equilibrium data and describe the adsorption type.

The Langmuir model is presented as follow [24]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \left(\frac{1}{q_{max}}\right) C_e \qquad (3)$$

Where q_{max} (mg/g) is the maximum amount of the CV^+ per weight unit of ATP to form a complete monolayer surface bound. K_L is the Langmuir constant in (L/mg) which can be calculated from plotting C_e/q_e against C_e, while C_e and q_e are the concentration at equilibrium (mg/L) of dye and the amount

adsorbed (mg/g) of dye onto ATP and ATP-SDS. The K_L and q_{max} were estimated by plotting C_e/q_e against C_e.

The Freundlich isotherm which normally used to describe the adsorption of heterogenous systems [25].The equation is shown:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (4)$$

Where K_f (slope, mg/g) and n (intercept, unit less) are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The K_f and n calculated by plotting Log q_e Vs Log C_e.

The Temkin can be calculated using equation (5) [26]

$$q_e = B \ln K_T + B \ln C_e \qquad (5)$$

Plotting q_e Vs ln C_e enables the determination of the Temkin constant (K_T and B).

Table 2 summarizes the isotherm parameters and their correlation coefficients, R^2. From the results shown in the table, we observe the non-applicability of the Langmuir isotherm. In conformity the high correlation coefficient in Freundlich and Temkin equations ($R^2 >$ 0.7324) at all temperatures, it shows that the Freundlich and Temkin isotherms are the

best fit of experimental data than the Langmuir model. In Freundlich isotherm, when n values being between 1 and 10, the removing process will be useful adsorption [27]. The n values for ATP and ATP-SDS are equal or more than 1 for all systems indicate favorable for corresponding adsorption. Furthermore, the values of K_f increased when the all temperatures increased for all adsorption systems of CV^+ by ATP and ATP-SDS except the adsorption of CV^+ onto ATP at 318 K which decreased to some extent.

Table 2: Langmuir, Freundlich and Temkin isotherm constants for the adsorption (CV+) by ATP and ATP-SDS

Isotherm	Adsorbent	298 K			308 K			318 K		
		K_L (L/mg)	q_{max} (mg/g)	R^2	K_L (L/mg)	q_{max} (mg/g)	R^2	K_L (L/mg)	q_{max} (mg/g)	R^2
Langmuir	ATP	0.0044	555.55	0.0578	0.0188	175.44	0.0507	-0.0171	-192.31	0.0365
	ATP-SDS	0.1554	26.39	0.7900	0.3472	23.64	0.8577	0.3908	26.1096	0.8555
Freundlich		K_F (mg/g)	n	R^2	K_F (mg/g)	n	R^2	K_F (mg/g)	n	R^2
	ATP	2.49	1.0257	0.9943	3.3892	1.0708	0.8983	3.3327	0.9539	0.9222
	ATP-SDS	5.11	2.0876	0.8951	6.6603	2.0703	0.8140	7.7714	2.0132	0.7324
Temkin		K_T	B	R^2	K_T	B	R^2	K_T	B	R^2
	ATP	0.7135	10.22	0.9455	0.9056	10.44	0.9615	0.9270	11.40	0.9336
	ATP-SDS	2.3847	4.89	0.8151	3.6142	5.2059	0.8120	4.2936	5.61	0.7974

Adsorption Kinetics

In this study two kinetic models were used to explore the behavior of the adsorption process and to test the mechanism of the CV^+ adsorption and also to examine the

$$\ln (q_e - q_t) = -k_1 t + \ln q_e \qquad (6)$$

Where, q_e and q_t (mg/g) are the amounts of (CV^+) adsorbed at equilibrium and at time (t), respectively, k_1 is the rate constant (min^{-1}), which were obtained from the slope of the

$$T/q_t = 1/k_2 q_e^2 + t/q_e$$

Where k_2 is the rate constant of (PSO) adsorption calculated from the slope of

experimental data. The adsorption data were analyzed using the pseudo-first-order (PFO) and pseudo-second-order (PSO).

The linear form of PFO is given as follows [28, 29]:

linear plot of ln ($q_e - q_t$) Vs (t) , as shown in Figure 8.

The (PSO) kinetic model can be expressed as in equation (7) [30]:

$$(7)$$

plotting t/q_t against time (t) as shown in Figure (9).

The values of q_e, k_1, and k_2 are listed in Table 3.There is an agreement between experimental q_e and calculated q_e values for the (PSO) model. In additional, the values of correlation coefficient (R^2) indicate that adsorption mechanism of CV^+ onto the ATP and ATP-SDS were fitted well to the PSO model.

Table 3: Kinetic parameters for the adsorption of (CV^+) onto ATP and ATP-SDS (C_o 250 mg/L)

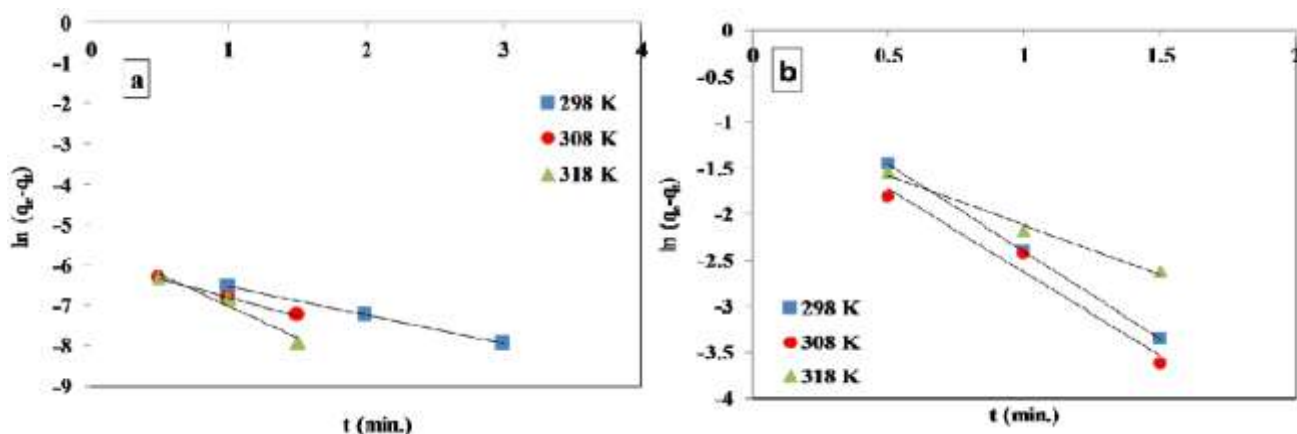| Adsorbent	T(K)	Pseudo-first order				Pseudo-second order		
		K_1(min^{-1})	$q_{e,exp}$ mg/g	$q_{e,calc}$ mg/g	R^2	K_2 (g.mg^{-1}.min^{-1})	$q_{e,calc}$ mg/g	R^2
ATP	298	0.6966	12.2295	0.0029	1	680.27	12.1359	1
	308	0.9218	12.3073	0.0028	0.9952	1136.36	12.1359	1
	318	1.5876	12.3174	0.0044	0.9583	854.70	12.1359	1
ATP-SDS	298	1.9065	12.2783	0.6070	1	6.5449	12.3609	1
	308	1.8122	12.4165	0.4417	0.9655	9.3729	12.3456	1
	318	1.0801	12.4487	0.3530	0.9908	9.3274	12.3762	1

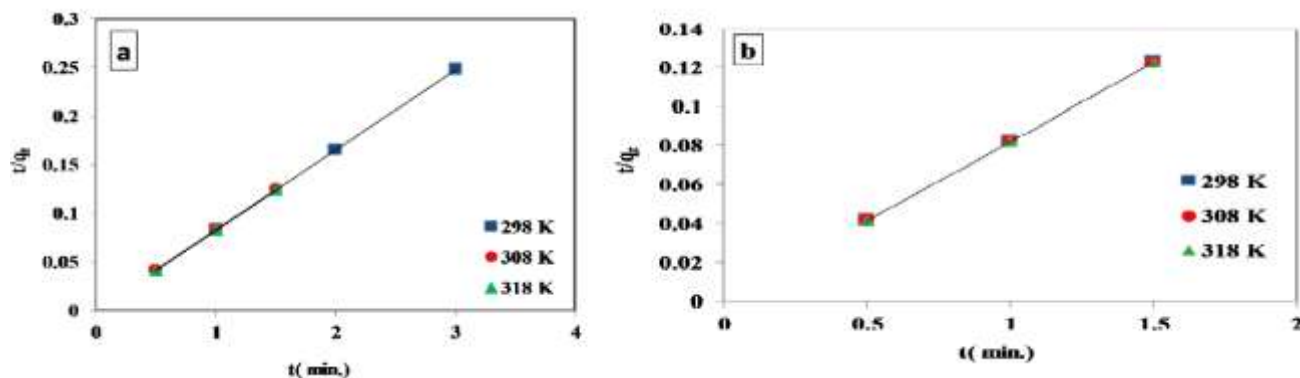Figure 8: pseudo-first-order plot of (CV^+) adsorption onto ATP (a) and ATP-SDS (b)

Figure 9: pseudo-second-order plot of (CV^+) adsorption onto ATP (a) and ATP-SDS (b)

Thermodynamic Parameters

Thermodynamic parameters such as ΔG^0 (Gibbs free energy), ΔH^0 (enthalpy), and ΔS^o (entropy) were calculated by studying the adsorption process at three temperatures (298K, 308K, and 318K).Gibbs free energy ΔG^0 was estimated using the following equation:

$$\Delta G^0 = -RT\ln K_{eq} \tag{8}$$

$$K_{eq} = (q_e/c_e) \times (m/V) \tag{9}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{10}$$

Where (R and T) are gas constant and the absolute temperature respectively. K_{eq} is the equilibrium constant for the adsorption process, q_e(mg/g) is the amount of (CV^+) adsorbed at equilibrium, C_e is the equilibrium dye concentration in solution (mg/L),V is the volume of (CV^+) solution used (L), and (m) is the mass of (ATP and ATP-SDS) used (g).

ΔH^0 (standard enthalpy), and ΔS^o (standard entropy) of adsorption were calculated from vent's Hoff equation (11):

$$\ln K_{eq} = \Delta S^0/R - \Delta H^0/RT \tag{11}$$

By plotting ln K_{eq} versus 1/T (Figure 10) the ΔH^0 and ΔS^o can be obtained from the slope and intercept, receptively. Table 4 shows the thermodynamic functions values at different temperatures. ΔG^0 showed negative values at all temperatures and becomes more negative as the temperature increased, suggesting that the process is more spontaneous at

higher temperature. The positive enthalpy change (ΔH^0)[31] suggest that the adsorption of CV^+ onto ATP and ATP-SDS is an endothermic process and the positive values of entropy change (ΔS^o) indicates the increase in disorder and randomness of solid -liquid interface during the adsorption process[32].

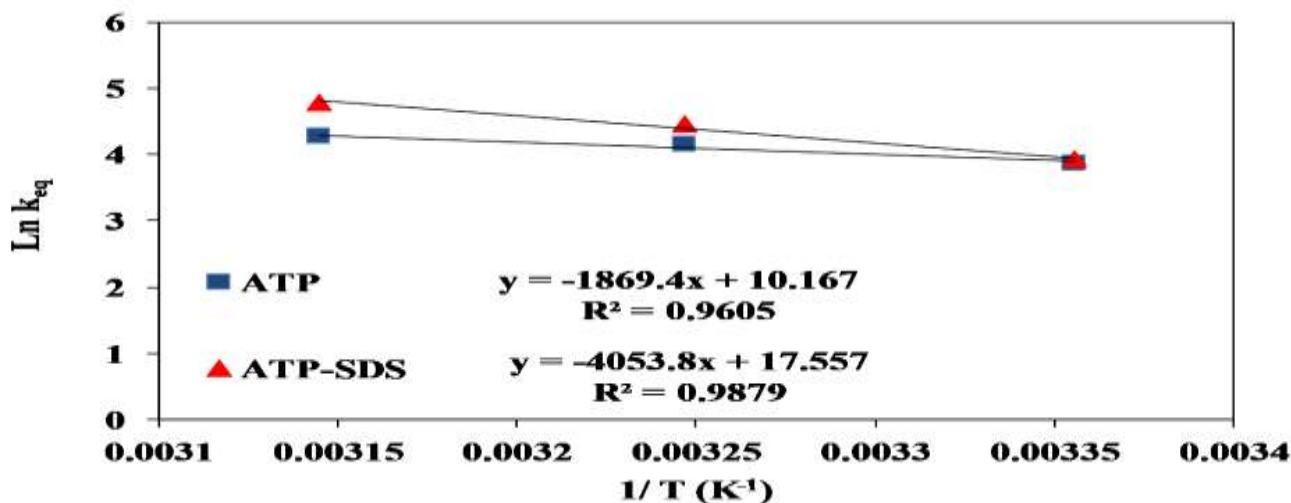Figure 10: Plotting ln k_{eq} Vs 1/T

Table 4: Thermodynamic parameters for the adsorption of (CV^+) by ATP and ATP-SDS

Adsorbent	T(K)	ΔG^0 (kJ.mol^{-1})	ΔH^0(kJ.mol^{-1})	ΔS^o (J. K^{-1}.mol^{-1})
ATP	298	-9.5904	+15.542	+84.528
	308	-10.6096		
	318	-11.2729		
ATP-SDS	298	-9.7277	+33.703	+145.969
	308	-11.3931		
	318	-12.6372		

Conclusions

In this study, an Iraqi attapulgite (ATP) and its modified form (ATP-SDS) were tested for the adsorption of CV^+ dye from aqueous solutions. The results indicated a higher adsorption of CV^+ using both Adsorbents and

the Freundlich and Temkin models showed better fit of experimental data than Langmuir model. The values of thermodynamic functions (ΔG^o, ΔH^o and ΔS^o) obtained indicated that the CV^+ adsorption was endothermic, spontaneous and randomness increasing for both adsorbents.

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