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Thermodynamic and Kinetic Study for Carmine adsorption on poly p-toluidine surface

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Abstract

In this approach, poly p-toluidine(PPT) was prepared based on the literature. The adsorption of carmine on the surface of poly p-toluidine(PPT). Different conditions affecting the adsorption process such as equilibrium time, initial concentration of studied dye , amount of polymer, and pH factor were studied. Isotropic experiments were performed and equilibrium adsorption data were fitted to the Langmuir and Freundliche isotherms. The thermodynamic and Kinetic study has also investigated the results that adsorption of carmine follow pseudo-second order. Also, the carmine was successfully extorted after adsorption. The morphology of surface was studied by scanning electron microscopy(SEM).

**Keyword :** Poly p-toluidine ,adsorption , Thermodynamically, kinetically.

Introduction
There are many synthetic dyes that are widely used in industries, photography, printing and textile dyeing, or as additives to some petroleum products and cosmetics, as well as their use in countless broad fields[1,2]. Dyes are also considered one of the serious environmental problems because they have an effect on the water environment and humiliated during their discharge into the water[3] . Over 7x105 tons and approximately 10000 different types of dyes and pigments are produced worldwide annually. It is estimated that 10 to 15% of the dye is lost in the effluent during the dyeing process[4]
which leads to their impact on the water environment and on the organisms present in it in general and on humans in particular, as they are considered one of the factors causing cancerous diseases, especially the amino dyes compounds[5]. After the exacerbation of pollution problems in previous years, many researchers have tended to think about finding appropriate ways to remove these pollutants, which have become a real problem, especially at low levels and concentrations
The techniques used to treat water pollution are adsorption on some surface, some chemical methods such as silica gel, activated carbon, ozonation, and osmosis reverse. One of the most important techniques used is adsorption due to its high efficiency of.

Water purification, its easy use for this purpose and its low economic cost by comparison with other methods [6].

The poly aromatic amines which is one of the most potentially useful conducting polymers and has received considerable attention in recent years because of its low cost of synthesis, easy process ability and environmental stability. It's generally used in rechargeable batteries, electro chromic devices, chemical sensors, photo voltaic cells, flexible LED, electromagnetic interference (EMI) shielding, solar cells, anticorrosion coatings, sensors etc.[7 ,8]. Conducting polymers have emerged as effective adsorbents in the field of waste water treatment due to their cost effectiveness and higher environmental stability[7]. The present investigation deals with the application of Poly p-toluidine, a potential conducting polymer, for the removal of a toxic dye carmine schem1 , as a surface for adsorption of neutral dye , the adsorption efficiency were studied and the factors affecting of adsorption
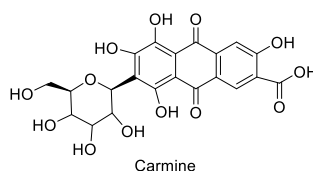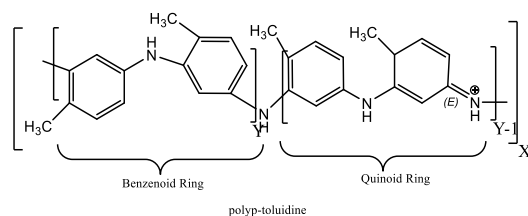

Scheme 1: Structure of carmine

2. Experimental

2.1. Martials

   p-Toluidine and Ammonium persulfate supplied by Fluka, Ammonium hydroxide supplied by sigma, ,carmine supplied by M&B ,Hydrochloric acid by J.T.Baker.

2.2. Preparation of poly p-Toluidine (PPT)(Adsorbent)

The (0.054) mole of p-Toluidine monomer dissolved in 54ml of an aqueous solution of 1M HCl in the round flask (250ml)was brought to a temperature of 0°C to 5°C in an ice bath , with stirred by a magnetic stirrer. 0.54M of ammonium persulphate was dissolved in 200ml of 1N HCl second solution was added to the first solution drop by drop. After a few minutes of the solution of the oxidant, the reaction became darker green by the time. Then the resulting polymer was treated with 120 ml of 25% ammonium hydroxide solution to obtain a formula of emeraldine base show schame 2. hours[9 ,10].

Scheme 2: Structure of polyp-toluidine

2.3. Adsorption Experiment

  The concentration of dye was determined by UV-vis spectroscopy . 20mg of **polyp-toluidine** was added to 50 ml of Carmine solution of different initial **concentrations**

(100-500 ppm) and shaken at 175 rpm for 24 h**r.** at room temperature. The filtered samples were collected at different time periods **from 5-240min.**. The amount of **carmine** dye per unit mass of **polymer** (mg/g) at any time (qt) and at equilibrium (qe) was calculated using Equations (1) and (2)[8].

$$q_t = \frac{(C_o - C_t)}{m} v \qquad (1)$$

$$q_e = \frac{C_o - C_e}{m} v \qquad (2)$$

Where Co, Ce and Ct are the initial concentration, equilibrium concentration and at any time dye concentration, m and v are the polymer mass (g) and the solution volume (L). The removal percentage was calculated using Equation (3).

$$R \% = \frac{A_o - A}{A_o} \times 100 \qquad (3)$$

where Ao is the initial absorbance of samples[11,12].

.

3.Results and discussion

3.1 Characteristics

Interprets the infrared spectrum that was measured at the University of Basra, College of Science, using a potassium bromide disc spectrophotometer. A Shimadzu FTIR-8400s by KBr disc technique for the IR investigation is represented in Figure (1) (a) of polyp-toluidine before adsorption, an absorption band appearing in the region 813.99 cm^{-1} C-H out plane deformation, and in the region 1114.98cm^{-1} C-H in plane deformation. An absorption band appearing in the region 1261.49 cm^{-1} could be attributed to stretching vibration for the C-N group. The absorption bands appearing at 1400.37 cm^{-1} and 1516.10 cm^{-1} attributed to stretching vibration for C=C in the benzenoid ring and in the quinoid ring respectively . The CH sterching of methyl group at 2920.32 cm^{-1}. The broadband at 3375. 54 cm^{-1} for starching vibration for the NH group. In Figure 1b polyp-toluidine after adsorption we showed all peaks of poylp-toluidine slightly shifted and intensity changed which indicates the bands of carmine with polymer, because of hydrogen bonding between amine group of polyp-toluidine and functional group of carmine. Absorption band of C-H in the peak C-H in plan deformation shifted to region 1126.43 cm^{-1}in carmine with polymer. Also N-H group shifted and board band   to region

337.50   cm^{-1}.
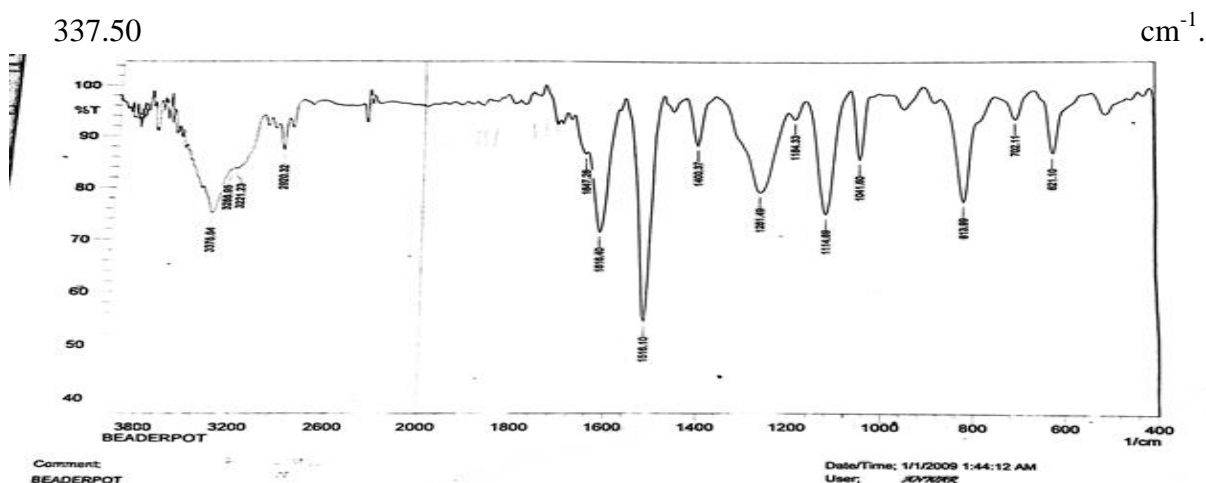
a
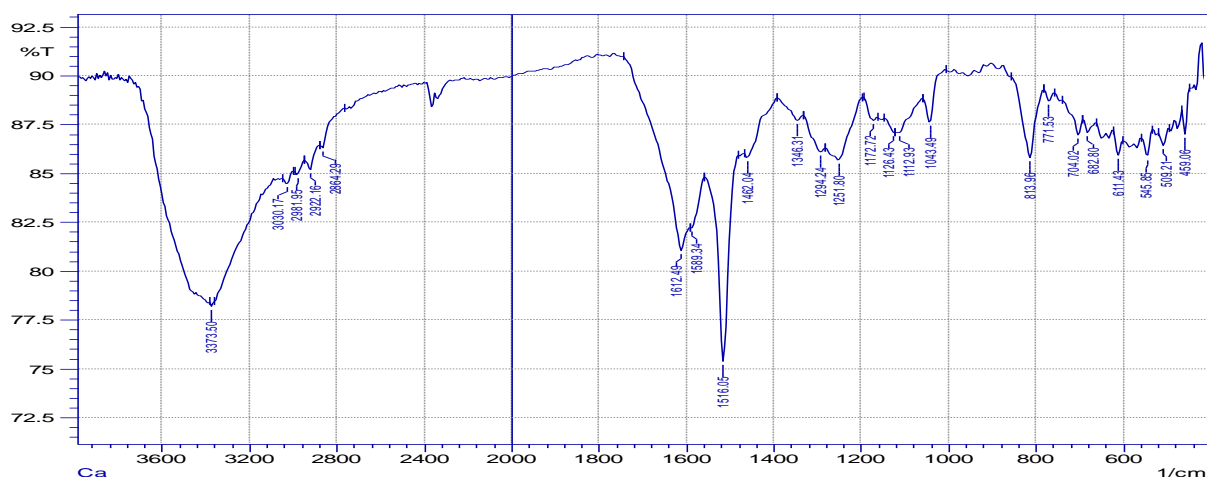
b

Figure 1:FTIR of (a) polyp-toliudin pure   (b)polyp-toliudin with carmine

3.2.The factors effecting of adsorption

To explain the adsorption mechanism, how it is obtained and the factors affecting it, which is important to choose the best results for designing adsorption models and to obtain important results in the processes of removing pollutants by the adsorption method. The initial dye concentration has an important role as a driving force to overcome the resistance to mass transfer of adsorbents between the liquid and solid phases.[11][12] .Carmine neutral dye in figure (2and 3) show variation of concentration carmine initial concentration of carmine 400mg\L in the presence of 20mg of polymer. We notice that the adsorption rate decreases with the increase in the initial concentration of the dye ,at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration[13][14] , The equilibrium time of carmine is 30 minutes.
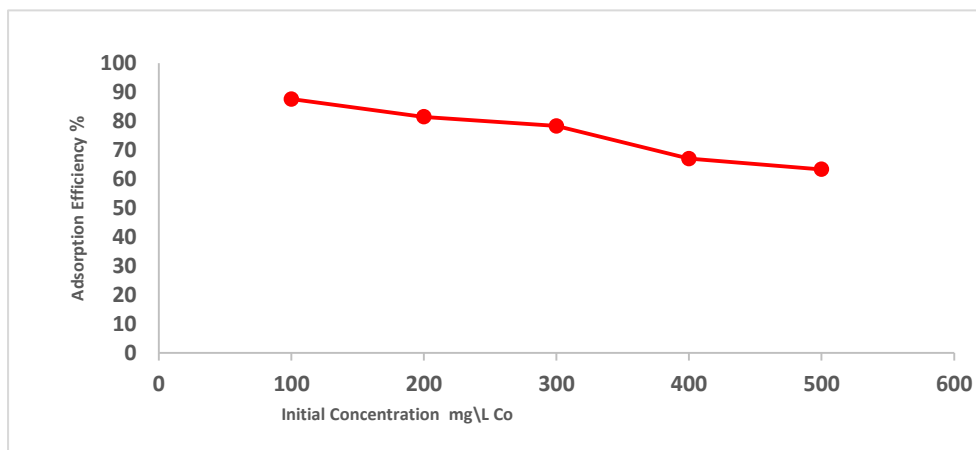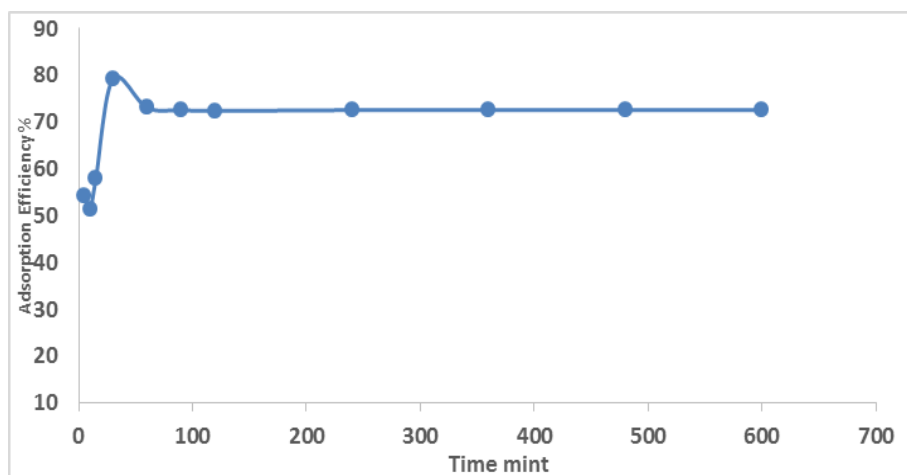
Figure 2: (a) Effect of Initial Concentration

Figure 2: (b) Effect of equilibrium time

Different weight of polymer taken with 500mg\L from the carmine notes on Figure (3) an increased percent adsorption efficiency with increasing of weight of polymer, after this stat at weight 0.15g decreasing percent due to the saturation of the polymer with carmine dye.
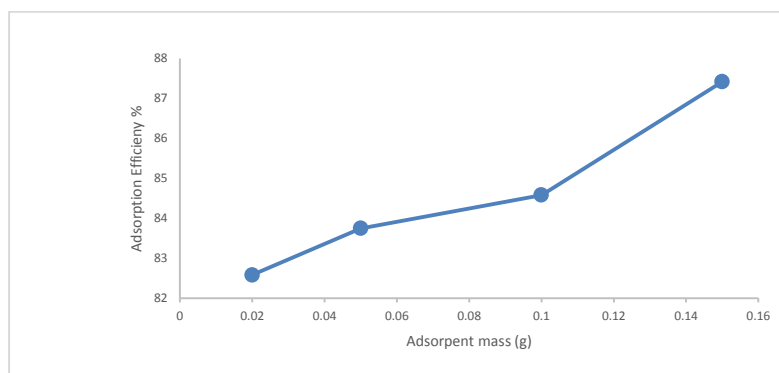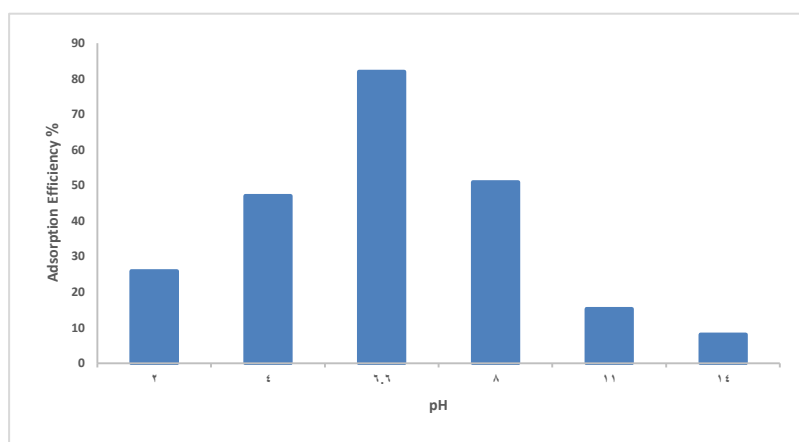
Figure 3: (a) Effect of weight of polymer

Figure 3: (b) Effect of change pH on polymer

The pH plays an important role in the adsorption of the dye ,from Figure 3b an increase in the percent of adsorption of the dye at 6.6 pH ,this is due to the interaction of the dye anion with the positive sites of the polymer ,while the adsorption rate decreased in the high acidity and high basic medium due to the lack of anionic centers to interact with the polymer .

2.4.2 Study adsorption isotherms

The adsorption isotherms were studied in which a weight 0.02g was taken from polymer with carmine concentrations (100-500 mg\L) and placed at different temperature degrees(20,30,40)^{o}C   and the amount   adsorbed material C_e was plotted against the equilibrium concentration q_e in order to obtain the general shape of the adsorption curves[15] as shown in Figure 4
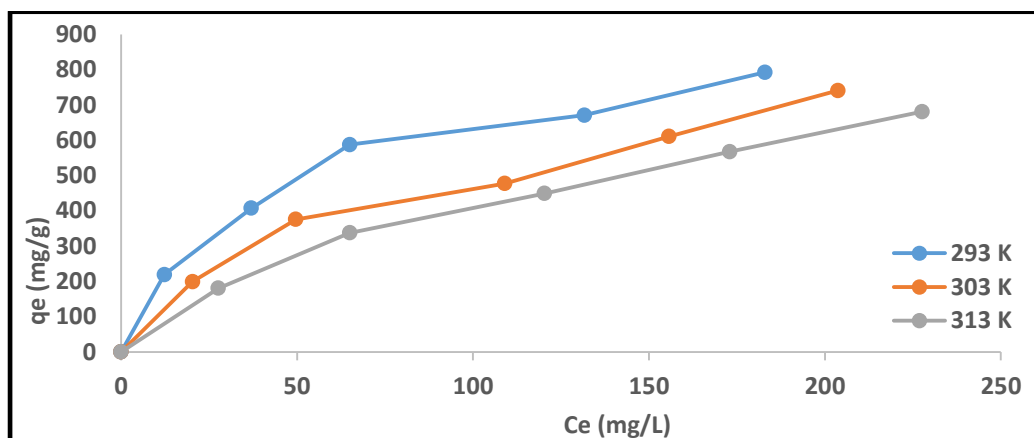
Figure 4:Adsorption isotherm for carmine with polymer

The results of the adsorption of carmine on polymer according to the classification of Giles follow the pattern of L2 [16]where the orientation of the adsorbent particles is horizontally on the surface [17]as shown in the Figure 5a, which shows that the amount of adsorbent at a temperature of 313 ^{o}k is the highest, then after This decreases slightly at the rest of the temperatures until it reaches the level of saturation at different temperatures, which indicates that the adsorption process is exothermic .

There are several adsorption isotherms that explain the results obtained from the Langmuir equation (4) [18]. Where the equation was applied to adsorption of carmine on polymer .from the slope and intersection, drawing Ce \ qe versus Ce   should be linear according to the following equation, where qe is the amount of dye adsorbed by polymer at equilibrium ,KL is the Langmuir constant in L\mg and a is the adsorption capacity in mg of dye\mg of polymer   as shown in Figure 5a

$$\frac{Ce}{qe} = \frac{1}{ak} + \frac{Ce}{a} \qquad (4)$$

Where from Freundlich equation (5) [19] was applied to adsorption of carmine on the polymer from the slope and intersection drawing ln q_e versus ln C_e according to the following equation, as shown in Figure 5b

$$lnqe = lnKf + \frac{1}{n}\ln Ce \qquad (5)$$

The Langmuir constants represented, q_m, K_L, and R^2, and the Freundlich constants represented n, which expresses the intensity of adsorption, is the amount of curvature of the curve in which the surface is saturated, and K_f which expresses the adsorption capacity of the surface, and the constants are shown in the Table(1)

Table (1) Langmuir and Freundlich constants

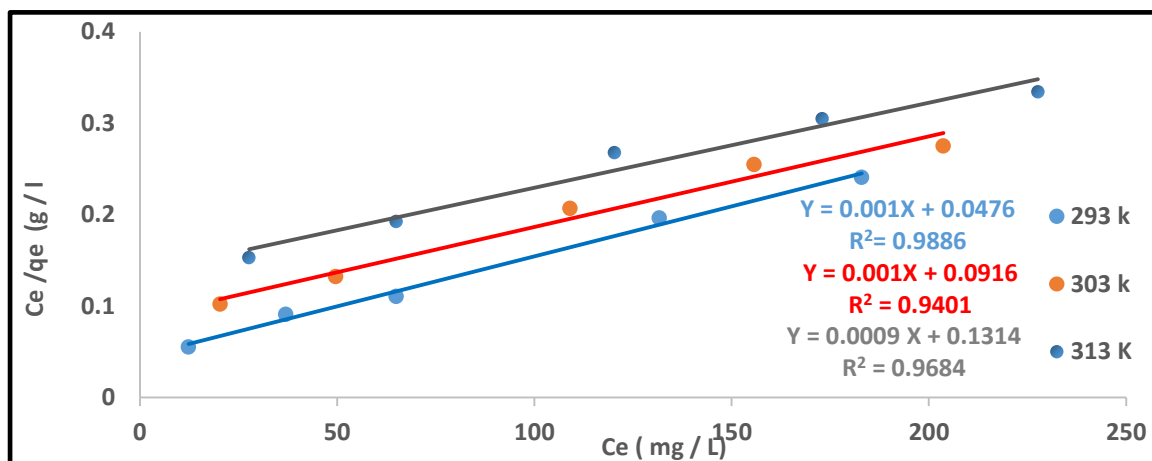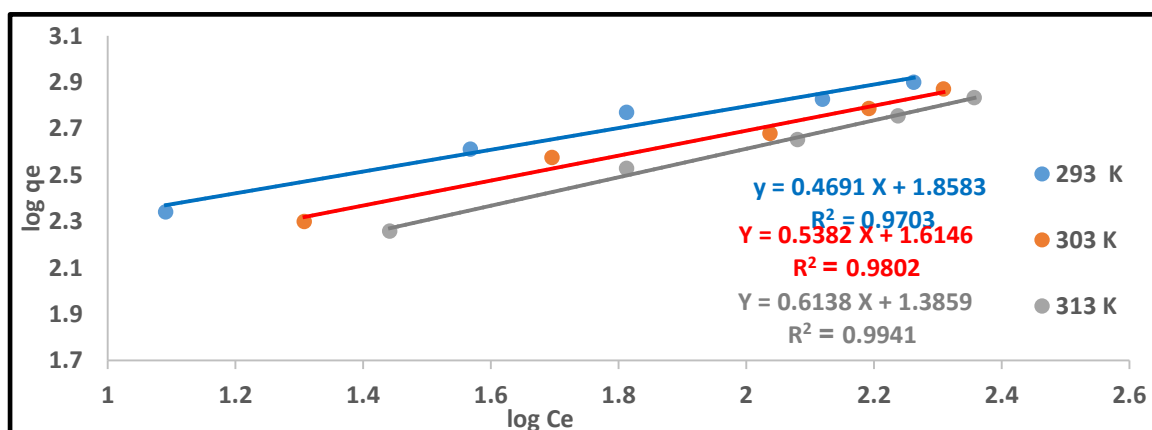| Dye	Temp.K	Longmire Constant			Freundlich Constant		
		q_m (mg\g)	R^2	KL	n	R^2	KF
Carmine	293.15	1000	0.9886	0.0210	2.13	0.9703	6,412
	303.15	1000	0.9401	0.0109	1.85	0.9801	5.025
	303.15	1111.11	0.9684	0.0689	1.62	0.9941	3.996

Figure 5: (a) Langmuir isotherm

Figure 5: (b) Freundlich isotherm

2.4.3 Thermodynamic Study

Thermodynamic parameters, namely the standard Gibbs free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) are estimated as follows. The change in ΔG^0 of the process is related to equilibrium constant Keq by the following equation:

$$\Delta G° = -RT \, lnKeq \qquad (6)$$

R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K).When Ko can be calculated by equation[20] :

$$Keq = \frac{qe}{Ce} \qquad (7)$$

Gibbs free energy change is also related to the enthalpy change (ΔH^0), and entropy change (ΔS^0) at constant temperature by the following expression[21]

$$\Delta G° = \Delta H° - T\Delta S° \qquad (8)$$

Combining equations (6) and (8) gives the integrated form of the Vent Hoff equation:

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (9)$$

Therefore, the values of ΔS^0, ΔH^0 and ΔG^O listed in Table (2) can be obtained from the intercept and the slope from the plot of ln Keq versus (1/T), respectively . the bonding process of particles adsorbed to the surfactant is in a different order from its form in solution the affinity of the adsorbent for adsorbed. [22,23].

The effect of temperature on the surface of the polymer of the carmine was studied, and a Vent Hoff relationship was drawn between ln Keq and 1\T as in the Figure6

Table (2) the values of ΔS^0 and ΔH^0 and ΔG^o

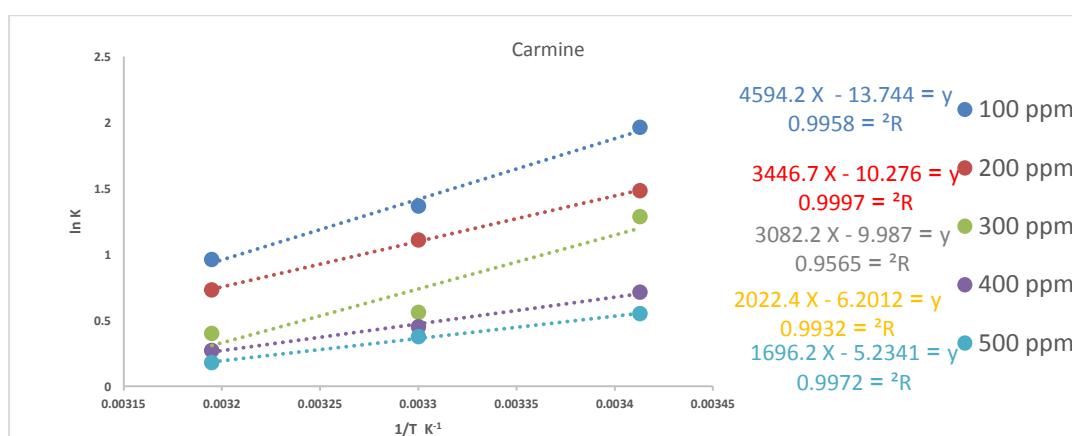| Dye	C_o ppm	ΔG^O KJ.mol^{-1}			ΔH^O KJ.mol^{-1}	ΔS^O J.mol$^-$k
		293.15 K	303.15 K	313.15 K		
	100	-4.777	-3.44	-2.50	-38.19	-114.23
Carmine	200	-3.612	-2.79	-1.90	-28.65	-85.43
	300	-3.130	-1.413	-1.043	-25.62	-83.03
	400	-1.734	-1.13	-0.70	-33.93	-51.55
	500	-1.338	-0.944	-0.46	-14.10	-43.51

Figure 6: Vant Hoff curved for carmine on the polymer

2.4.4 Kinetic Study

The Lagergren equation was used to derive the equation for the velocity of the adsorption process on the surface of the polymer and the equation of the pseudo-first-order[24], and it was studied at temperatures (20,30 and 40°C) at the initial concentration of carmine in the neutral solution, can be explained by plotting the adsorption capacity ln(qe-qt) versus time as shown in Figure7a It was found that the extracted value of qe from the drawing is far from the practical value. Therefore, the pseudo-second-degree equation[25] was applied, as shown in Figure 7b and plotting the t\qt versus time. By applying the pseudo-second-degree equation, he found that the value of qe computed from the equation is an approximation to its practical value, and Table(3)shows the Lagergren constants obtained from the pseudo-first-order equation[26] and the pseudo-second-order equation[27].

$$\ln(qe - qt) = \ln qe - K1t ----- (10)$$

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{1}{qe}t ----------- (11)$$

Table (3)The Lagergren constants of pseudo-first-order equation and the pseudo-second-order equation.

Dye	Temp.K	qe(exp.) mg\g	Pseudo-first-degree			Pseudo-second-degree		
			q_e (mg\g)	R^2	K1	q_e (mg\g)	R^2	K2
Carmine	293.15	667.5	5.424	0.964	0.0407	666	0.9998	0.0020
	303.15	629.1	48.92	0.957	0.033	625	0.9997	0.0021
	303.15	610.8	62.00	0.976	0.045	625	0.9998	0.0018
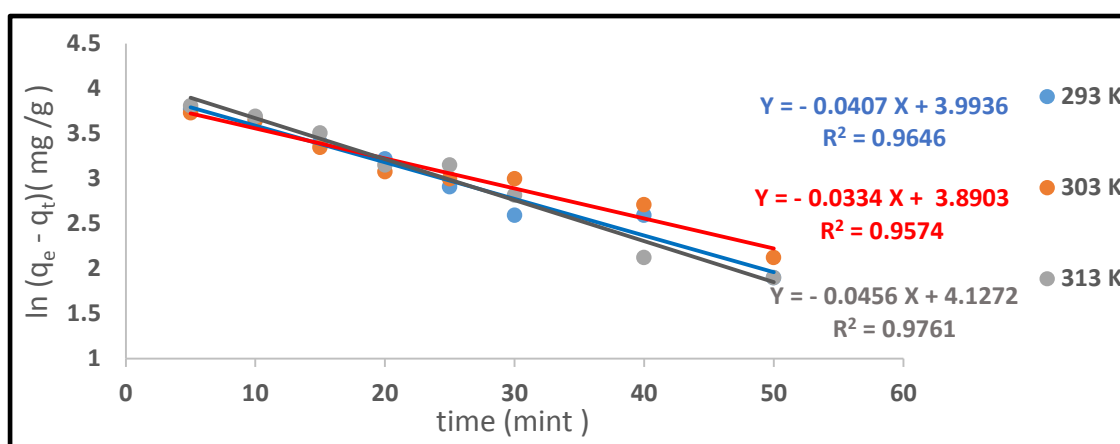
Figure:7 a Lagergren pseudo-first equation

Y = 0.0015 X + 0.0011
$R^2 = 0.9998$

Y = 0.0016 X + 0.0012
$R^2 = 0.9997$

Y = 0.0014 X + 0.0016
$R^2 = 0.9998$

● 293 K
● 303 K
● 313 K
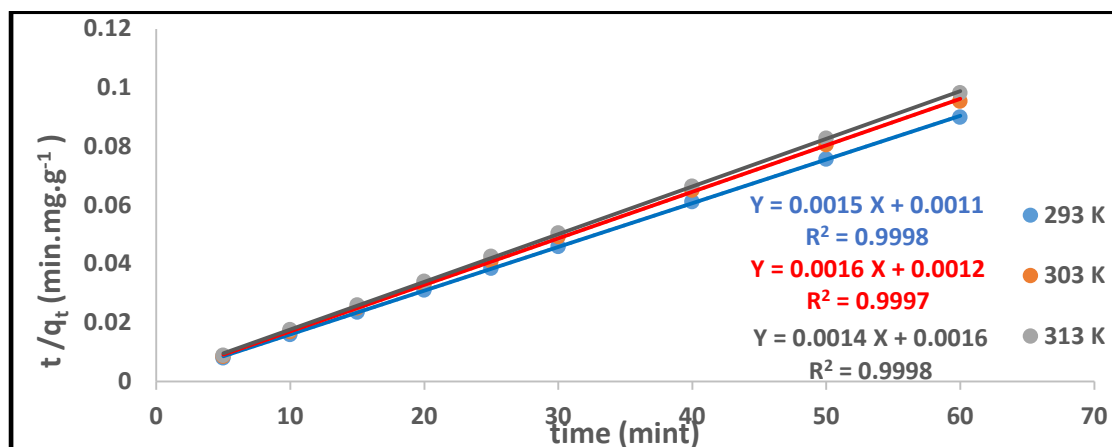
Figure:7 ,b Lagergren pseudo-second equation

2.4.6 Desorption experiment

After the adsorption process, carmine was extracted from the medium at a temperature of 343.15K, then the absorbance was measured, and the results showed the possibility of recovering the dye after the adsorption process, as shown in the Figure(8).
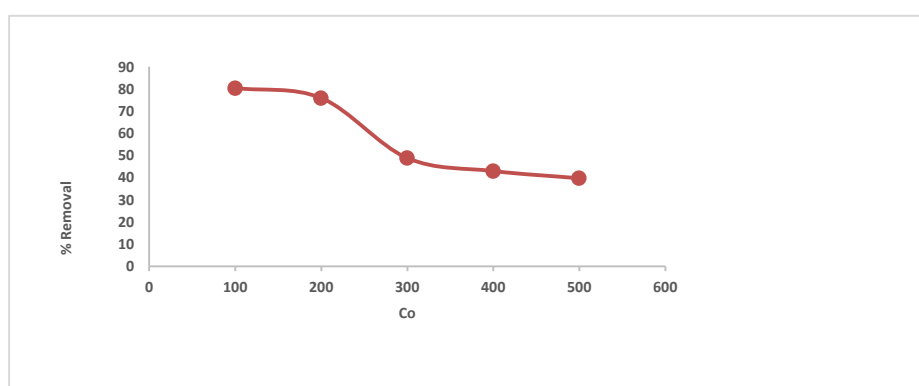

Figure 8: desorption process

2.4.7 Morphology of adsorbent

The surface morphology of polymer before and after adsorbent studied by scanning electron microscopy (SEM) images was studied to evaluate the morphology and changes of adsorbent surface before and after dye adsorption Figure (9a)show the SEM images of pure polymer before adsorption illustrates tubular shape but in Figure (9b) after adsorbent with dye we note homogeneity of surface .
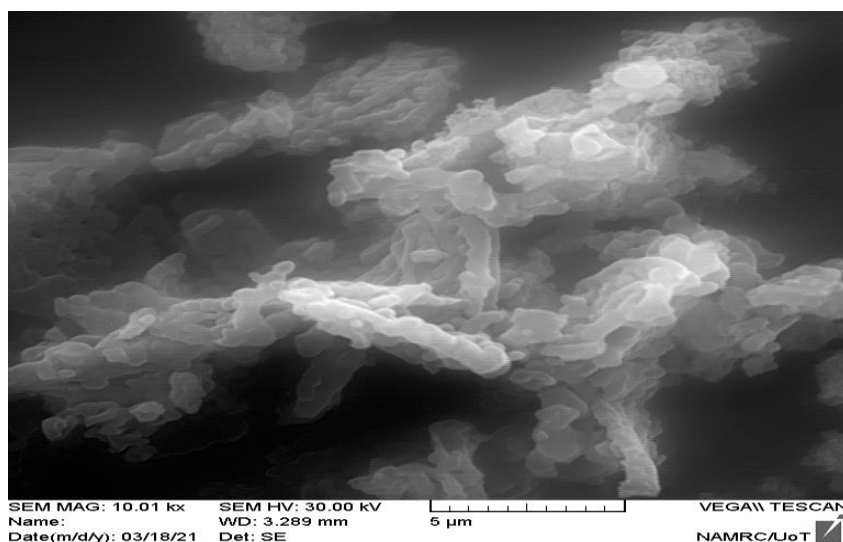
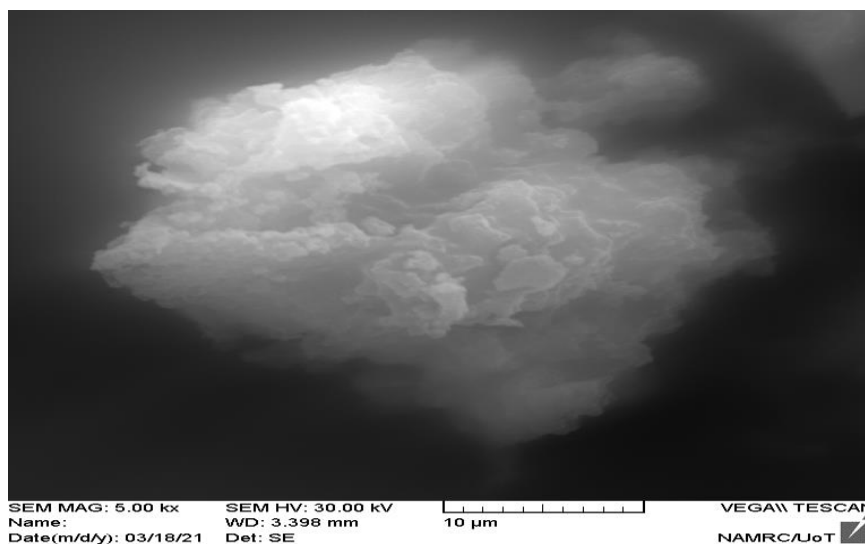Figure (9) SEM image of adsorbent (a) pure poly p-toluidine before adsorbent

Figure (9) SEM image of poly p-toluidine with Carmine after absorbent .

Conclusions

Through the thermodynamic and kinetic study of adsorption, the success of poly p-toluidine for adsorption of neutral dye. Through the study of surface formation by SEM, homogeneity of the dye with the polymer confirms the success of the adsorption process and the possibility of activating the surface and using it again for adsorptio

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الملخص

في هذه البحث، تم تحضير البولي بارا توليدين بالاعتماد على الادبيات. لدراسة امتزازالكارمين. تم دراسة الظروف المختلفة التي تؤثر على عملية الامتزاز مثل وقت التوازن ، والتركيز الأولي للصبغة المدروسة ، وكمية البوليمر ، وعامل الأس الهيدروجيني. تم دراسة ايزوثرمات الامتزاز (لانجموير وفريوندليش). لقد أوضحت الدراسة الديناميكية الحرارية أن عملية تفاعل امتصاص صبغة الكارمين المدروسة كانت تلقائية من قيم ΔG السالبة ، وتفاعل امتصاص الأصباغ الطاردة للحرارة بالقيمة السالبة لـ ΔH^o ، بينما كانت القيمة السالبة لـ ΔS^o مؤشراً على أن تكون عملية الترابط بين الجسيمات الممتصة بالمادة الخافضة للتوتر السطحي في ترتيب مختلف عن شكلها في المحلول . حققت الدراسات الحركية أيضًا في النتائج التي تفيد بأن امتزاز الأصباغ يتبع الدرجة الثانية الوهمية. أيضا ، تم ابتزاز الأصباغ بنجاح بعد الامتزاز.تم تشخيص البوليمر المحضر قبل وبعد الامتزازباستخدام تقنية FT-IR و دراسة شكل السطح عن طريق المسح المجهري الإلكتروني SEM .