Removal Dye Disperse red 1 From Waste Water by Using Novel Graft Nano Co-Polymer, As A Health Study

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Abstract
This work was done by synthesis a nano-co-polymer by available monomers through the esterification process, by dissolution by preparing the linear copolymer as the first step in the reaction of Terphthalic acid with glycerol. Then an amount of maleic anhydride was added to the resulting linear copolymer solution to get the nano co-polymer. This nano polymer was characterized by FT-IR spectroscopy, ^{1}H-NMR, and Atomic Force microscopy (AFM), and the average particle height was equal to 8.3 nm, The effect of three different temperatures (298, 308, and 318 K) and four different concentrations (1, 3, 5 and 7 ppm) of nano co-polymer has been studied and it is clear that they play a critical part in the adsorption process, and the experimental results showed that the adsorption of dyes (Disperse Red 1) on the surface of this nano polymer increases when the temperature rises, which means that the process is an endothermic process. The effective of nano co-polymer was also found to complete the effective bile removal from aqueous solution.
Keyword: Graft nano co-polymers; Nano co-polymer; co-polymer; Characterization; Pollutions; Adsorptions; Disperse Red 1.

1. Introduction

Nanomaterials are materials with a small size range (1 to 100 nm). Controlling the size and Fig of the nanoscale enables the characterization, design, installation, and application of materials, systems, and devices [1]. Pollution is one issue that needs great attention. Pollutants must be eliminated because they endanger people, health and aquatic life, and among the most important water pollutants (dyes, organic compounds, heavy metals, medicines and everything that spoils and changes the natural properties of water). Industrial dyes are used in a variety of areas in the modern era, for example, to color textiles, hair, leather, papers, meals and cosmetics [2]. There are many toxic and dangerous dyes, and some of them consume 2% in wastewater after their production, such as painting dyes, and the other 10% used in textile coloring. What increases its danger is water (the universal solvent)[3,4] .Where the dyes show a high solubility in water and make their removal more difficult through traditional procedures, one of the most important of these methods is the adsorption method on the surface of a nanopolymer. Many harmful components from the water system, where we note that many researchers have tended to develop new high-quality materials using nanomaterials, more and larger adsorbents because the particles on the nanoscale interact in a way that is different from what they are in their natural size [5] .Our research also reveals the adsorption of dyes by manufacturing poly(terephthalic acid - glycerol - G - maleic anhydride) nanoparticles and the results obtained The nanopolymer was shown to be quite effective. at getting rid from pollutants.

2. Materials and Mouthed

All chemicals were used in this work as analytical grade.

Synthesis of graft PTGM nanoparticles

Poly (Terphthalic acid-co-Glycerol-G-Maleic anhydride) nanoparticles was synthesis by two steps; The esterification technique was used to make the nanopolymer, and the preparation method is shown below: The initial stage is: They were assembled together in a 200 mL beaker (332gm, 2.0 mol) of terephthalic acid and (50 mL) of dimethyl sulfoxide (DMSO). A thermostat is built into this beaker. Using a magnetic stirrer, gently heat the mixture to 40 °C to form a clear liquid, and add (92gm ,1.0 mol) glycerol to the solution We next gently heat the mixture to 120 °C, then add 25 ml of xylene to the reaction flask in 2-drop increments until the water from the esterification process is drained and the flask is softly heated. After (80 minutes at 145 °C), the heating was stopped because the water no longer prepared the nanopolymer. Then. As suggested by the equation, the reaction beaker was allowed to cool to about 50 °C , as shown in The initial stage 1. In the second stage; We dissolved (0.5 mol, 58 g) maleic anhydride in 10 mL DMSO, heated to 40°C, and added it to the mixture (made in the first step above). The beaker was slowly heated to 90 °C, then droplets of xylene were introduced in batches (2 drops per batch) until the water stopped leaking at

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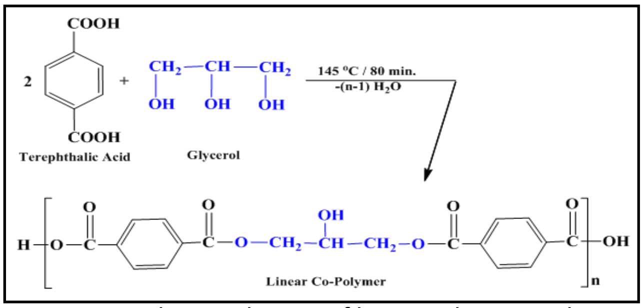
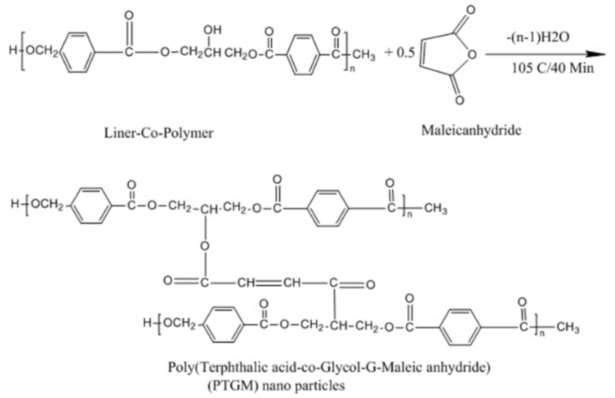
105°C after 40 minutes. To make PTGM nanoparticles. Allow the reaction flask to cool to room temperature before adding cold distilled water to the suspension solution generated after 6 hours. Then, as stated in equation 2, permit the suspension solution to precipitate overnight before filtering, washing with distilled water, and drying.



Equation 1: The initial stage of linear polymer synthesis



Equation 2: The second stage of the Synthesis of graft PTGM nanoparticles

Polymer Purification

Since the nanopolymer can be contaminated in trace amounts by solvents or monomers that did not react or in the presence of other contaminants, it must be filtered. After separation, an appropriate solvent was used to dissolve the synthesized nanopolymer, as well as to precipitate it. A 5% concentration was added while vigorous "stirring" was continued according to the proposed protocols [6]. Polymers and solvents are miscible with non-solvents, separate the solid polymer from the solution as soon as it settles. To increase the purity of the polymer, repeat the melting and re-deposition process three times [7]. After purification, the nano polymer is ready for use. The new composite polymer was dried at 57°C and stored in a vacuum desiccator, to be performed and tested for diagnosis[8].

Adsorption behavior of Graft Nano Co-polymers

The adsorption of a new nano-polymer on dyes was examined using the following technique to generate dye solutions (Disperse Red 1): A solution of Disperse Red 1dye was made by immersing (0.5 g) of the dye in a certain amount of distilled water and then diluted to (1000 ml) to establish a concentration (500 parts per million.From this concentrated solution, the dilute solutions were prepared in concentrations (1, 3, 5 and 7 ppm) by taking the appropriate volume of the concentrated solution and then diluting it with (100 ml) distilled water. Its absorption was measured after 60 minutes of taking the vials containing the solution, which consists of a nanopolymer adsorbent surface with a weight of (0.01) and the dye adsorbent (Disperse Red 1), from being placed in the vibrator at a temperature of 298 K. Then samples were taken from them at successive times and the absorbance was measured through the spectral changes of visible and ultraviolet rays over time. The amount of adsorbed dyes (Disperse Red 1) on the surface of the new nanopolymer was calculated From before the next equation[9].

$Qe = (Co-Ce) .Vsol / Wt$ (3)

3. Discussion and Results

The nanopolymer was generated through the esterification process, and analyzed using (FT-IR, 1H-NMR, AFM) technology. The first step is as follows: The FT-IR spectra of a linear copolymer are depicted in Fig 1, which reveal a strong broad band at 3,423 cm-1 owing to OH alcohols due to hydrogen bonding, as well as a faint band at roughly 2,902 cm-1due to -OH of carboxylic acid, whereas the bands It occurred at around 2902 cm-1because of the carboxylic acid's -OH. CH hybridized with sp3 and sp2 at 2544 and 2,654 cm-1, respectively and the spectra indicated a strong band to the ester group's OC band at about 1726 cm1. The spectra reveals faint sharp bands at 1597 cm1 - 1158 cm - 1 result [1]. Due to the C = C of the benzene ring coupling system, the spectrum reveals faint sharp bands between 1597 and 1158 cm-1 as well as bands between 1284 and 1259 cm-1. The ester adsorption (CO) bands are responsible for these bands, as Van explained. This spectrum matches the linear copolymer's suggested structural structure from the first step.

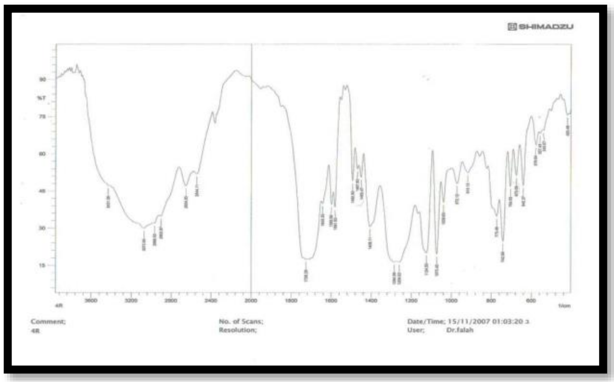


FIG (1): FTIR linear copolymer spectrum.

Fig 2, 1 HNMR spectrum elucidating the signal at 13.24 ppm of the carboxylic acid group proton, as well as the a number of in the 7.53 - 8.10 ppm range for every proton in the aromatic ring, while the signals that appeared at 6.27 - 6.46 ppm for four methylene protons in the copolymer structure, and doubled at 4.24-4.50 ppm for methyl protons, while the triple signal appeared at 3.44 because of the alcoholic proton and our polymer was confirmed by this spectrum [2].

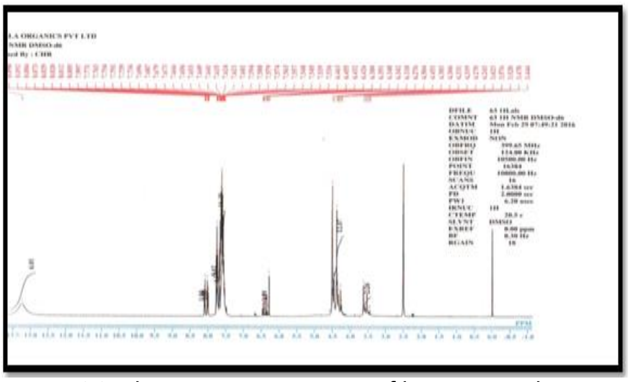


FIG (2): The 1HNMR spectrum of linear co-polymer

second-stage personalized nano-co-polymer prepared by second-infrared spectroscopy Fig 3 shows the FT-IR spectrum of the copolymer, which revealed a strong broadband at 3500 cm-1 for alcohols-OH, as well as aliphatic CH, aromatic C=H, and alkenes. = CH at 3140 cm-1, and 3050 cm-1 respectively, plus a strong in situ sharp band (1740 cm-1) belongs to the esteric bond (C = O), and a band in it belongs to (CO) ester, and based on the foregoing, this spectrum corresponds to the proposed structural structure of the as-processed polymer.

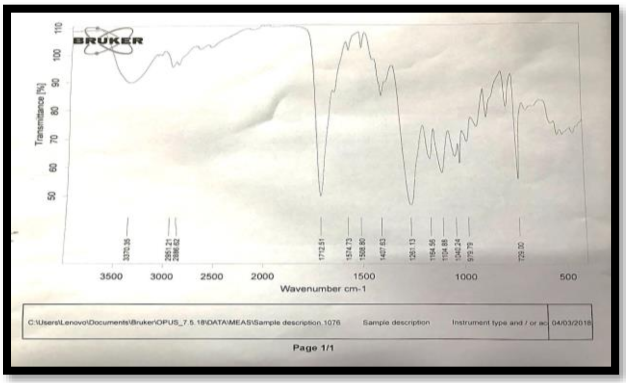


FIG (3): Graft co- polymer's FT-IR spectra

FIG (4), 1HNMR spectra, revealed DMSO has a single signal at 2.5 ppm., multiple signals in the range 3.5-4.8 ppm that is attributable to the groups [CH2-OC = O, -CH = CH-], Protons with aromatic properties as a double signal at 6.81–8.02 ppm, and carboxylic acid protons 12.77 ppm in a single signal.

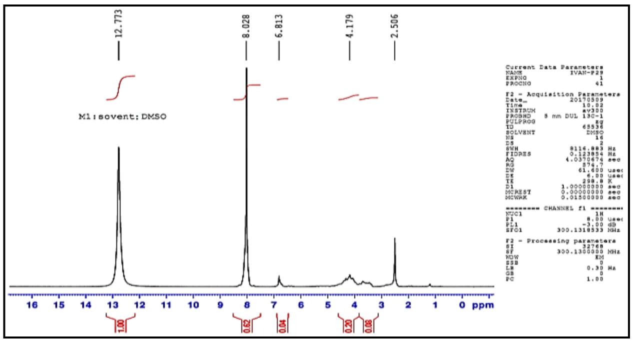


FIG (4): Graft spectrum of polymer 1H NMR

The prepared polymers were measured using the first-stage melting process by atomic force microscopy (AFM); By FIG. (5a,b,c) which expresses the outside surface of linear copolymer nanoparticles. Show the results The coefficient of roughness is 1.19 nm for a linear polymer surface and the square root is 1.37 nm. This implies that dark size of The roughness of the surface is influenced by nanoparticles. and homogeneity, its regular crystal system, the surface, and the average height of the particles, shown in Figure (5a) was equal to 4.80. Table (1) considers the overall rate and different ratios of common linear nanoparticle sizes; The results showed that the molecular size was equal to 94.09 for the linear nanoparticle and Figure (6) It illustrates the The various linear nanoparticle size ratios of the copolymer were distributed. The polymers were discovered to be copolymer nanoparticles, as seen below: Yin Figure (5a,b,c) The outside of the building of linear copolymer nanoparticles.

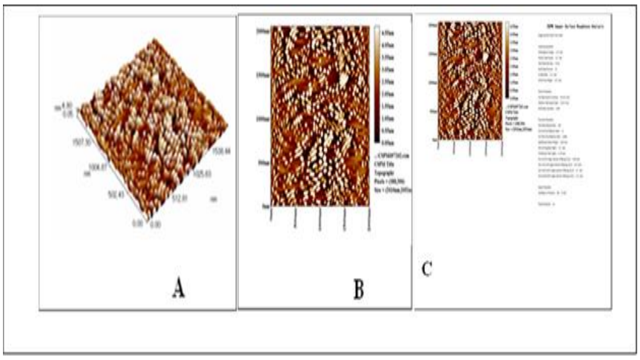


FIG. (5A, B,C) The outer surface of the linear copolymer nanoparticle

Table (1): The total rate of the particle sizes of the linear co-polymer nanoparticle and the different proportions of these volumes

Sample:1					Code: Sample Code			
Line No.: lineno					Grain No.:139			
Instrument: CSPM					Date:2021-06-23			
Avg. Diameter: 94.09 nm					<=10% Diameter:75.00 nm			
<=50% Diameter: 90.00 nm					<=90% Diameter:115.00 nm			
Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume (%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
75.00	7.19	7.19	100.00	8.63	68.35			
80.00	12.95	20.14	105.00	7.19	75.54	125.00	1.44	93.53
85.00	16.55	36.69	110.00	7.19	82.73	130.00	5.76	99.28
90.00	11.51	48.20	115.00	5.04	87.77	145.00	0.72	100.00
95.00	11.51	59.71	120.00	4.32	92.09			

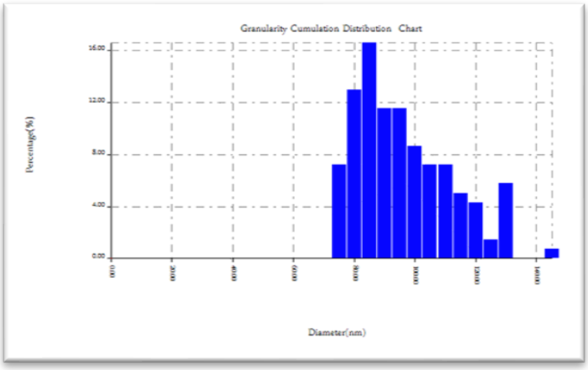


FIG (6): The diameters of linear co-polymer nanoparticles are distributed in varied ratios.

The secondary copolymer particle size, on the other hand, was determined using a two-stage atomic force microscopy (AFM) approach. The exterior surface of the graft copolymer nanoparticles is seen in Figures 7a,b,c. The surface of the co-grafted polymer has a coefficient of roughness of 2.12 nm, with a square root of 2.44 nm. The average height of the particles was 8.3 nm, indicating that the dark size of the nanoparticles has a vital influence on the surface roughness, regular crystal structure, and surface homogeneity, as shown in Fig7a. Table (2) considers the overall average sizes of copolymer nanoparticles and the various ratios of these sizes; the results show that the molecular size of the copolymer nanoparticles from the graft was 74.39 nm, and Figure (8) depicts the distribution showing the various particle size ratios of the copolymer nanoparticles

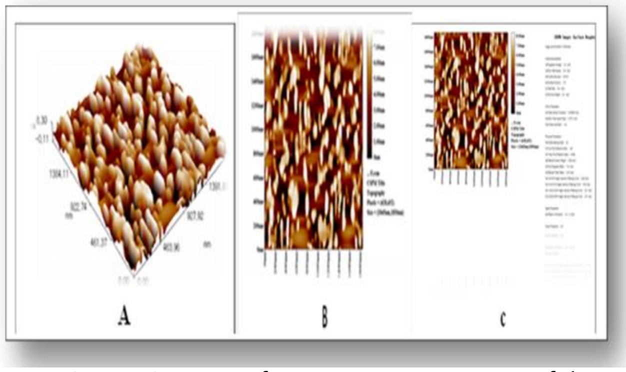


Fig (7A,B,C): Atomic force microscopy image of the grafted polymer showing the outer surface of the copolymer nanoparticle and some of its propertie.

Table (2): The overall rate of graft co-polymer nanoparticle particle sizes and the varied proportions of these volumes

Sample:2				Code: Sample Code				
Line No.: lineno				Grain No.:208				
Instrument: CSPM				Date:2021-07-31				
Avg. Diameter:74.39 nm				<=10% Diameter:0 nm				
<=50% Diameter:70.00 nm				<=90% Diameter:95.00 nm				
Diameter(nm)<	Volume (%)	Cumulation (%)	Diameter(nm)<	Volume (%)	Cumulation (%)	Diameter(nm)<	Volume (%)	Cumulation (%)
55.00	10.58	10.58	85.00	7.69	75.96			
60.00	12.98	23.56	90.00	6.73	82.69	115.00	1.44	98.56
65.00	10.10	33.65	95.00	4.81	87.50	120.00	0.48	99.04
70.00	12.50	46.15	100.00	4.33	91.83	125.00	0.48	99.52
75.00	7.21	53.37	105.00	2.88	94.71	140.00	0.48	100.00
80.00	14.90	68.27	110.00	2.40	97.12			

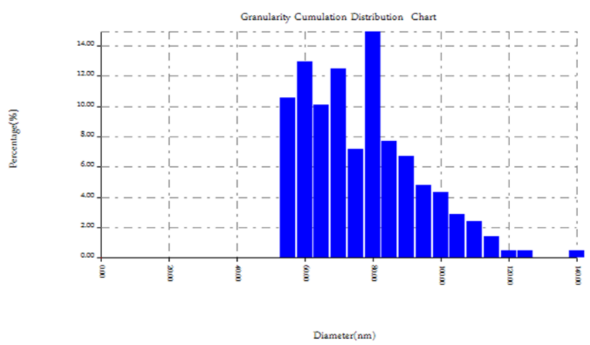


Figure (8) : Distribution of the different ratios of the sizes of the graft co- polymer nanoparticles

Adsorption Disperse Red 1

The titration curve represents the relationship between absorbance and concentration through the graph as shown in Figure (10). . Four generate (1, 3, 5 and 7 ppm) from the (Disperse Red 1) solution utilized in the investigation were employed to Identifies it. As indicated in Fig. 1, These concentrations' absorbance was measured at their highest wavelength (max. = 536 nm) (9).

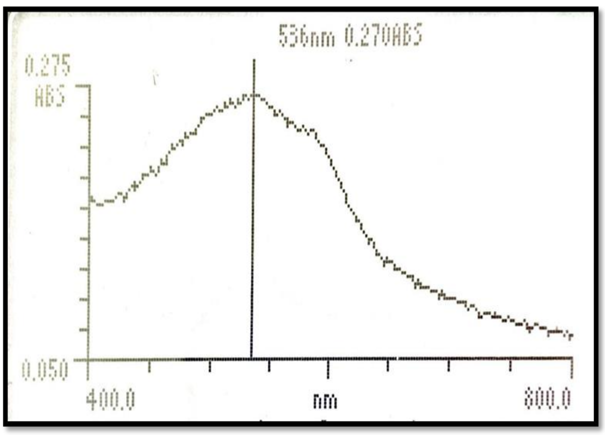


Fig (9)maximum wavelength (λ max) for the (Disperse Red 1)

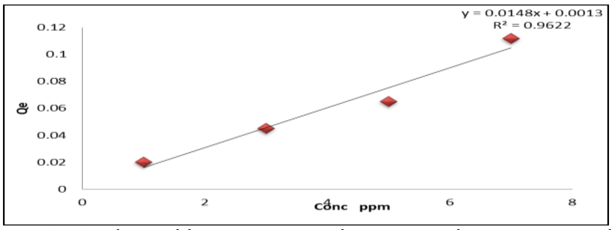


Fig (10): The calibration curve between absorption and concentration of Disperse Red 1dye

Table (3) shows the effect of temperature on dye adsorption (Disperse Red 1) on the surface of newly synthesized PTGM nanoparticles within the thermal range [298-308-318K]. Experimental results showed that the absorption of red dye dispersed on the surface of grafted PTGM nanoparticles increases with increasing temperature. The process is endothermic. [10] i.e. the occurrence of chemical adsorption (it needs high temperatures) [11]. by increasing the temperature the speed of diffusion of molecules increases and this indicates the occurrence that is, the processes of adsorption and absorption occur, and thus this leads to an increase in the removal percentage when the temperature is increased [12]. as shown in the figure (11).

Table (3) effect of temperature on the adsorption of the dye (Disperse Red 1)						
Conc	298k		308k		318k	
	Ce	Qe	Ce	Qe	Ce	Qe
1	0.2500	7500.000	0.1824	8176.0000	0.11486	8851.4000
3	0.6554	23446.000	0.5202	24798.0000	0.25000	27500.0000
5	0.8581	41419.000	0.7905	42095.0000	0.38510	46149.0000
7	0.9932	60068.000	0.9256	60744.0000	0.45270	65473.0000

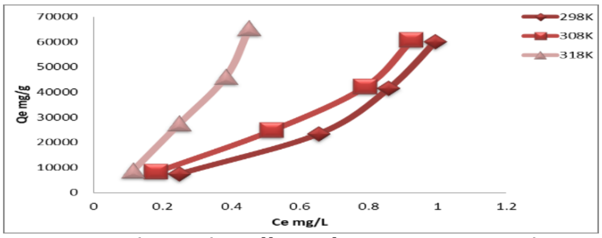


Fig11. shows the effect of temperature on the polymer at concentrations (1, 3,5 and 7 ppm) and temperatures (298, 308 and 318).

Adsorption Isotherms

The adsorption of dyes (Disperse Red 1) on the nano-copolymer was investigated, and adsorption isotherms were determined. at a temperature of 298 K, as shown in Figure (12), indicating that the adsorbent surface is not homogeneous and that the general Fig of the adsorption isotherms according to Giles classification, which Back to Frendelsh Basics from Type S1[13]

Table (4): adsorption of Disperse Red 1on the roof of the graft co-polymer at a temperature of 298K.			
Temp	Con.(ppm)	Ce (mg/L)	Qe (mg/g)
298K	1	0.2500	7500.0000
	3	0.6554	23446.0000
	5	0.8581	41419.0000
	7	0.9932	60068.0000

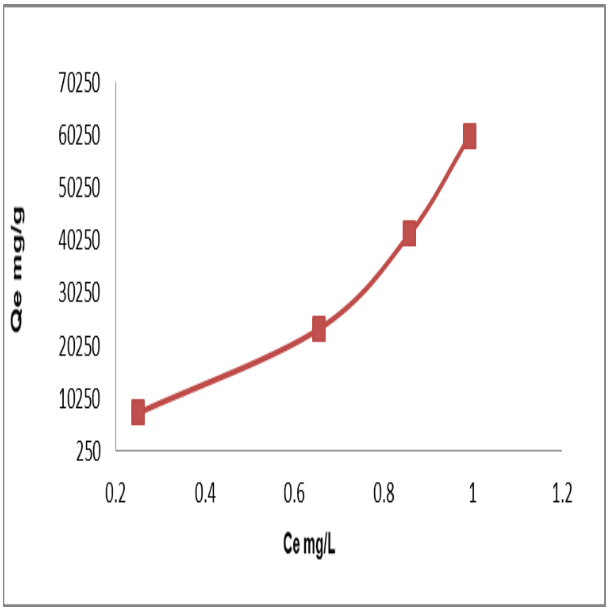


Fig (12): Adsorption isotherm Disperse Red 1dye on the roof of graft co-polymer.

Frendlich's adsorption equation

Frendlich's adsorption equation is one of the most important equations that expresses the adsorption of materials on heterogeneous surfaces and there are many equations. As for Frendlich's adsorption equation, It is one of the most significant isothermal equations expressed as follows [14] .

Qe = Kf. Ce1/n) (4)

When entering th

e logarithm on the equation No. (4), the equation becomes as shown in Equation No. (5) and through it The adsorption data of the dyes were processed according to the following linear equation of the logarithmic Frendelich equation: -

Log Qe = Log Kf + (1/n) Log Ce (5)

Ce: the equilibrium concentration of adsorbents (mg/L). While **Qe**: the amount of adsorbent at equilibrium (mg/g). **K f, n** are isothermal constants indicating the adsorption amplitude and density, respectively. Table (5) and Figure (13) show the extent of adsorption of Disperse Red 1 color on the surface of the newly synthesized nanopolymer with Freundlich's equation, By sketching the connection between Log Qe vs Log Ce, we get straight lines As indicated below.

Table (5): adsorption of Disperse Red 1dye on the roof of a synthetic graft co-polymer at 298 K (by applying the Freundlich equation).						
Conc	298K		308K		318K	
	LogCe-	LogQe	LogCe-	LogQe	LogCe-	LogQe
1	0.6020	3.8750	0.7389	3.9125	0.9400	3.9470
3	0.1834	4.3700	0.2838	4.3944	0.6020	4.4393
5	0.0664	4.6171	0.1020	4.6242	0.4144	4.6641
7	0.0029	4.7786	0.0335	4.7835	0.3441	4.8160

TABLE 6. Freundlich constant value of Disperse Red 1adsorbed on roof of graft co-polymer at (298K)			
R^2	K_f	N-	Temp
0.9746	5234.9887	0.6920	298K
0.9877	59197.0411	0.8425	308K
0.9965	192264.8972	0.7037	318K

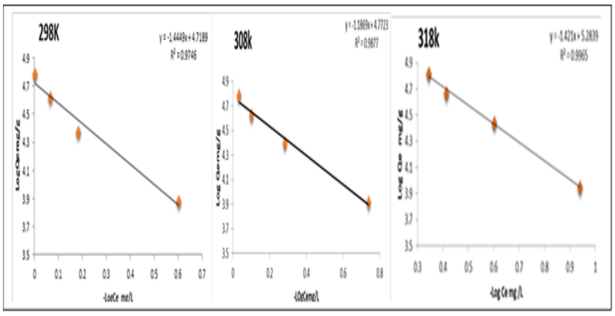


Fig13. The Freundlich isothermal absorbs the Disperse Red 1dye on the surface of the new graft co-polymer at

a) 298 K, b) 308 K, c) 318 K.

4. Conciusion

The novel nano co-polymer was synthesized from the reaction of Terphthalic acid with Glycerol to produce in the first step a linear co-polymer, and then maleic anhydride was added as step two. It has been shown that the nano-grafted copolymer is highly effective for removing dyes and pollutants at a temperature of 25 degrees and neutral acidity by using an adsorbent surface for the adsorption of the effective yellow dye in our research. Having a crystal structure

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