



Removal of Pollution with Methyl Orange Dye Waste Water by Using Novel Graft Nano Co-polymer

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ABSTRACT

The grafted nanocopolymers were synthesized via an esterification process, where the first step was to generate a linear copolymer by reacting terephthalic acid with glycerol. Then, a certain amount of maleic anhydride was added to the resulting linear copolymer solution to obtain the grafted PTGM nanoparticles. The prepared nanopolymers were characterized using FT-IR spectroscopy, ¹H-NMR, and atomic force microscopy (AFM). The average particle height was 8.3 nm and was exposed to three different temperatures (298, 308, and 318 K). Four different concentrations (1, 3, 5, and 7 ppm) of the nanocopolymers were examined and it was evident that they play a vital role in the adsorption process. The experimental results showed that the average surface area of this nanopolymer for adsorption of dye (methyl orange) decreased with increasing temperature, indicating that the process is endothermic. It was also observed that the highly efficient nanocopolymers were able to successfully remove (methyl orange) from aqueous solutions.

NOMENCLATURE

DMSO	DiMethyl SulfOxide	Log	Logarithm
PTGM	Poly(Terphthalic acid-CO-Glycol-G-Maleic anhydride)	N	Number of malls
Wt	weight	g	gram
Vsol	Volume solvent	ppm	part pear million
Co	The concentration at zero	nm	nanomater
Ce	The concentration at equilibrium	Temp.	Temperature
Qe	The amount of adsorbate substance	N	The adsorption intensity
Eq.	equation	Kf	The adsorption amplitude
K	Kalvin	R ₂	Reagen
mL	milliliter	λ	Wave length
AFM	Atomic force Microscope	Conc.	Concentration

1. INTRODUCTION

Nanomaterials are materials with a limited size range (1-100)nm[1, 2]. Controlling the size and shape at the nanoscale allows for the characterization, design, installation and utilization of materials, systems and devices [3, 4]. Pollution is one of the greatest concerns. Pollutants should be removed as much as possible, since

they pose a threat to humans, health and aquatic organisms, and are the most significant water pollutants (dyes, organic compounds, heavy metals, pharmaceuticals and anything that affects or changes the natural properties of water). Industrial dyes are common in many modern fields including the dyeing of fabric, hair, leather, paper, food and cosmetics[5]. Many toxic and deadly dyes are consumed by 2% of the wastewater produced, which is similar to the amount produced by

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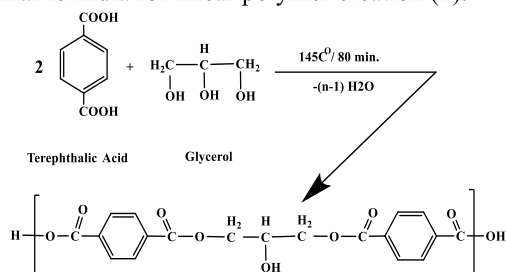
painting, and another 10% is used for textile coloring. Water (universal solvent) increases their susceptibility [6, 7]. Since dyes have a strong affinity for water, and are more difficult to remove via traditional methods, one of the most significant methods is the adsorption method on the surface of nanopolymers. Many toxic components in water systems, including many scientists, tend to utilize nanomaterials, larger and more effective adsorbents to create new and effective materials because the particles in question have a different interaction with each other than when they are naturally sized [8]. Our research also showed the capacity of poly (terephthalic acid-glycerol-G-maleic anhydride) toads to successfully adsorb dyes. Nanopolymers were found to be effective [9] for the purpose of eliminating pollutants.

2. MATERIALS and METHODS

Terephthalic acid, glycerin maleic anhydride, and other chemicals were used. All chemicals used in this work were of analytical grade procured from E. Merck Ltd.

2. 1. Synthesis of Graft PTGM Nanoparticles

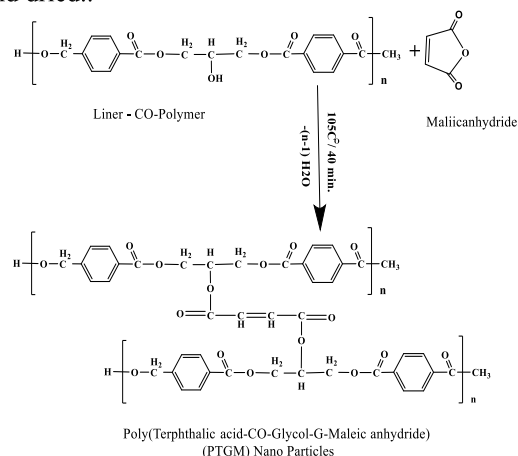
The nanoparticles consist of terephthalic acid and glycerol in a ratio of 2:1 (200 mL, 2.0 mol) terephthalic acid and (50 mL, 2.0 mol) DMSO. A temperature-sensitive cup is integrated into the vessel. The mixture is heated to 40 degrees Celsius with a magnetic stirrer and then (92 g, 1.0 mol) Glycerol is incorporated into the mixture. Next, heat the mixture to 120 degrees Celsius and then add 25 ml of xylene to the vessel in 2 drop increments until the water from the esterification process is expelled and the vessel is only marginally heated. After the 80-minutes incubation at 145 degrees Celsius, the temperature will be decreased because the water no longer facilitates the generation of nanopolymers. The proposed equation would then state that the reaction vessel should be decreased to around 50 degrees Celsius. This is evident in the figure. The original formula for linear polymer creation (1).



Equation 1. The initial stage of linear polymer synthesis.

In the second step, the anhydride maleic (0.5 mol, 49 g) was solving in 10 mL DMSO, heated to 40 °C and added it to the mixture (created in the first step). The beaker was gradually heated to 90 degrees Celsius,

and then xylene was added in small doses. (2 drops per batch to remove water) until no more water came out after 40 mins at 105 °C. This was used to produce PTGM nanoparticles. The reaction flask was allowed to cool to room temperature and then cold distilled water was added to the resulting suspension after 6 h. The suspension was then allowed to settle overnight as shown in Eq. (2) and then filtered, washed with distilled water and dried..



Equation 2. The second stage of the synthesis of graft PTGM nanoparticles

2. 2. Polymer Purification

Since the nanopolymers may be contaminated with trace amounts of unreacted solvent or monomers, they must be filtered. After separation, the synthesized nanopolymers are dissolved and precipitated using an appropriate solvent. According to the recommended protocol, a concentration of 5% is added while continuing to "stir" vigorously [10]. The polymer and solvent are miscible with the non-solvent. Once the solid polymer is formed, it is separated from the solution. To enhance the purity of the polymer, repeat the melting and re-emplacement process 3 times [11]. After cleaning, the nanopolymers are prepared for use. The new synthetic polymers are heated to 57 degrees Celsius and kept in a desiccator with a vacuum for processing and diagnostic testing [12].

2. 3. Adsorption Behavior of Grafted Nanopolymers

The process of adsorption of the new polymers onto dyes was studied to produce solutions containing Methyl orange dye (active ingredient). This was achieved by first preparing a solution of the dye in water (0.5 g) and then diluting it to 1000 mL to achieve a concentration of 500 ppm. From this concentrated solution, dilution solutions with concentrations of 1, 3, 5, and 7 ppm were prepared, all by taking an appropriate volume of the concentrated solution and then diluting it

with 100 mL of water. The vials containing the solution consisting of the surface-adsorbed nanopolymer and the surface-adsorbed dye were left for 60 minutes and their absorbance was measured after 60 minutes. The solution came from a vibrator set at a temperature of 298K. Samples were then taken and the absorption of the solution was determined by observing the changes in the visible and ultraviolet spectra as time progressed. After determining the amount of dye (Methyl orange) adsorbed on the surface of the new polymer material, the following equation was established[13].

$$Q_e = (C_o - C_e) * \frac{V_{sol}}{W_t} \quad (3)$$

3. DISCUSSION and RESULTS

Nanopolymers were created through an esterification process and studied using FT-IR, ¹H-NMR, and AFM. The first step is demonstrated in Figure 1: The spectrum of the linear copolymer's FT-IR is demonstrated in Figure 1. The spectrum has a strong, broad band at 3,423 cm⁻¹ caused by the presence of OH in the copolymer, and a weak band at approximately 2902 cm⁻¹ caused by the -OH of the carboxylic acid. Additionally, the band at around 2902 cm⁻¹ is attributed to the -OH acid. The composition of CH sp³ and sp² is 2544 and 2654 cm⁻¹, respectively, and the spectrum exhibits a strong association with the OC band of the ester band at around 1,726 cm⁻¹. The spectrum exhibits weak and sharp bands at 1597 cm⁻¹ – 1158 cm⁻¹ [14]. The spectrum shows weak, but distinct bands between 1597 and 1158 cm⁻¹ and a band between 1284 and 1259 cm⁻¹ due to the C=C system of the benzene ring. Van states that the esterification of the oil (CO) is responsible for these bands. The spectrum is in agreement with the pattern of the linear copolymer that was proposed in the first step.

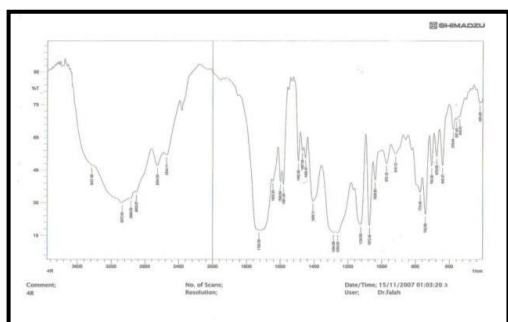


Figure 1. FTIR linear copolymer

Figure 2, ¹H-NMR spectrum shows the signal of the carboxylic acid group protons at 13.24 ppm and counts of each proton in the aromatic ring in the range of 7.53 - 8.10 ppm, while the signal is located at 6.27 - 6.46 ppm. The four methylene protons in the copolymer structure appear, the methyl protons double at 4.24-4.50

ppm, and the triplet signal from the alcohol protons appears at 3.44ppm. Our polymer was confirmed by this spectrum[5].

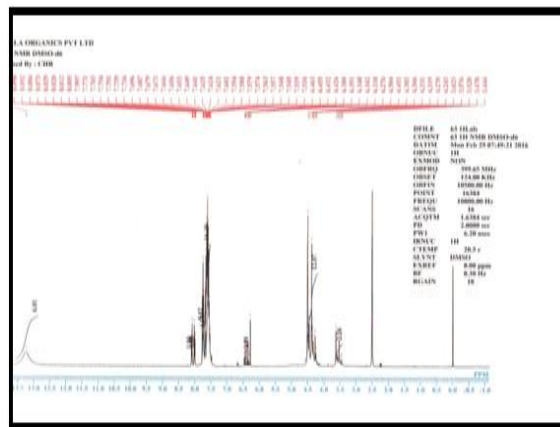


Figure 2. The ¹H-NMR spectrum of linear copolymer The individualized second stage polymer was created by second step infrared spectroscopy. Figure 3 depicts the FT-IR spectrum of the copolymer, which exhibits numerous broad bands at 3550 cm⁻¹ for alcohol -OH as well as aliphatic CH, aromatic C=H and Olefins. = CH at 3140 cm⁻¹ and 3050 cm⁻¹, respectively, plus a strong, sharp band in place (1740 cm⁻¹) that is associated with the ester bond (C=O), a band inside of it that is linked with (CO) ester, and, based on the spectrum's composition. It can be deduced that the processed polymer has a structural composition similar to that proposed in the proposed structure[15, 16].

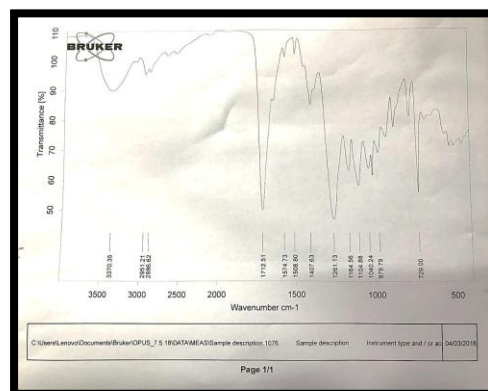


Figure 3. Graft co- polymer's FT-IR spectra

Figure 4, The ¹H-NMR spectrum demonstrates that DMSO has a signal at 2.5 ppm, multiple signals in the 3.5-4.8 ppm range, which are associated with the [CH₂-OC = O, -CH = CH-] group, protons that have a chemical composition similar to that of aromaticity, as well as protons which are connected with the carboxylic acid. These protons are considered to have a single signal at 12.77 ppm...

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

TABLE 2. The average rate of graft copolymer's particle sizes and the various percentages of these volumes.

Sample:1			Code: Sample Code		
Line No.: lineno			Grain No.:208		
Instrument: CSPM			Date:2019-05-31		
Avg. Diameter: 74.39 nm			<=10% Diameter:0.00 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	115.0	1.44	98.56
60.00	12.98	23.56	90.00	6.73	82.69	120.0	0.48	99.04
65.00	10.10	33.65	95.00	4.81	87.50	125.0	0.48	99.52
70.00	12.50	46.15	100.0	4.33	91.83	140.0	0.48	100.00
75.00	7.21	53.37	105.0	2.88	94.71			
80.00	14.90	68.27	110.0	2.40	97.12			

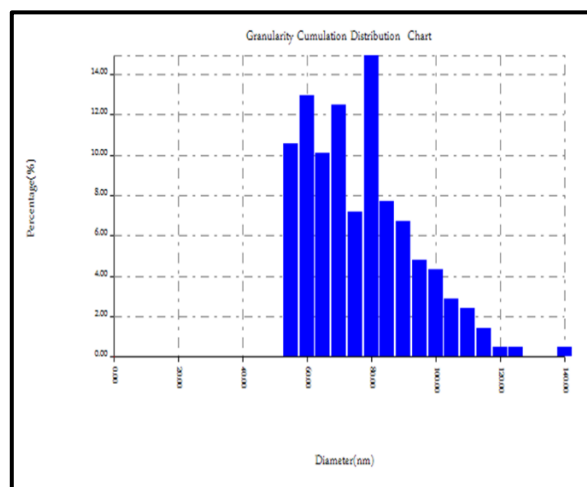


Figure 8. Distribution of the different ratios of the sizes of the graft co- polymer nanoparticles.

3. 1. Adsorption of Methyl orange

The titration graph is a representation of the relationship between absorption and concentration via a graph that is shown in Figure (10). Four different concentrations (1, 3, 5 and 7 ppm) of the (methyl orange dye) solution employed in the study were engaged to differentiate them. The absorption at these concentrations was recorded at their greatest wavelength as clarified in Figure 9 (max. = 418 nm).

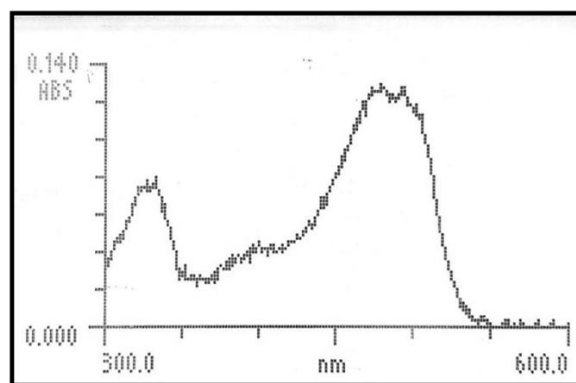


Figure 9. Maximum wavelength (λ_{max}) for the (Methyl orange)

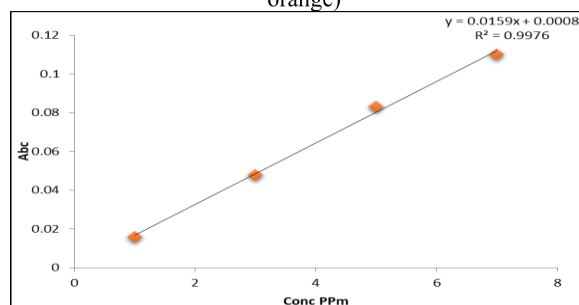


Figure 10. The calibration curve between absorption and concentration of methyl orange dye.

The effect of temperature on dye adsorption (methyl orange dye) on the surface of freshly prepared PTGM nanoparticles in the temperature range [298-308-318 K] is shown in Table 3. The data show that authors observed that the amount of orange G adsorbed on the surface of grafted PTGM particles decreased as the temperature increased [12]. The procedure is temperature-supporting. As the temperature increases, any physical association (requiring a low temperature) [17] decreases the rate of particle diffusion on the surface of PTGM nanoparticles [18]. This implies that there is a procedure by which the particles that are adsorbed by the layer are separated from it and reenter the liquid state [13]. as revealed in Figure 11.

TABLE 3. Effect of temperature on adsorption of methyl orange dye.

Conc.	298K		308K		310K	
	Ce	Qe	Ce	Qe	Ce	Qe
1	0.2641	0.7359	0.1383	0.8617	0.0754	0.9246
3	0.6415	2.3585	0.3899	2.6101	0.2012	2.7988
5	0.8301	4.1699	0.5157	4.4843	0.2641	4.4834
7	0.9559	6.0441	0.6415	6.3585	0.3270	6.6730

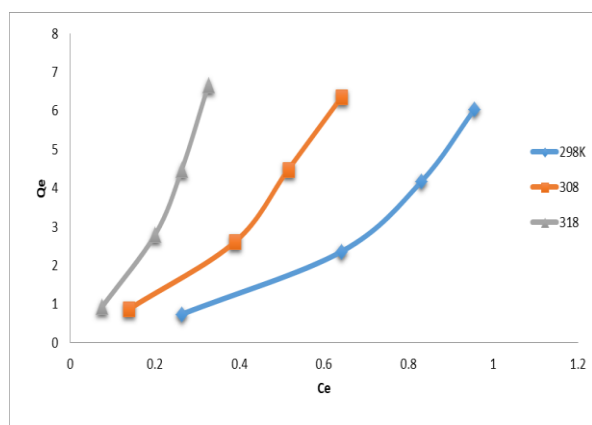


Figure 11. The effect of temperature on the polymer at concentrations (1, 3, 5 and 7 ppm) and temperatures (298, 308 and 318)K.

3.2. Adsorption Isotherms

The association of the dye (Methyl orange) with the nanocopolymer was investigated, and the isotherms of relationship were determined. At a temperature of 298 K, as demonstrated in Figure (12), this demonstrates that the surface of the adsorbent is not uniform and that the general shape of the isotherm according to Giles' classification is similar to the Frenelsh principle of type S1 [19, 20].

TABLE 4. adsorption of methyl orange on the roof of the nano copolymer at a temperature of 298K.

Temp.	Conc. (ppm)	Ce	Qe
298K	1	0.2641	0.7359
	3	0.6415	2.3585
	5	0.8301	4.1699
	6	0.9559	6.0441
	7	0.2641	0.7359

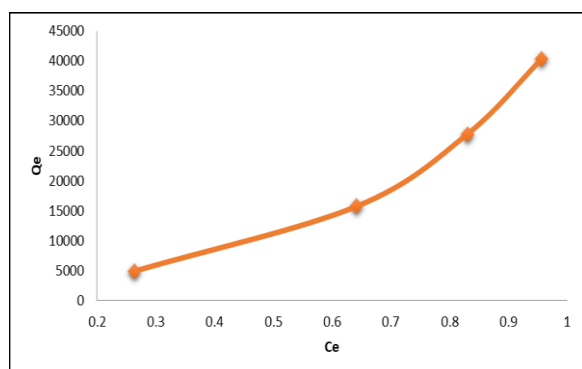


Figure 12. Adsorption isotherm methyl orange dye on the roof of graft co-polymer.

3.2. Freundlich's Adsorption Equation

The Freundlich equation is one of the most significant equations used to describe the attachment of

substances to different surfaces. Many equations exist. The Freundlich equation for adsorption is one of the most significant isotherms, and its expression is as follows [21, 22]:

$$Q_e = K_f \cdot \frac{C_e}{n} \quad (4)$$

When entering the 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 Freundlich equation[23, 24]:

$$\text{Log} Q_e = \text{Log} K_f + \left(\frac{1}{n}\right) \text{Log} C_e \quad (5)$$

Ce: the equilibrium concentration of the adsorbent in (mg/L). Qe: the amount of adsorbent at the equilibrium (mg/g). Kf and n are isothermal constants that represent the amplitude and density of adsorption, respectively. Table (5) and Figure (13) determine the degree to which disperse red 1 coating is adsorbed on the surface of the newly created nanopolymer using the Freundlich equation. If ore connect Log Qe with Log Ce, we will get a direct line as illustrated below..

TABLE 5. adsorption of Methyl orange dye on the roof of a synthetic graft co-polymer at 298 K (By applying the Freundlich equation).

	298K		308K		318K	
Con.	LogCe-	LogQe	LogCe-	LogQe	LogCe-	LogQe
1	0.5782	-0.1331	0.8591	-0.0646	1.1226	-0.0344
3	0.1982	0.3726	0.409	0.4166	0.6963	0.4468
5	0.0808	0.6201	0.2876	0.6516	0.5782	0.6754
7	0.0195	0.78133	0.1928	0.8033	0.4854	0.8243

TABLE 6. Freundlich constant value of adsorbed on roof of graft co-polymer at (298K)

Temp.	-N	Kf	R2
298K	0.7566	284315.1486	0.9866
308K	0.7003	82186.4080	0.9725
318K	0.6282	43641.5332	0.9574

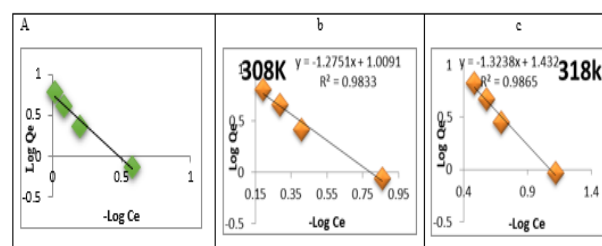


Figure 13. The Freundlich isothermal absorbs the methyl orange dye on the surface of the new graft co-polymer at a) 298 K, b) 308 K, c) 318 K.

4. CONCIUSION

This new nano-doped copolymer was synthesized by reacting terephthalic acid with glycerol to form a linear copolymer and adding malic anhydride in the first step. This is how the nano-doped copolymer

was prepared. Our study showed that the nano-grafted copolymer was very effective in removing dyes and pollutants at a temperature of 25 degrees and neutral acid by adsorbing the effective methyl orange dye on the adsorbent surface. It has a crystalline structure.

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Arabic Abstract

تم تصنيع البوليمرات النانوية المطعمة من خلال عملية الأسترة، حيث كانت الخطوة الأولى هي تحضير بوليمر مشترك خطي عن طريق تفاعل حمض التريفتاليك مع الجلسرين. بعد ذلك، تمت إضافة كمية معينة من أنهيدريد المالتيك إلى محلول البوليمر الخطي الناتج للحصول على جسيمات PTGM النانوية المطعمة. تم تشخيص وتشخيص البوليمرات النانوية باستخدام التحليل الطيفي FT-IR، $^1\text{H-NMR}$ ، ومجهر القوة الذرية (AFM). كان متوسط ارتفاع الجسيمات 8.3 نانومتر وتعرض لثلاث درجات حرارة مختلفة (298، 308، و318 كلفن). تمت دراسة أربعة تراكيز مختلفة (1، 3، 5، و 7 جزء في المليون) من صبغة (الميثيل البرتقالي) ومن الواضح أنها تلعب دوراً حيوياً في عملية الامتزاز. أظهرت النتائج التجريبية أن امتزاز صبغة (الميثيل البرتقالي) انخفض في متوسط مساحة السطح والسبب في ذلك أنه امتز البوليمر النانوي عدد كبير من الجزيئات مع زيادة درجة الحرارة، مما يدل على أن العملية ماصة للحرارة. ولوحظ أيضاً أن البوليمرات النانوية عالية الفعالية نجحت في إزالة صبغة الميثيل البرتقالي من المحاليل المائية.