# Adsorption Of Methyl Orange from Aqueous Solutions by Using a Novel Nano Co-Polymer: As A Model of Heyyalth Study

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**Abstract**

In this piece, a developed graft of nano co-polymer by esterifying glycerol and phthalic anhydride. X-ray diffraction analysis, differential scanning calorimetry, atomic force microscopy, and infrared spectroscopy were used to analyse the nano co-polymer. It was determined whether synthetic nano co-polymers propensity could remove methyl orange from aqueous solutions. The effects of three distinct concentrations (1, 3, 5 and 7 ppm) and temperatures (298, 308 and 318 k) on nano polymers have been studied. The height of the nano-average polymer was 22.04 nm. The results of the experiment clearly showed that synthetic nano-polymers were very good at totally eliminating methyl orange from aqueous solutions.

Keyword: Adsorption, Characterisation, Nano Co-Polymers; Methyl Orange, Pollutions

## 1. Introduction

Industrial growth in the countries has resulted in the rapid chemical synthesis d and the expensive solid waste production, which has led to environmental issues and an increase in pollution flows (dyes, heavy metals, phenols, pharmaceuticals, and so on) [1-2]. Even in tiny amounts, these poisons pose a major threat to both people and other living things. Industrial dyes are employed in a number of contemporary technological domains [3]. Dyes are used to give colors to paper, skin, hair, food, cosmetics, and textiles. They are soluble in water. Due to its toxicity, color removal from local or industrial effluents has received more attention lately [4]. Materials having colouring qualities were derived from natural sources, mainly plants or animals, before the middle of the nineteenth century [5]. However, synthetic compounds had largely taken the role of natural colors by the early 20th century [6]. All commercially available stains today are industrial, with a few inorganic dyes as an exception [7]. Annually, novel colour chemicals in abundance enter the market and find their way into a range of applications [8]. According to Guaranine and Zanonia [9], dispersed dyes that are insoluble in water-based solutions are nonetheless applied to cellulose fibers and other dirty fibres by suspension. The insoluble component of the origin is slowly deposited in the form of differentiation on cellulose acetate as a result of the dye's hydrolysis throughout the dyeing process.. The process is frequently carried out in when there was long chain reasons for dispersion, which maintain the dye's suspension and allow interaction with water-damaged fibres. The bulk of the dyes in this layer, AZURE dyes, have been used to colour, artificial fibres like cellulose acetate nylon, polyester, and polyamide [10-12]. Technology's scope in the twenty-first century is either anatomical or molecular. The development of nanoscale manufacturing has so far demonstrated its adaptability in terms of pollution disposal and environmental sustainability [13]. To reduce color pollution, a novel nanomaterial was created and used in this project (methyl orange).

## 2. Material and Methods

The chemicals used in this experiment, such as glycerol and phthalic anhydride, were of analytical purity.

### Preparation of Nano Particles co-polymer

Phthalic anhydride (3.0 moles, 444 g) and DMSO (48 mL) were combined in a 200 mL beaker. A thermometer was included with this beaker. Glycerol (1.0 mole, 92 g) was gradually included into the mixture after it had been carefully heated with a hot plate magnetic stirrer to 70°C. The esterification water was drained, the reaction beaker was gently heated, and 15 mL of xylene was added in batches of three drops: after carefully bringing the mixture to 100°C. After turning off the heating (71 Min, 125°C); Once no more water is released, keep preparing the nano co-polymer. The suspension solution is created when the cold distilled water has been added. In the morning, filter the suspension solution, wash it in distilled water, and let it air dry.

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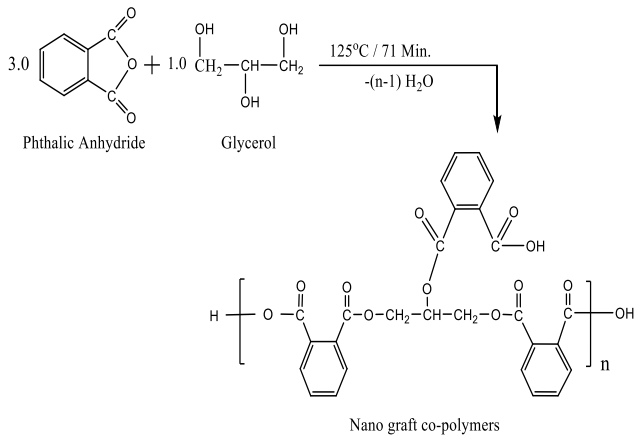



*Figure 1: Polymer preparation processes*

## Purification of Polymer

Purification is essential after separation because the produced polymer may contain solvent residues, an unreacted monomer, or other contaminants. The polymer was dissolved in the suitable solvent, and 5% non-solvent was added while the mixture was forcefully agitated, as reported in [14].

The solvent and polymer were miscible with the non-solvent. Precipitation caused the solid polymer to separate from the solution. To increase the polymer's quality, the entire re-dissolving and re-precipitating operation was repeated three times [15]. The nano co-polymer was purified prior to vacuum drying at 50°C and storage in a vacuum desiccator until it could be further described and used [16].

## Adsorption Behaviour of Graft Nano Co-Polymers

Examining a novel's absorption of nano-polymer on dyes, The following "methyl orange" dye solution was produced.: To prepare a methyl orange dye solution, dissolve (0.5 g) of the dye in a specified amount of distilled water and dilute the solution to (1000 ml) to get a concentration of (500 parts per million)., The concentrated solution was diluted by adding the necessary amount to it, diluting it with (100 ml) distilled water, and then concentrating it (1, 3, 5 and 7 ppm). The solution's absorption was evaluated 60 minutes after its vials were placed in the vibrator at a temperature of 298 K with a nano polymer adsorbent surface weighing (0.016) and the dye adsorbent surface weighing (0.016). (Methyl orange). After then, the absorbance was calculated by taking samples at regular intervals and seeing how the spectral characteristics of visible and ultraviolet light changed over time. The number of dyes (methyl orange) adsorbed on the surface of the equation was used to calculate the new nano polymer. [17].

(Co-Ce) = Qe (Co-Ce). /Wt Vsol ……..(1)

## Outcomes and Debate

### Characterization of Graft Nano Co-polymers

Figure 2 shows in the FT-IR spectrum, a broad and weak peak appears at (3093 cm-1) belonging to the (OH) carboxylic bond, as well as the appearance of peaks that extend at (3067 cm-1 and 2887 cm-1) belonging to the aromatic (C-H) bond. The asymmetric aliphatic bond (C-H) as well as the development of a prominent tip at (1757 cm-1) is due to the ester bond (C=O), as well as the presence of a potent peak at (1107 cm-1) because of the bond (C-O) as well as extending peaks at (1402, 1468 and 1595 cm-1) is attributed to the aromatic (C=C) bond, with the appearance of two peaks at (709 and 903 cm-1) ascribed to an aromatic ring substitution.

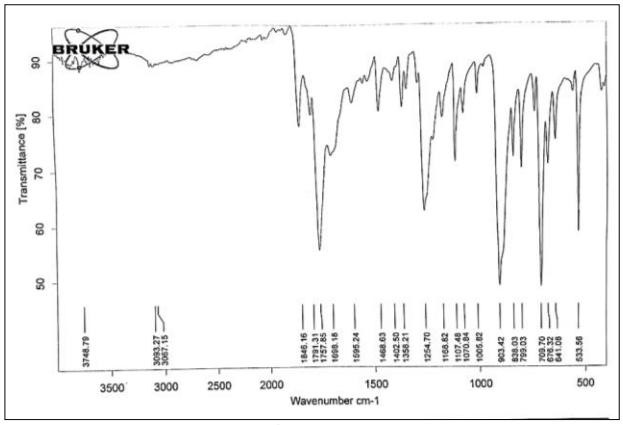



*Figure 2. shows graft nano co-FT-IR. polymer's*

Figure 3 a demonstrates the 1H-NMR spectrum, which explains the singlet signal of the special proton of the carboxylic acid group at 13.04 ppm. Furthermore, the evidence for four methylene protons at 4.26-4.28 ppm in the co-polymer structure, as well as many signals for methyl protons at 4.15 ppm, suggest the creation of a graft co-polymer.

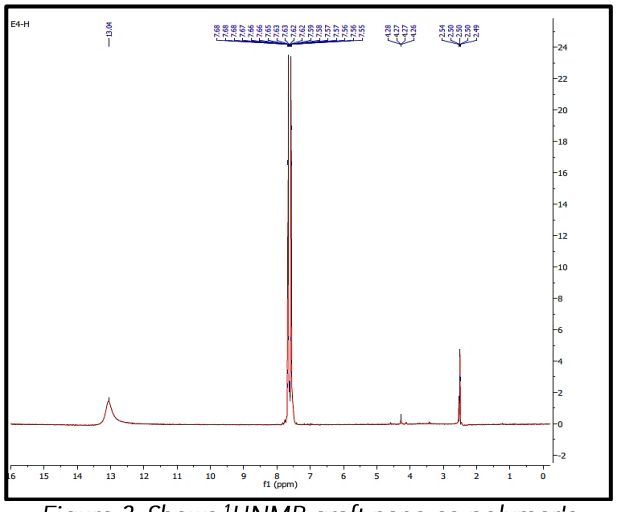
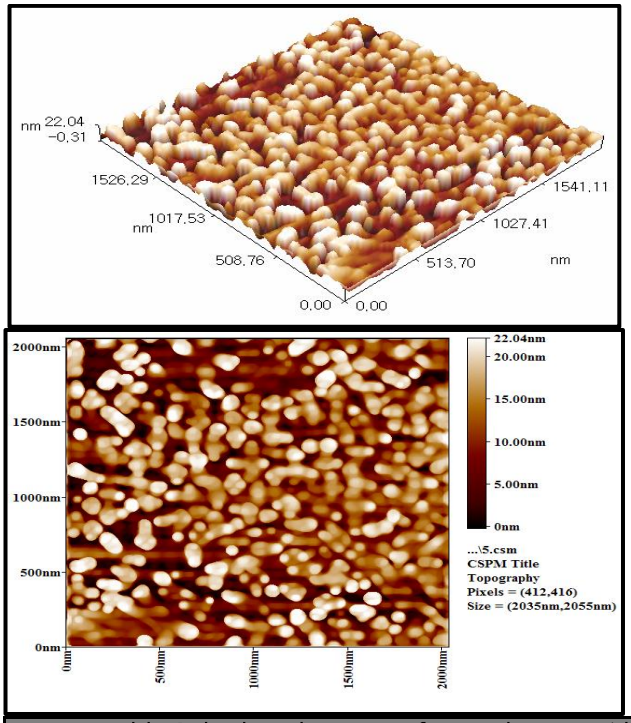



*Figure 3. Shows [1]HNMR graft nano co-polymer's*

Figure 4, represent the square root square was 5.94 nm, while the co-polymer surface roughness coefficient was 5.08 nm. This shows how the nanoparticles' huge size affects surface roughness, Consistent crystalline structure, and surface homogeneity. Additionally, the nanoparticle co-polymer's molecular size was 68.62 nm, and Figure (4) demonstrates how the various sizes of particle are distributed that makes up nanoparticle. Table displays the overall rate of the common nanoparticle's particle sizes as well as the various volumes' proportions



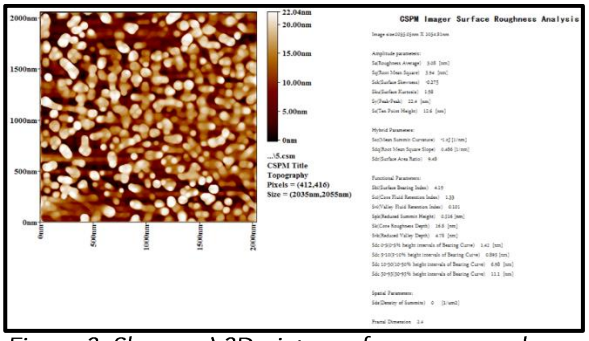




*Figure 3, Shows; a) 3D picture of a nano co-polymer captured by an atomic force microscope, b) 2D picture of a nano co-polymer is shown by an atomic force microscope image and c) 2D picture of a nano co-polymer with all of the particles' characteristics.*

| Table 1; The total rate of the particle sizes of the nanoparticle co-polymer and the different proportions of these volumes | |
|---|---|
| Sample: 1 | Code: Sample Code |
| Line No.:lineno | Grain No.:264 |
| Instrument: CSPM | Date: 2021-09-24 |

| Table 2 displays the ratios of atom distances (d-spacing) and crystallite sizes in a nano co-polymer. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Avg. Diameter: 68.62 nm | | | <=10% Diameter: 50.00 nm | | | | | |
| <=50% Diameter: 65.00 nm | | | <=90% Diameter: 80.00 nm | | | | | |
| Diameter(nm)< | Volume (%) | Cumulation (%) | Diameter(nm)< | Volume (%) | Cumulation (%) | Diameter(nm)< | Volume (%) | Cumulation (%) |
| 45 | 1.52 | 1.52 | 65.00 | 17.80 | 40.91 | | | |
| 50 | 4.17 | 5.68 | 70.00 | 12.12 | 53.03 | 85.00 | 11.74 | 90.91 |
| 55 | 9.09 | 14.77 | 75.00 | 13.64 | 66.67 | 90.00 | 9.09 | 100.00 |
| 60 | 8.33 | 23.11 | 80.00 | 12.50 | 79.17 | | | |

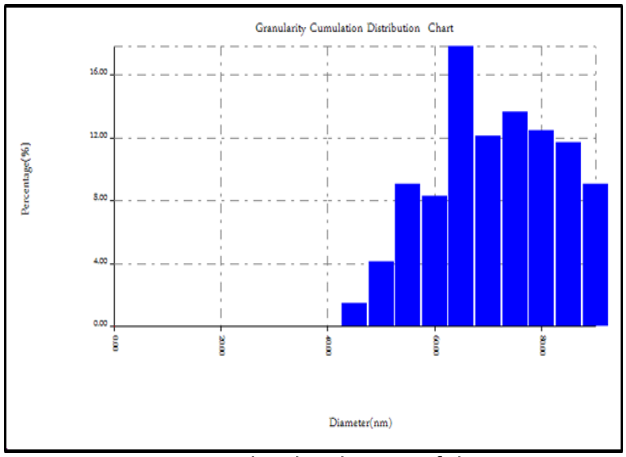



*Figure 4, Depicts the distribution of the nano co-particle polymer's size proportions.*

Peaks at two temperatures are shown in Figure 5, co-polymer of the nanoparticles (15.4°, 18.5°, 21.2°, 22.2°, 26.9°, and 30.5°). With fewer amorphous carbon atoms, these peaks showed the new co-polymer was effective a crystalline molecule. Using Bragg's Law: n = 2dsin, the origin program determined that the average inter spherical distance ($d_{hkl}$) between atoms was 0.415 nm.

The total average crystallite size was detected by Scherrer's equation to be 68.48 nm.

$D=k\lambda/\beta\cos\theta$

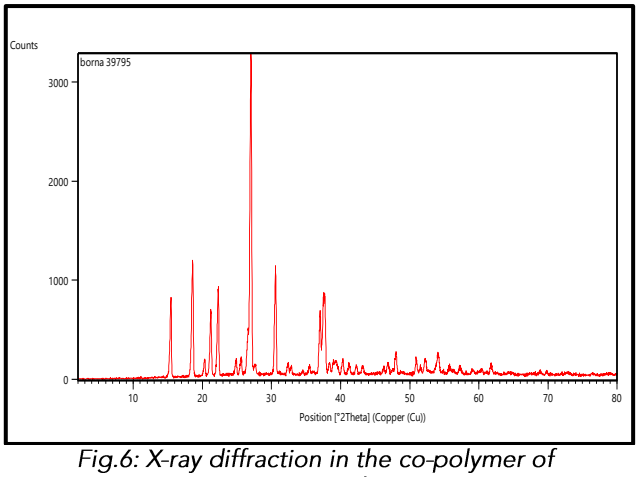



*Fig.6: X-ray diffraction in the co-polymer of nanoparticles*

| Table 3 displays the ratios, diameters, angles, and the nano co-polymer's standard deviations | | | | | | |
|---|---|---|---|---|---|---|
| $d_{hkl}$ (Av.) nm | D (Av.) nm | $d_{hkl}$nm | Dnm | FWHM | θ | 2 θ |
| 0.4152 | 68.4874 | 0.57421 | 77.77159 | 0.10308071 | 7.70944 | 15.41888 |
| | | 0.477637 | 66.10961 | 0.12176233 | 9.28079 | 18.56158 |
| | | 0.418681 | 69.58317 | 0.11615246 | 10.60181 | 21.20363 |
| | | 0.398978 | 68.94823 | 0.11743049 | 11.13191 | 22.26382 |
| | | 0.32998 | 61.54072 | 0.13275784 | 13.4996 | 26.9992 |
| | | 0.292302 | 66.97155 | 0.12296861 | 15.27956 | 30.55913 |

Figure (7) shows TEM images of the co-polymer nanoparticles. With irregular particles such as vertebrae with various thickness, layers of semi-spherical forms, and rod shapes, the nanoparticle's co-polymer was seen in a variety of sizes and shapes. The co-polymer nanoparticle had an average particle size of 68.08 nm. Figure (7) shows the histogram for the breakdown of the various ratios of the nano co-polymer particle sizes, and Table (3) lists the ratios of the diameters, angles, and the nano co-polymer's standard deviations were discovered with imaging software.

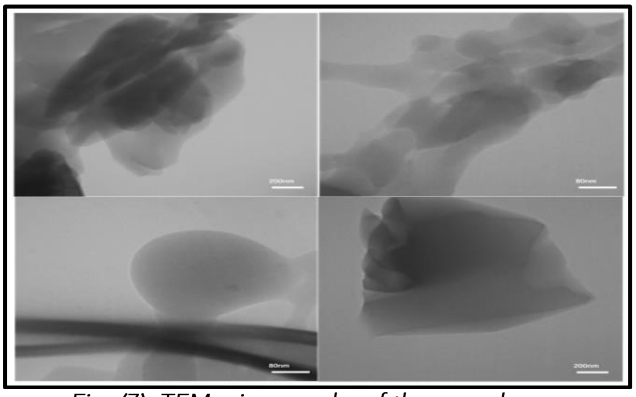


*Fig. (7): TEM micrographs of the co-polymer nanoparticles*

| Area | StdDev | Angle | Diameter nm | D (av.) nm |
|---|---|---|---|---|
| 14.775 | 7.288 | 8.13 | 45.617 | **68.084** |
| 14.879 | 6.905 | -51.843 | 45.944 | |
| 16.231 | 13.912 | -78.111 | 50.104 | |
| 17.896 | 7.185 | 90 | 55.481 | |
| 21.225 | 11.734 | 90 | 65.803 | |
| 21.954 | 17.472 | -76.759 | 67.6 | |
| 22.578 | 22.617 | -93.18 | 69.781 | |
| 22.682 | 6.093 | 94.236 | 69.864 | |
| 20.393 | 8.205 | -135.83 | 72.958 | |
| 24.555 | 10.457 | -48.447 | 75.862 | |
| 19.457 | 9.157 | -37.117 | 79.868 | |
| 27.364 | 10.744 | 23.429 | 84.371 | |
| 19.04 | 5.677 | -74.745 | 88.844 | |
| 30.486 | 9.79 | -88.431 | 94.223 | |
| 31.942 | 9.633 | 52.98 | 98.575 | |
| 32.566 | 15.94 | -80.417 | 100.755 | |

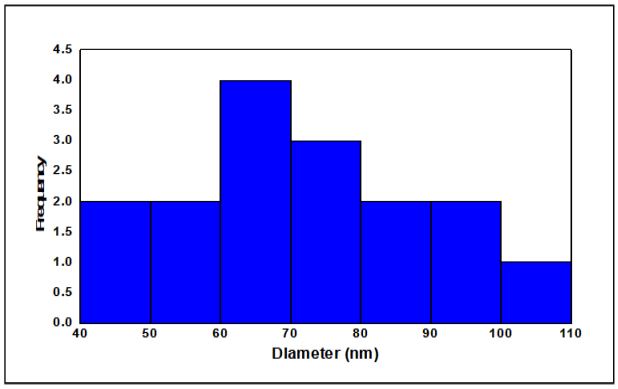



*Figure 8. displays a histogram of the distribution of the various nano co-particle polymer ratio sizes.*

The DSC thermograms (Figure 9 ), for the nano co-polymer are shown in the first thermal transition at the peak of the nano co-polymer, which is 48.68oC, corresponds to the glass transition temperature (Tg), the second transition at the peak, which is 134.10oC, to the crystallization temperature (Tc), and the third and fourth transitions at the peak, which are 197.60 and 302.19 oC, respectively, to the melting temperature (Tm1 and Tm2).

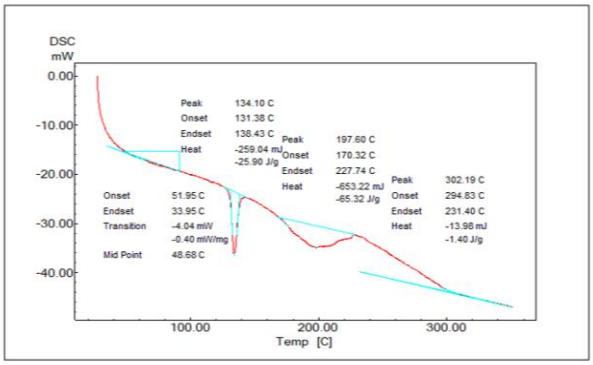



*Fig. (9) shows grams of nano co-polymer in a DSC thermos.*

## Adsorption of methyl orange

Figure 10 shows how the titration curve represents the connection between absorbance and concentration. Four samples were taken from the (methyl orange) solution used in the experiment (1, 3, 5, and 7 ppm). The absorbance of these concentrations at their respective places was measured to determine it (highest wavelength 464 nm).

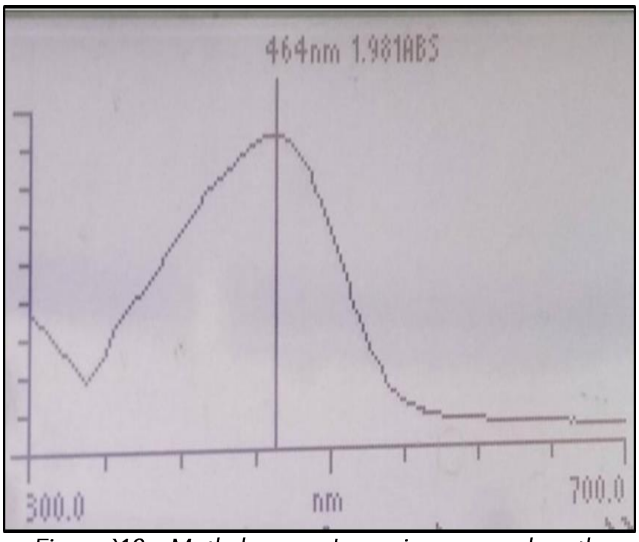



*Figure `10a: Methyl orange's maximum wavelength (max).*

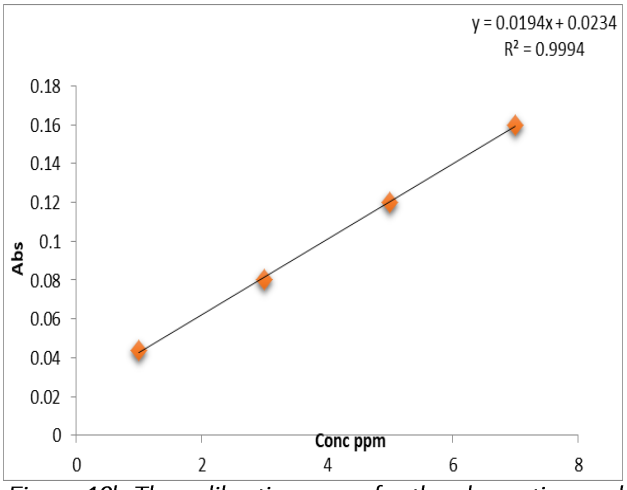



*Figure 10b.The calibration curve for the absorption and concentration of methyl orange is shown*

The "methyl orange" dye standard curve between absorbance and concentration Table 4 shows the findings of a study on the impact of temperature and thermal range on methyl orange pigment adsorption on the surface of polymer nanoparticles (298, 308 and 318 K). The adsorption of methyl orange pigment on the surface of these nanoparticles decreased as temperature increased, which is consistent with the experimental findings that the process is exothermic [19]. This reveals the existence of a desorption process, which is the separation of adsorbed particles on the adsorbent surface and their return to solution [20], which slows molecular diffusion as temperature rises [21]. as seen in Figure (10).

Table (4): impact of temperature on adsorption of methyl orange

| Conc(ppm) | 298K | | 308K | | 318K | |
|---|---|---|---|---|---|---|
| | Ce mg /L | Qe mg/g | Ce mg/L | Qe mg/g | Ce mg/L | Qe mg/g |
| 1 | 0.0994 | 0.8443 | 0.1518 | 0.7951 | 0.2565 | 0.6970 |
| 3 | 0.2041 | 2.6211 | 0.4659 | 2.3757 | 0.6753 | 2.1794 |
| 5 | 0.2565 | 4.4476 | 0.623 | 4.1034 | 0.8848 | 3.858 |
| 7 | 0.3089 | 6.2729 | 0.7277 | 5.8802 | 0.9895 | 5.6348 |

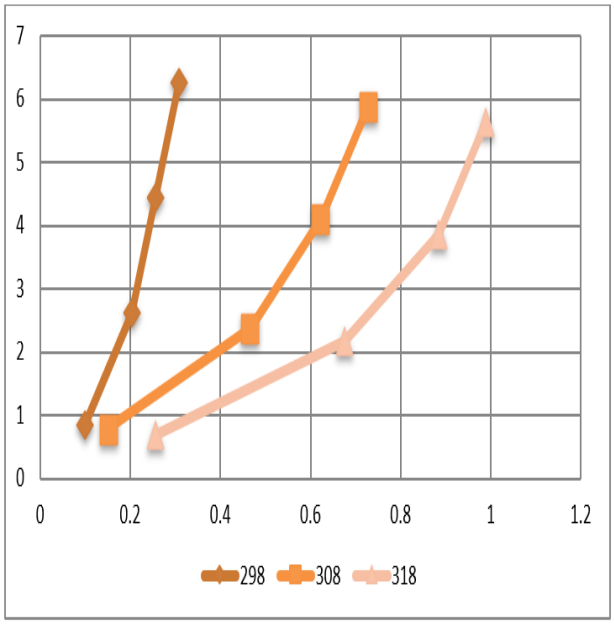



*Fig. (11): Effect of temperature on adsorption of graft co-polymer at (1, 3 ,5and 7ppm) of methyl orange dye*

## Adsorption Isotherms

Researchers measured adsorption isotherms for dyes (methyl orange) on the nano-copolymer at 298 K, as shown in Figure (12), implying that the adsorbent's surface is not uniform. Furthermore, the overall shape of the adsorption isotherms is Type S1 according to the Giles classification [22].

Table (5): Adsorption of methyl orange dye on the surface of nano co-polymer at 298K

| Temp | Con.(ppm) | $C_e$ (mg/L) | $Q_e$ (mg/g) |
|---|---|---|---|
| 298 | 1 | 0.0994 | 0.8443 |
| | 3 | 0.2041 | 2.6211 |
| | 5 | 0.2565 | 4.4470 |
| | 7 | 0.3089 | 6.2729 |

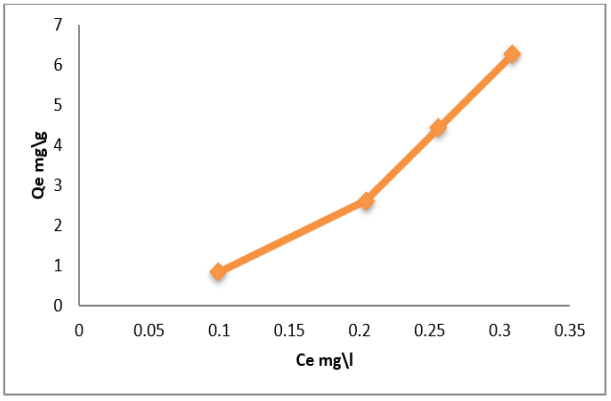



*Figure (11): Adsorption isotherm methyl orange dye on the surface of graft co-polymer.*

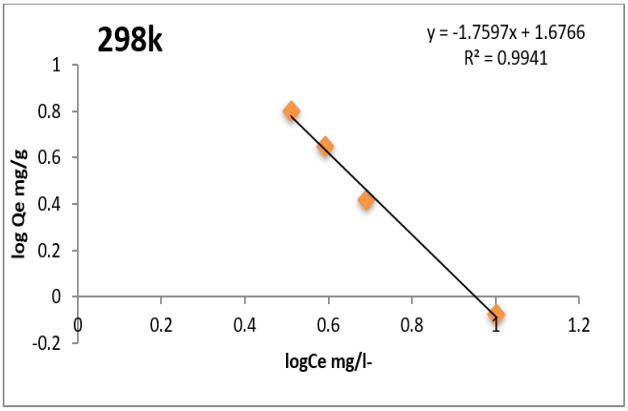
## Adsorption Freundlich equation

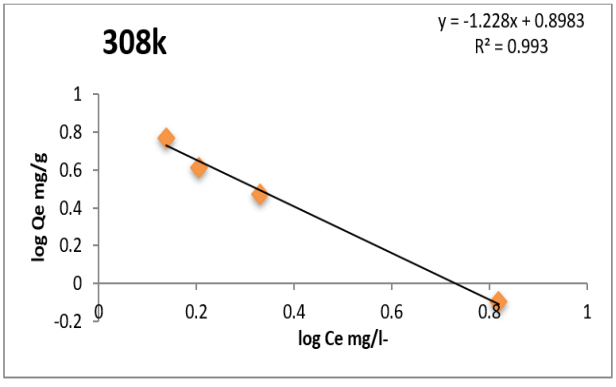
Freundlich, a German physicist, developed one of the most important isothermal equations to explain solution adsorption on the surfaces of heterogeneous materials [18]. The mathematical formula for the second Freundlich equation is as follows: Ce1/n + Qe = Kf (2)

Figure 9 illustrates what occurs when a straight line is used to link Log Qe with Log Ce. Tables 3 and 4 display the findings of the Freundlich equation for the adsorption of methyl orange dye on a nano co-polymer surface at 298 K.

Table (6): Graft co-polymer surface methyl orange dye adsorption at 298K, 308K, and 318K (by applying Freundlich equation).

| Conc. (ppm) | 298K | | 308K | | 318K | |
|---|---|---|---|---|---|---|
| | -LogCe | LOgQe | -LOgCe | LogQe | -LogCe | LogQe |
| 1 | 1.0026 | -0.0735 | 0.8187 | -0.0995 | 0.5909 | -0.1567 |
| 3 | 0.6901 | 0.4184 | 0.3317 | 0.3757 | 0.1705 | 0.3383 |
| 5 | 0.5909 | 0.6480 | 0.2055 | 0.6131 | 0.0531 | 0.5863 |
| 7 | 0.5101 | 0.7974 | 0.1380 | 0.7693 | 0.0045 | 0.7508 |



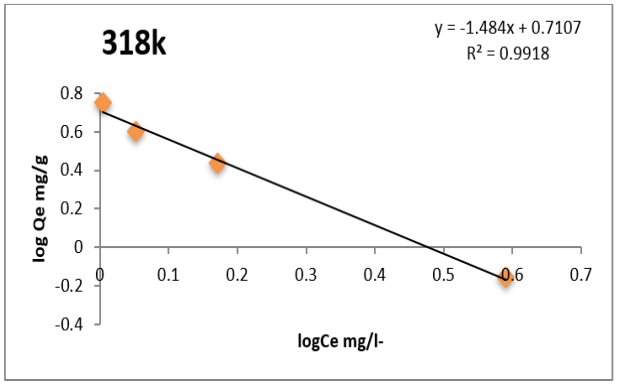



*Figure (12): Apply Freundlich equation on adsorption of methyl orange dye on the surface of graft co-polymer at 298K,308K and318K*

| Table13: Freundlich constant values for methyl orange dye adsorption on the surface of a nano co-polymer at 298K | | | |
|---|---|---|---|
| R2 | KF | -N | Temp |
| 0.9941 | 47.48976 | 0.56828 | 298 |
| 0.993 | 7.91225 | 0.81433 | 308 |
| 0.9918 | 5.136887 | 0.67385 | 318 |

## 3. Conclusion

With a specific temperature, the unique nano-copolymer of phthalic anhydride and glycerol was created. The AFM photos supported the polymer's nanostructure, while the XRD measurements demonstrated the presence of a crystal structure. Methyl orange dye was examined for its ability to adsorb to a nano polymer, and the findings indicated that this adsorption was successful at normal temperature and pH.

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