Research Article

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# Removal of Pollution with Eosin Yellow Dye from Waste Water by Using a Novel Nano Co-polymer

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## Abstract

In this study, graft nano co-polymer was synthesized by esterification method of phthalic anhydride and glycerol. Nano polymer was diagnosed by infrared spectroscopy FT-IR, atomic force microscopy technique (AFM), X-ray diffraction analysis (XRD) and differential scanning calorimetry (DSC). Tendency of fabricated nano-polymer to adsorb Eosin yellow from aqueous solutions was evaluated. The average size of the height density of the nano-polymer was 22.04 nm. The effects of three different temperatures (298, 308 and 318 K) and concentrations (1, 3, 5 and 7 ppm) for nano polymer have been studied. The study's findings made it abundantly evident that manufactured nano-polymers were highly effective in completely removing Eosin yellow from aqueous solutions.

**Keywords:** Nano co-polymer; Characterization; Adsorption; Eosin yellow

## Introduction

A study on the design, installation, characterization and applications of materials, devices and systems controls the shape and size of the nanoscale. As the size of nanomaterials ranges from 1 to 100 nm according to the US National Nano Initiative, the presence of pollutants such as dyes, heavy metals, phenols, drugs and others is very dangerous to the health of human and aquatic life, and artificial dyes are used everywhere in the era of modern technology [1–3]. Since water-soluble dyes are used to colour papers, leather, hair, foods, cosmetics, and clothing, the removal of dyes from industrial wastewater is extremely necessary and has attracted great interest in the past few years due to its toxicity [4]. And the demand for clean water, which

is expected to rise rapidly with an accelerating pace of industrialization, poses the disposal of industrial liquid pollutants threats to the environment and becomes a great matter of concern for the sustainable development of human society, and that the reclamation of polluted water and its recycling are among the objectives and improvement of environmental quality [5, 6].

In the last few decades, great emphasis has been placed on the exploration of biodegradable polymers for specific applications such as controlled drug delivery, insecticides and pesticide vectors as well as sorbents to remove many harmful components from the aqueous system [7]. The adsorption method on a nano polymer's surface is one of the most crucial of these techniques. When we observe that most researchers have a propensity to making use of nanoparticles to

create novel and high-quality materials, larger and more adsorbents are required because the particles on the interactions at the nanoscale differ from those at larger scales [8]. Although many commercial polymers are available, they are almost resistant to microbial attack, and survival of such polymers is a major problem and a potential source for creating an environment. Therefore, the aim of the study was to develop new nano-polymers of phthalic anhydride and glycerine specifically designed to absorb some pollutants such as dyes from wastewater. There are various ways that monomers can be arranged into a common polymer along the spine. Sequence-controlled polymers are co-polymers with carefully chosen monomer arrangements. Simple examples of sequentially managed polymers are mass copolymers, cyclic and co-rotating polymers [9].

## Material and Methods

The chemicals employed in this investigation, including phthalic anhydride, glycerol, and others, were of analytical high quality chemical compounds.

### Synthesis of nanoparticles co-polymers

About 200 mL beaker (3.0 mole, 444 g) of phthalic anhydride and (48 mL) of DMSO, were mixed together. This beaker was equipped with a thermometer. The mixture warmed carefully with a hot plate magnetic stirrer to 70 °C until clear liquor is formed and added (1.0 mole, 92 g) of glycerol to the solution. The mixture warmed carefully to 100 °C then 15 mL of xylene was added carefully to the reaction beaker, in the form of batch, withdrawal of water formed by the esterification process, and the beaker was gently heated. Heating was stopped after (71 min at 125 °C), until no more water came off to prepare the nano co-polymer. Then add the cold distilled water, where the suspension solution is formed. Leave the suspension solution to precipitate overnight, then filtrat and wash with distilled water and leave to dry [10].

### Purification of polymer

After isolation, purification is required because the generated polymer can contain traces of solvent, an unreacted monomer, or other impurities. The polymer was dissolved in the appropriate solvent, in accordance with the described procedure [10], and 5% concentration of non-solvent was added while being violently agitated.

The non-solvent was miscible with the polymer and the solvent. The solid polymer was separated from the solution as a result of precipitation. The entire re-dissolving and re-precipitating procedure was completed three times in order to improve the polymer's quality [11]. After being purified, the nano co-polymer was vacuum dried at 50 °C and maintained in a vacuum desiccator until it could be further characterized and used [12].

### Adsorption behavior of grafting nano co-polymers

The adsorption of a new nano-polymer on dyes was examined using the following technique to generate dye solutions (Eosin yellow): A solution of Eosin yellow dye 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
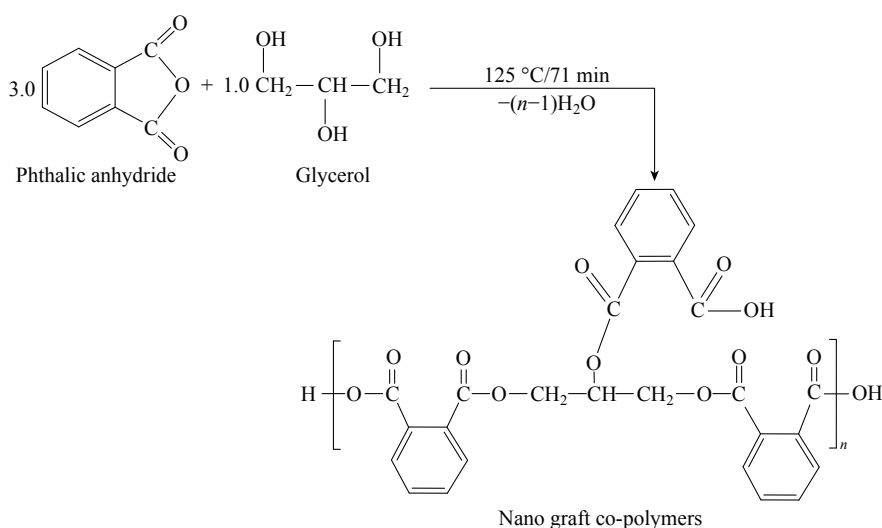


**Fig. 1** Steps of polymer preparation

274

*Nano Biomed. Eng.*, 2022, Vol. 14, Iss. 3

solutions were prepared in concentrations of 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 min of taking the vials containing the solution, which consists of a nano polymer adsorbent surface with a weight of 0.02 and the dye adsorbent (Eosin yellow), 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 number of adsorbed dyes (Eosin yellow) on the surface of the new nano polymer was calculated from the next equation [13]:

$$Q_e = (C_o - C_e) V_{sol} / W_t \tag{1}$$

## Results and Discussion
### Characterization of grafting nano co-polymer

Figure 2 showed the FT-IR spectrum which appears a very weak broad band at (3093—3401 cm$^{-1}$) attributed to the bond (O—H) carboxylic acid and

H-bond, showed a stretching band at (3067 cm$^{-1}$ and 2887 cm$^{-1}$) attributed to the bond (C—H) aromatic and a asymmetric (C—H) aliphatic bond, also a strong stretching band at (1757 cm$^{-1}$) attributed to the carbonyl bond (C $=$O) and stretching bands at (1402, 1468 and 1595 cm$^{-1}$) attributed to (C—C) aromatic, showed strong sharp peak at (1107 cm$^{-1}$) attributed to the bond (C—O) ester, and showed bands at (709 and 903 cm$^{-1}$) attributed to disubstitution of aromatic ring.

Figure 3 shows the 1H-NMR spectrum, which explains the singlet signal at 13.04 ppm of characteristic proton in the carboxylic acid group. Moreover, the multiple in the region 7.55—7.68 ppm attributed to all protons in the aromatic ring, the signals at 4.26—4.28 ppm for four methylene protons in the co-polymer structure, and multiple at 4.15 ppm of methyl protons, but aliphatic alcohol signal has disappeared indicating the formation of a graft co-polymer.

Figure 4 shows the outer surface of the nanoparticles of co-polymer. The roughness coefficient of co-
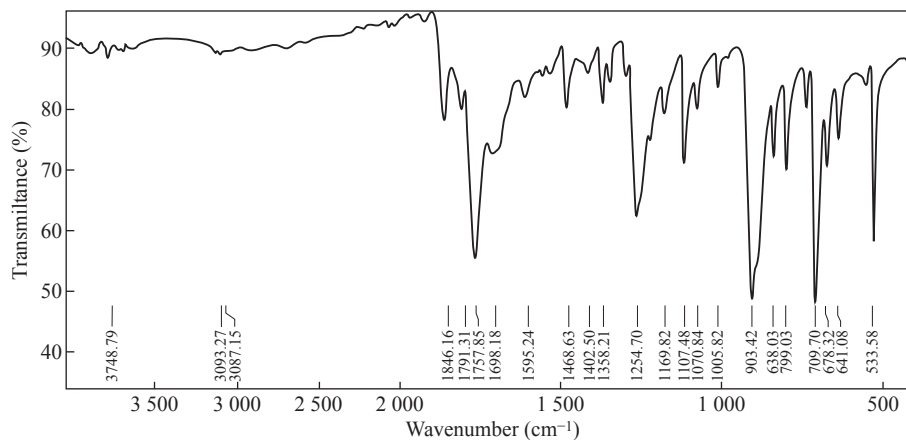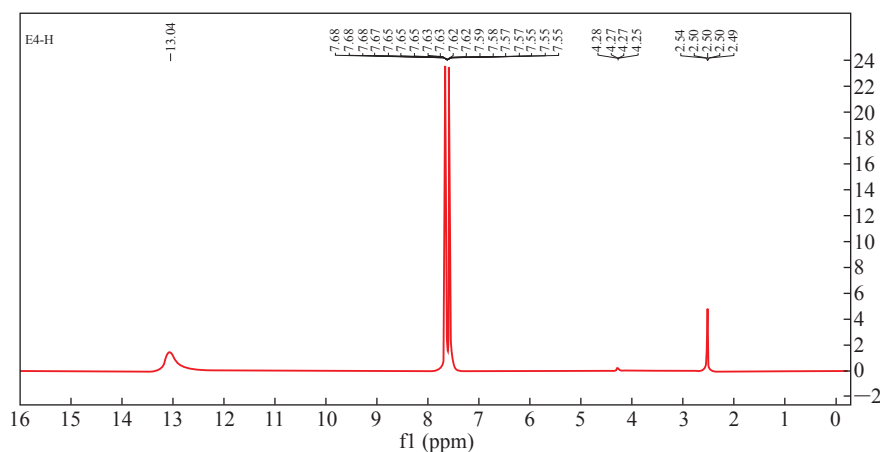


**Fig. 2** FT-IR of graft nano co-polymer
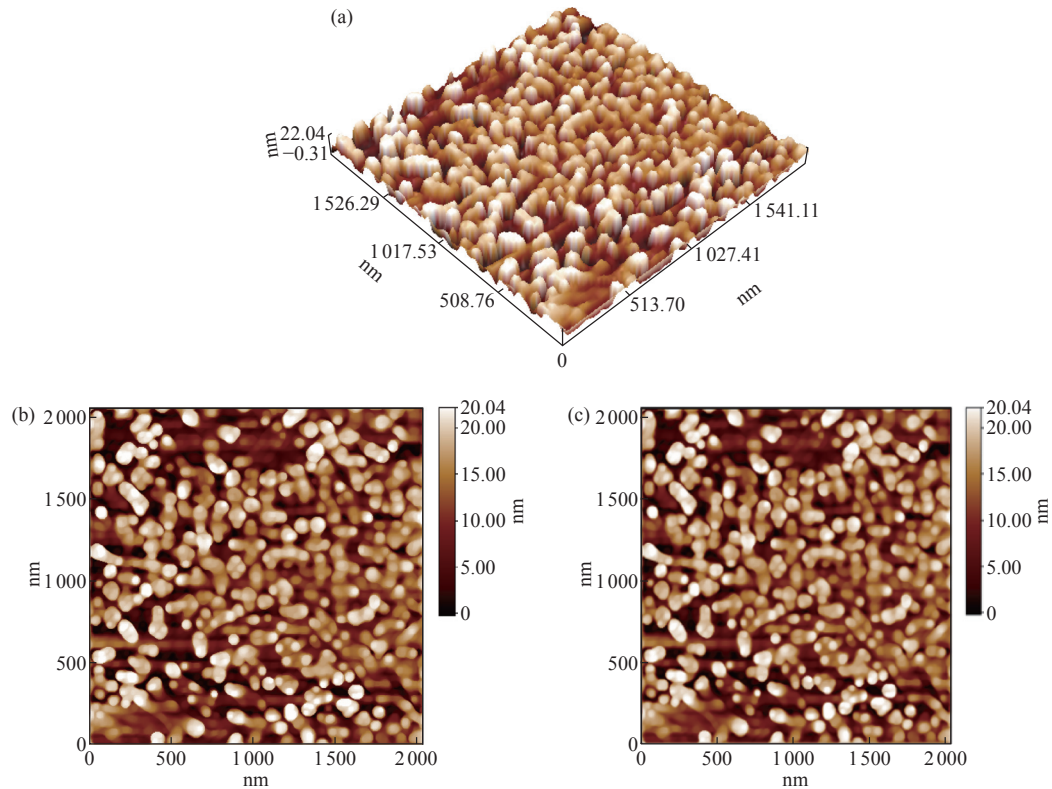


**Fig. 3** 1H-NMR spectrum of nano co-polymer

(a)



**Fig. 4** Image of atomic force microscope for nano co-polymer: **(a)** 3D image, **(b)** 2D image, and **(c)** 2D image showing all details of particles

polymer surface was 5.08 nm and the square root square was equal to 5.94 nm. This indicates that the bold size of the nanoparticles plays an important role in the roughness of the surface, its uniform crystalline system, and the surface homogeneity. Also, the average of height of the particles was equal to 22.04 nm, as observed in Fig. 4(a). Table 1 represents the total rate

of the particle sizes of the common nanoparticle and the different proportions of these volumes; the results indicate that the molecular size of the co-polymer nanoparticle was 68.62 nm.

The X-ray diffraction (XRD) in the nanoparticle's co-polymer (Fig. 5) shows peaks at $2\theta$ values of 15.4°, 18.5°, 21.2°, 22.2°, 26.9° and 30.5°. These peaks

**Table 1** Total rate of the particle sizes of the nanoparticle co-polymer and different proportions of these volumes

| Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) |
|---|---|---|---|---|---|---|---|---|
| 45.00 | 1.52 | 1.52 | 65.00 | 17.80 | 40.91 | 85.00 | 11.74 | 90.91 |
| 50.00 | 4.17 | 5.68 | 70.00 | 12.12 | 53.03 | 90.00 | 9.09 | 100.00 |
| 55.00 | 9.09 | 14.77 | 75.00 | 13.64 | 66.67 | | | |
| 60.00 | 8.33 | 23.11 | 80.00 | 12.50 | 79.17 | | | |
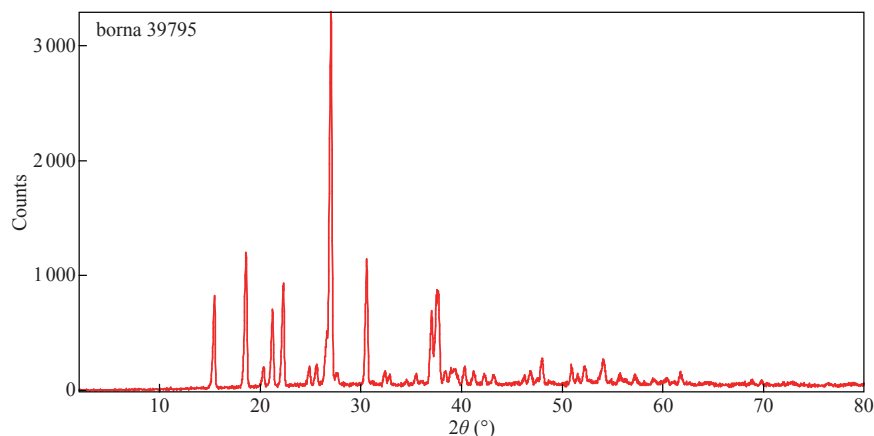


**Fig. 5** X-ray diffraction in the nanoparticle's co-polymer

276

*Nano Biomed. Eng.*, 2022, Vol. 14, Iss. 3

**Table 2** Proportions crystallites sizes and distances between atoms (d-spacing) in the nano co-polymer

| $2\theta$ (°) | $\theta$ (°) | FWHM | $D$ (nm) | $d_{hkl}$ (nm) | $\bar{D}$ (nm) | $\bar{d}_{hkl}$ (nm) |
|---|---|---|---|---|---|---|
| 15.41888 | 7.70944 | 0.10308071 | 77.77159 | 0.57421 | | |
| 18.56158 | 9.28079 | 0.12176233 | 66.10961 | 0.47764 | | |
| 21.20363 | 10.60181 | 0.11615246 | 69.58317 | 0.41868 | **68.4874** | **0.4152** |
| 22.26382 | 11.13191 | 0.11743049 | 68.94823 | 0.39898 | | |
| 26.99920 | 13.49960 | 0.13275784 | 61.54072 | 0.32998 | | |
| 30.55913 | 15.27956 | 0.12296861 | 66.97155 | 0.29230 | | |

indicated that the new co-polymer has been formed as a crystalline compound with less of amorphous carbon atoms. By using origin software, the average inters planer spacing between atoms (dhkl) was 0.415 nm according to Bragg's law:

$n\lambda = 2d\sin\theta$

The total average crystallites size was 68.48 nm relative to Scherrer's equation:

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

The TEM micrographs of different sizes and shapes of the nanoparticle's co-polymer (Fig. 6) were observed with irregular particles such as vertebras with different thicknesses shapes, semi-spherical in the form of layers and rods shapes. An average particle size of the co-polymer nanoparticle was found to be 68.08

nm. Table 3 shows the proportions diameters, angels and standard deviations of the nano co-polymer using image software and Fig. 7 represents the histogram for distribution of the different proportions of particle
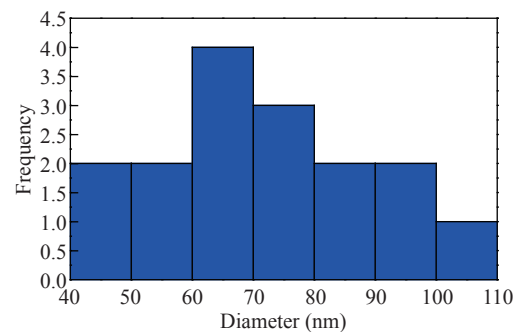


**Fig. 7** Histogram for distribution of the different proportions of particle sizes of the nano co-polymer
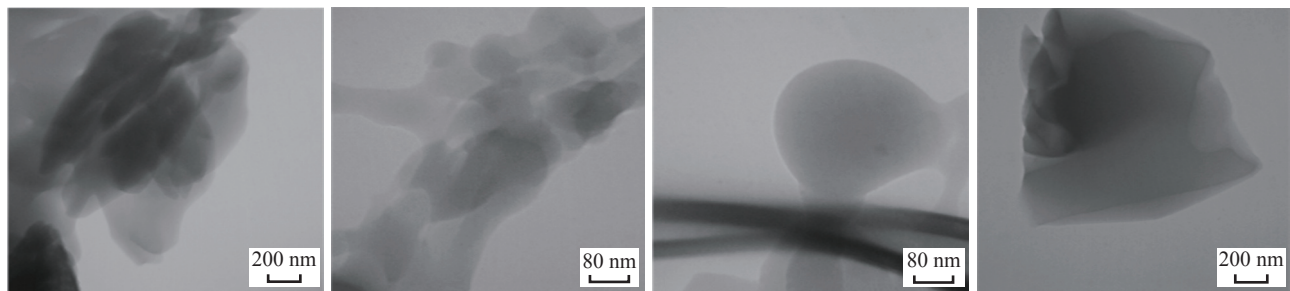


**Fig. 6** TEM micrographs for the nanoparticle's co-polymer

**Table 3** Proportions diameters, angels and standard deviations of the nano co-polymer

| Area | StdDev | Angel (°) | $D$ (nm) | $\bar{D}$ (nm) |
|---|---|---|---|---|
| 14.775 | 7.288 | 8.130 | 45.617 | **68.084** |
| 14.879 | 6.905 | −51.843 | 45.944 | |
| 16.231 | 13.912 | −78.111 | 50.104 | |
| 17.896 | 7.185 | 90.000 | 55.481 | |
| 21.225 | 11.734 | 90.000 | 65.803 | |
| 21.954 | 17.472 | −76.759 | 67.600 | |
| 22.578 | 22.617 | −93.180 | 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 | |
| 19.040 | 5.677 | −74.745 | 88.844 | |
| 30.486 | 9.790 | −88.431 | 94.223 | |
| 31.942 | 9.633 | 52.980 | 98.575 | |
| 32.566 | 15.940 | −80.417 | 100.755 | |

sizes of the nano co-polymer.

Figure 8 showed the DSC thermos grams for the nano co-polymer, the first thermal transition at the peak (48.68 °C) represents the glass transition temperature ($T_g$), the second transition at the peak (134.10 °C) represents the crystallization temperature ($T_c$), and the third and fourth transitions at the peaks (197.60 °C and 302.19 °C) represents the melting temperature ($T_{m1}$ and $T_{m2}$) respectively for the nano co-polymer.
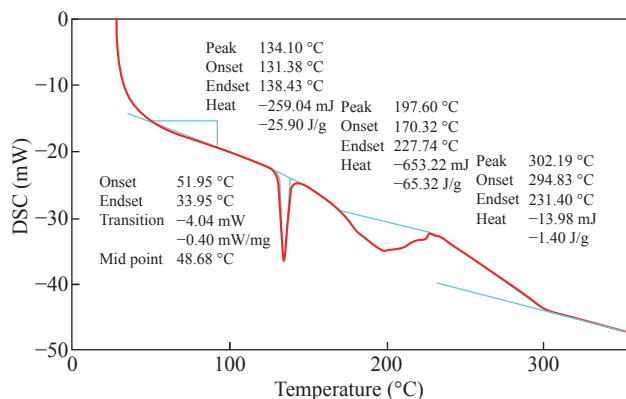
**Fig. 8** DSC thermos grams of nano co-polymer

### Adsorption of Eosin yellow

The titration curve represents the relationship between absorbance and concentration through the graph as shown in Fig. 9. Four generations (1, 3, 5 and 7 ppm) from the Eosin yellow solution utilized in the investigation were employed to identify it, and these concentrations' absorbance was measured at their highest wavelength (520 nm).
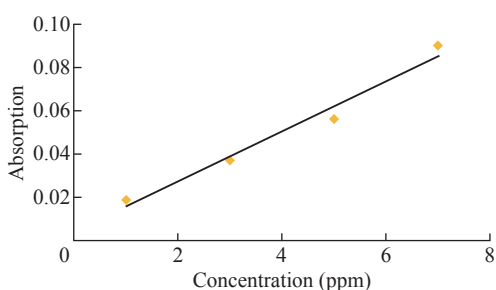
**Fig. 9** Calibration curve between absorption and concentration of Eosin yellow

Table 4 displays the results of a study on the thermal range effects of temperature on the adsorption of Eosin yellow pigment on the surface of polymer nanoparticles (298, 308 and 318 K). The Eosin yellow pigment's adsorption on the surface of these nanoparticles that were created decreased with increasing temperature, indicating that the process is exothermic, according to the experimental data [14]. This suggests the existence of a desorption process, which is the separation of the adsorbed particles on the adsorbent surface and their return to the solution [15], lowering the speed of molecular diffusion with an increase in temperature [16], as illustrated in Fig. 10.
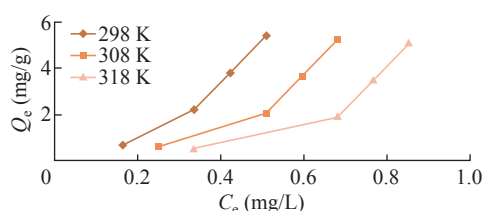
**Fig. 10** Effect of temperature on adsorption of graft co-polymer at 1, 3, 5 and 7 ppm of Eosin yellow dye

### Adsorption isotherms

Researchers looked at the adsorption of dyes (Eosin yellow) on the nano-copolymer and calculated adsorption isotherms at a temperature of 298 K, as shown in Fig. 11, and this suggests that the adsorbent's surface is not uniform. Additionally, the overall shape of the adsorption isotherms, as determined by the Giles classification, is Type S1 [17].
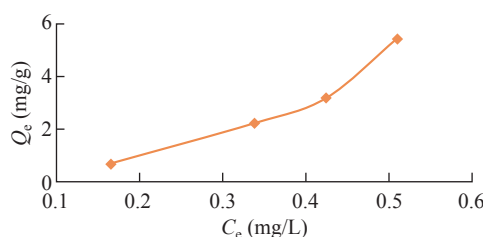
**Fig. 11** Adsorption isotherm Eosin yellow dye on the surface of graft co-polymer

### Freundlich equation for adsorption

One of the most significant isothermal equations

**Table 4** Effect of temperature on adsorption of Eosin yellow

| Concentration (ppm) | 298 K | | 308 K | | 318 K | |
|---|---|---|---|---|---|---|
| | $C_e$ (mg/L) | $Q_e$ (mg/g) | $C_e$ (mg/L) | $Q_e$ (mg/g) | $C_e$ (mg/L) | $Q_e$ (mg/g) |
| 1 | 0.1637 | 0.6969 | 0.2500 | 0.6250 | 0.3362 | 0.5531 |
| 3 | 0.3362 | 2.2198 | 0.5086 | 2.0761 | 0.6810 | 1.9325 |
| 5 | 0.4224 | 3.8146 | 0.5948 | 3.6710 | 0.7672 | 3.5273 |
| 7 | 0.5086 | 5.4095 | 0.6810 | 5.2658 | 0.8534 | 5.1221 |

**Table 5** Adsorption of Eosin yellow dye on the surface of nano co-polymer at 298 K

| Concentration (ppm) | $C_e$ (mg/L) | $Q_e$ (mg/g) |
|---|---|---|
| 1 | 0.1637 | 0.6969 |
| 3 | 0.3362 | 2.2198 |
| 5 | 0.4224 | 3.1846 |
| 7 | 0.5086 | 5.4095 |

was created by German scientist Freundlich to describe the adsorption of solutions on the surfaces of heterogeneous materials [18]. The Freundlich equation has the following mathematical formula:

$$Q_e = K_f C_e^{1/n} \tag{2}$$

Figure 12 illustrates the result of depicting the link between $\log Q_e$ and $\log C_e$ as a straight line. While Tables 6 and 7 provide the findings of the Freundlich equation for the adsorption of Eosin yellow dye on the surface of nano co-polymer at 298 K.
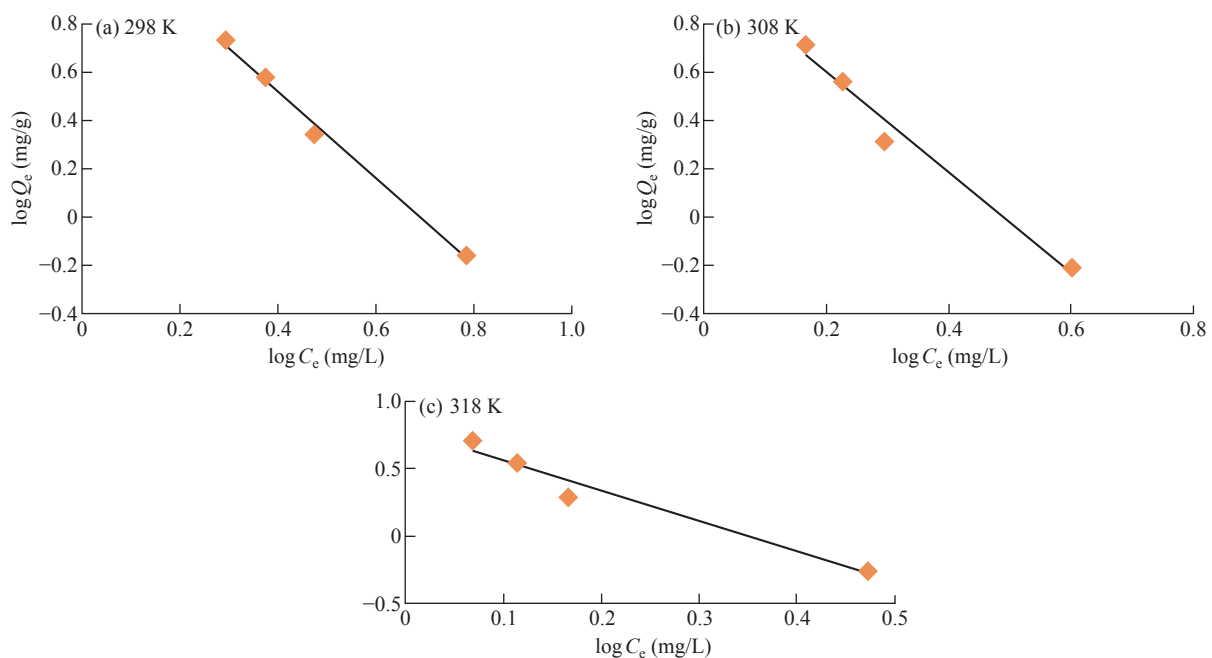


**Fig. 12** Apply Freundlich equation on adsorption of Eosin yellow dye on the surface of graft co-polymer at **(a)** 298 K, **(b)** 308 K and **(c)** 318 K

**Table 6** Adsorption of Eosin yellow dye on the surface of graft co-polymer at 298 K, 308 K and 318 K by applying Freundlich equation

| Concentration (ppm) | 298 K | | 308 K | | 318 K | |
|---|---|---|---|---|---|---|
| | $-\log C_e$ | $\log Q_e$ | $-\log C_e$ | $\log Q_e$ | $-\log C_e$ | $\log Q_e$ |
| 1 | 0.7859 | −0.1568 | 0.6020 | −0.2041 | 0.4734 | −0.2571 |
| 3 | 0.4734 | 0.3463 | 0.2936 | 0.3172 | 0.1668 | 0.2861 |
| 5 | 0.3742 | 0.5814 | 0.2256 | 0.5647 | 0.1150 | 0.5474 |
| 7 | 0.2936 | 0.7331 | 0.1668 | 0.7214 | 0.0688 | 0.7094 |

**Table 7** Values of Freundlich constants for adsorption of Eosin yellow dye on the surface of nano co-polymer at 298 K

| $R^2$ | $K_f$ | $-N$ | Temperature (K) |
|---|---|---|---|
| 0.9941 | 17.49444 | 0.55577 | 298 |
| 0.9761 | 10.34904 | 0.48412 | 308 |
| 0.9581 | 6.146105 | 0.44096 | 318 |

# Conclusion

The novel nano-copolymer between phthalic anhydride and glycerol was synthesized with a certain temperature. The XRD results indicated the presence of a crystal structure, while the AFM images confirmed the nanostructure of the polymer. The adsorption of Eosin yellow dye on the nano polymer was studied and the results showed that the adsorption of Eosin yellow dye was effective at normal temperature and neutral pH.

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