Removal of Pollution with Dye Orange-G from Waste Water by Using Novel Nano Co-polymer

Sajid H. Guzar1*, Ameer S. Al-mayali2, Mohammad N. Al-Baiati3

Abstract
Through this study, nanocomposite co-polymer was prepared by reaction between Pentaerythritl phthalic anhydride. Infrared spectroscopy and AFM technique was used for the purpose of distinguishing the nanopolymer. Thus, the ability of the synthetic polymer to absorb the Orange-G pigment present in aqueous solutions was found. It was found that the nanopolymer had an average height of 5.26 nm. Therefore, three different temperatures were used (298, 308 and 318 K). Also, three concentrations of parts units per million (1, 3 and 5) of the nanopolymer synthesized were used for the study. Through this study, it was found that the nanopolymer is effective in removing Orange-G from all aqueous solutions.

Key Words: Newly Created Nan Co-polymer, Characterization, Pollutions, Adsorption, Orange-G.

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Introduction
Based on the US National Nanoscale Program, the size of nanomaterials ranges from 1 to 100 on the nanometer scale (A.R. Khudhair et al, 2020). Large quantities of water and the many types of chemicals used in the textile industry (such as washing, bleaching, dyeing, preparation... etc.) generate a large amount of industrial wastewater, and these quantities of polluted liquids can cause damage if discharged into the water environment Bio-without treatment, which leads to a reduction in the percentage of dissolved oxygen in these waters in addition to toxic effects (M.J. Abd Ali et al, 2020). Industrial wastewater contains various types of synthetic dyes, suspended solids, fibers, solvents, heavy metals, urea, detergent foam, toxic materials, biological and chemical materials that depress dissolved oxygen. In water, as industrial dyes are one of the common types of water pollutants because of their high solubility in water, and industrial wastewater needs chemical treatment to remove dangerous chemicals to comply with legal limits so that it can be discharged into public sewage networks or into surface water (L.C. Teong et al, 2011). It also contains solid waste that includes fibers, strings, fabrics, winding exhausts (empty rollers and cardboard), empty containers for dyes, chemicals and impurities of wax materials, which are considered hazardous wastes, and dealing with them may expose workers to toxic effects, that the release of this polluted water into the ecosystem and due to its high toxicity which pose a great threat to living organisms and the environmental balance, so it is necessary and absolutely necessary to remove these dyes from wastewater and make them usable, while continuing to develop new technological systems to remove organic pollutants in the water, such as dyes and heavy metals from their aqueous solutions.

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Although there are many commercial polymers, they are almost all antimicrobial, and dumping such polymers has major problems and is a potential source of environmental differences (A. George et al, 2019). Therefore, the purpose of this research is to develop a new type of phthalic anhydride and pentatriol nano-copolymer, its purpose is to absorb some pollutants such as dyes from impure water containing the pollutant.

**Materials and Mouthed**
The chemicals and reagents used for the purpose of this study are from E. Merck's limited analytical class.

**Synthesis of Novel Nano Co-Polymer**
(269 g, 2.0 mol) of phthalic anhydride was dissolved in (20 ml) ml of dimethyl sulfoxide, and (136 g, 1.0 mol) of pentehtritol in (15 ml) dimethyl sulfoxide and then the two solutions were mixed. The temperature was raised externally to 130°C and 10 mL of xylene was added gradually to remove the water particles. The total reaction time was 65 min and the reaction was at 140°C. Finally the resulting solution was immersed in an ice-cold water bath. The final precipitate was filtered, washed with deionized water, and labeled with FT-IR and NMR.

![Figure 1. Synthesis the novel nano co-polymer](image)

**Polymer Purification**
Sometimes the nanopolymer is contaminated in trace amounts through solvents or monomers remaining without reaction Or the presence of various impurities, so it needs to be purified. after separation A suitable solvent was used for the purpose of dissolving the composite nanopolymer and for the purpose of precipitationA concentration of 5% has been added while continuing vigorous” stirring” according to the recommended procedures (B. Jeong et all, 2000). Non-solvents are miscible with polymers and solvents. After precipitation Separate the solid polymer from the solution. Repeat the whole process of dissolution and reprecipitation three times to improve the purity of the polymer (K.S. Chang et al, 1991). After purification, the prepared nano-copolymer It was dried in vacuum at 55°C and for storage, a vacuum dryer was used, after which characterization and further application were performed. (J. Pham et all, 2018).

**Adsorption Behavior of Novel nano Co-Polymer**
adsorption properties of the synthesized nano-copolymer for Orange-G were studied. 0.5 grams of Orange-G dye was taken and dissolved in an amount of distilled water to prepare a Orange-G dye solution. For the purpose of preparing the solution at a concentration of 500 parts per million, it was diluted to 1000 mlWhile shaking the flasks with their contents, the shaking temperature was stabilized at 25°C, and the bottles and their contents were kept in the container for 20 minutes.The absorption of the dyes was defined by recording the spectral changes of UV and VIS over time. In order to know the concentration of the Ce solutions in mg / L units, a titration curve was used for this purpose, after which the absorbed Qe was determined in mg / g units in several stages with the formulas shown below (A.F. Hasan et all, 2020):

\[
Q_e = \frac{(C_i - C_f) \cdot V_{sol}}{W_t} \ (1)
\]

**Discussions and Results**

**Characterization Related to the Novel Nano Co-polymer**
Figure 2, Displays the characteristic peaks of the FT-IR spectrum. The peaks appearance at 3072 cm\(^{-1}\) returns OH alcoholic, the peaks at 3003 cm\(^{-1}\) refers to aromatic C-H, while the peak at 2889 and 2957 cm\(^{-1}\) refers to pentarythritolic linkage C-H, the sharp band at 1671 cm\(^{-1}\) indicates the C=O, the two bands at 1582 and 1492 cm\(^{-1}\) becomes to C=C, and the peak which appear at 1069 cm\(^{-1}\) returns to C-O, finally the peaks at 735 and 898 cm\(^{-1}\) refers to di substituted aromatic rings.

Figure 3, represent the 1H-NMR spectrum of a novel nano co-polymer, and showed exchangeable singlet signal for the hydroxyl group at 13.15 ppm. The aromatic protons appeared within the 7.81-7.52 ppm region. It also showed a singlet signal at 2.55
ppm for the hydroxyls group of the Pentarythrytol linkage, they appear at this position due to its exchangeable prosperity with the deuterium and the methylene groups showed a singles peaks at 4.38 and 3.25ppm; On the other hand.

Figure 2. FT-IR Spectrum of novel nano co-polymer

Figure 3. 1HMNMR Spectrum of novel nano co-polymer

Figure (4 a,b and c) Illustrate the External surface For nanoparticles related to the new co-nanopolymer. Show that the co-polymer surface has a roughness coefficient of 1.37 nm and As for the squal root of the co-polymer, it was equal to 1.58 nm. It shows us that the bold size of the nanoparticles has an effective role in the roughness of the surface as well as its crystal system, which are important factors in the homogeneity of its surface. From Figure (3a), it appears that the average height of the particles was 5.26. Table 1 includes the total rate for the common sizes of nanoparticles and the various proportions related to these sizes; It was found through the results that the co-polymer nanoparticle had a molecular size of the that was equal to 97.23 nm.
Figure 4. Illustrates an atomic force microscope image of the new nanopolymer; a) shows 3D Image, b) an atomic force microscope shows a nanopolymer image showing a two-dimensional image and c) It shows all the properties related to the particles

Table 1. Illustrates the produced results from AFM analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Code: Sample Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line No.:lineno</td>
<td>Grain No.:130</td>
</tr>
<tr>
<td>Instrument: CSPM</td>
<td>Date: 2021-01-15</td>
</tr>
<tr>
<td>Avg. Diameter: 97.23 nm</td>
<td>&lt;=10% Diameter: 65.00 nm</td>
</tr>
<tr>
<td>&lt;=50% Diameter: 95.00 nm</td>
<td>&lt;=90% Diameter: 125.00 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diameter (nm)&lt;</th>
<th>Volume (%)</th>
<th>Cumulation (%)</th>
<th>Diameter (nm)&lt;</th>
<th>Volume (%)</th>
<th>Cumulation (%)</th>
<th>Diameter (nm)&lt;</th>
<th>Volume (%)</th>
<th>Cumulation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.00</td>
<td>0.77</td>
<td>0.77</td>
<td>85.00</td>
<td>6.92</td>
<td>30.77</td>
<td>115.00</td>
<td>7.69</td>
<td>79.23</td>
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<tr>
<td>60.00</td>
<td>1.54</td>
<td>2.31</td>
<td>90.00</td>
<td>8.46</td>
<td>39.23</td>
<td>120.00</td>
<td>2.31</td>
<td>81.54</td>
</tr>
<tr>
<td>65.00</td>
<td>3.08</td>
<td>5.38</td>
<td>95.00</td>
<td>6.92</td>
<td>46.15</td>
<td>125.00</td>
<td>3.85</td>
<td>85.38</td>
</tr>
<tr>
<td>70.00</td>
<td>7.69</td>
<td>13.08</td>
<td>100.00</td>
<td>8.46</td>
<td>54.62</td>
<td>130.00</td>
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<td>75.00</td>
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<td>7.69</td>
<td>23.85</td>
<td>110.00</td>
<td>8.46</td>
<td>71.54</td>
<td>140.00</td>
<td>2.31</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure 5. It includes the distribution of the various proportions related to the particle sizes of the nanoparticles related to the copolymer

**Adsorption Orange-G dye**

A calibration curve was used by graphing between concentration and absorption, using three previously prepared concentrations (1, 3 and 5 ppm) through (Orange-G dye) solution of that was used in the search. Then the concentration absorption was measured by fixing maximum wavelength (480 nm) For Orange-G dye, as shown in Fig. 6, after which the curve between absorption and concentrations was updated as shown in Fig. 7.
Figure 6. Ultraviolet–Visible spectrum (λ_{max}) of the Orange-G dye

Table 2 showed that the Orange-G dye is affected by temperature when absorbed on the surface of the polymer when using different temperatures (298, 308, and 318 K).

From the results shown to us, we can conclude that the absorption of the Orange-G dye when using a nano-polymer as a mas surface increases with increasing temperature, indicating that the process is endothermic (M.N. Al-Baiati, 2017). This explains the occurrence of the absorption process, meaning that two absorption processes take place in addition to the adsorption process (L. Illum et al., 1999). Consequently, the velocity of particle diffusion increases with increasing temperature (D.N. Simavilla et al., 2017), as shown in Fig. 8.

Table 3. Shows adsorption of Orange-G dye on the surface of the newly prepared polymer nanoparticles at 298 K

<table>
<thead>
<tr>
<th>Temp</th>
<th>Conc.(ppm)</th>
<th>C_e</th>
<th>Q_e</th>
</tr>
</thead>
<tbody>
<tr>
<td>298K</td>
<td>1</td>
<td>0.275</td>
<td>6041.66</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.726</td>
<td>18950</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.077</td>
<td>32691.66</td>
</tr>
</tbody>
</table>

Freundlich Equation

There are several equations that deal with adsorption of solutions over heterogeneous surfaces of materials. Freundlich’s equation is one of...
these special isotherm equations (C. Namsiveayam et al, 2005).

\[ Q_e = K_f \cdot C_e^{1/n} \]  

(2)

From the above equation, \( C_e \) is the concentration of the absorbent in units of mg per liter at equilibrium. While \( Q_e \) the amount of absorbent in mg from the above equation, \( C_e \) is the concentration of the absorbent in units of mg per liter at equilibrium. While \( Q_e \) is the amount of absorbent, in units of mg per g, at equilibrium g units at equilibrium. They are affected by the nature of the adsorbent, the adsorbent surface, and temperature. By taking the logarithm as shown in the equation below 3.

\[ \log Q_e = \log K_f + \left( \frac{1}{n} \right) \log C_e \]  

(3)

By plotting a calibration curve between (Log \( Q_e \)) and (Log \( C_e \)), We were able to get straight line as shown in the figure 10. In contrast, the results are through the Freundlich equation for absorption of the Orange-G Dye using the newly synthesizing nanopolymer surface at 298 K.

Table 4. Demonstrates the absorption of Orange-G dye on the surface of the newly prepared nanopolymer at 298 K (using the Freundlich equation)

<table>
<thead>
<tr>
<th>Conc</th>
<th>298K</th>
<th>308K</th>
<th>318K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LogCe</td>
<td>LogQe</td>
<td>LogCe</td>
</tr>
<tr>
<td>1</td>
<td>-0.5606</td>
<td>3.7811</td>
<td>-0.6989</td>
</tr>
<tr>
<td>3</td>
<td>-0.139</td>
<td>4.2776</td>
<td>-0.3001</td>
</tr>
<tr>
<td>5</td>
<td>0.0322</td>
<td>4.5144</td>
<td>-0.17</td>
</tr>
</tbody>
</table>

Table 5. Freundlich constant value of Orange-G dye adsorbed on surface of nano-co-polymer at (298K) and (pH = 6)

<table>
<thead>
<tr>
<th>Temp</th>
<th>N</th>
<th>Kf</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298K</td>
<td>0.8157</td>
<td>29087.071</td>
<td>0.9986</td>
</tr>
<tr>
<td>308K</td>
<td>0.7399</td>
<td>57491.018</td>
<td>0.9926</td>
</tr>
<tr>
<td>318K</td>
<td>0.6834</td>
<td>232166.738</td>
<td>0.9596</td>
</tr>
</tbody>
</table>

Figure 10. The Freundlich isothermal absorbs the Orange-G dye on the surface of the new nano-polymer at a) 298 K, b) 308 K, c) 318 K

**Conclusion**

This new type of a nano-co-polymer is successfully synthesized between phthalic anhydride and pentaerythritol. It is found that at temperatures below (250°C), it has very high stability. The AFM image confirms the nano-structure of the copolymer. The study showed a very high effectiveness of the synthesis novel nano co-polymer in removing pollution at room temperature, which indicates the possibility of removing pollution from the polluted waste water, and reuses it again.

**References**

Khudhair AR, Sherazi STH, Al-Baiati MN. Adsorption of methylene blue from aqueous solutions by using a novel nano co-polymer. *In AIP Conference Proceedings 2020: 2290(1).*


