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## Adsorption of Maxilon Blue ( GRL) from Aqueous Solutions by using a novel nano-composite polymer

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**Keyword:** Nano –composite, active carbon, adsorption, Graft- co- polymer, Nano graft co- polymer.

### Abstract

In this work, preparation of nano-composite polymer from nano graft co-polymer with active carbon and its tendency to adsorbed textile dyes (Maxilon blue GRL), from aqueous solutions were communicated in this study. Different experimental factors like; pH, temperature, size, surface morphology and concentration, play a very important role in the adsorption operation. After addition the composite to the GRL solution were noted the increase in initial pH in the range of (3 to 11), increase the yields removal of Maxilon blue dye, with increasing temperatures and mass of nano-composite co-polymer.

### Introduction

Industrial development in the nations has led to environmental challenges resulting from the rapid synthesis of chemicals and the generation of high-cost solid waste, resulting in an increased flow of pollutants (dyes, heavy metals, phenols, medicines, etc.) [1-2], The presence of these pollutants with a few concentrations is a serious intimidation of human creatures and other organisms. Industrial dyes are used in many areas of modern technology [3]. Dyes are soluble in water and are used for coloring paper, skin, hair, food, cosmetics and textiles. The removal of color from industry or local effluents has attracted considerable attention in the last few years, due to the toxicity of its existence [4]. Before the middle of the 19th century, materials with coloring properties were extracted from natural sources, especially from animals or vegetables [5]. However, natural dyes were almost entirely replaced with synthetic materials at the beginning of the 20th century [6]. Today, almost all commercially available dyes are industrial, with the exception of some inorganic dyes [7]. Every year hundreds of new colored compounds flow into the market, evolving into a series of different applications [8]. According to Guaratini and Zanoni [9], there



are still dispersed dyes that are insoluble in water products, applied to cellulose fibers and other foul fibers by suspension. During the dyeing process, the dye undergoes hydrolysis and the insoluble composition of the origin is slowly deposited in the form of differentiation on cellulose acetate. In general, the process occurs in the presence of dispersion factors for long chains that fix the suspension of the dye, and facilitate contact with water-damaging fibers. This layer of dyes is mainly made up of Azure dyes and has been used in dyeing synthetic fibers, such as cellulose acetate, nylon, polyester and polyamide [10-12]. The technology that has been used in the 21st an atomic or molecular scale by size. The increase in nano scale production has so far shown its diversity in pollutant disposal and environmental sustainability [13]. In this work, a new nano material was prepared and used to remove dye contaminant (Maxilon blue GRL)

## Experimental Part

### 1-Materials

A- All chemicals were used in this work analytical grade.

B- Preparation of nano graft co-polymer

#### 1-Preparation of a nano linear co-polymer

In 200 ml two-necked round bottom flask, (2.0 mole, 332gm) of terphthalic acid and (50 ml) of DMSO, were mixed together. This flask was equipped with a thermometer. The mixture warmed carefully with a hot plate magnetic stirrer to 40 °C until clear liquor is formed and added (1.0 mole, 92gm) of glycerol to the solution. The mixture warmed carefully to 120 °C, then about 25 ml of xylene was added carefully to the reaction flask, in the form of batch (two drops in each batch), withdrawal of water formed by the esterification process, and the flask was gently heated. Heating was stopped after 80 min. at 145 °C, until no more water came off. Leave the reaction flask to cool to about 50 °C.

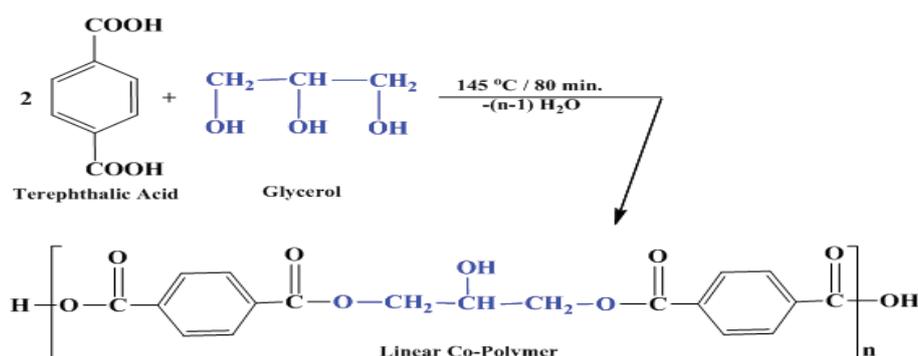


Figure (1) represents the FT-IR spectrum [14] of the linear co-polymer. It showed the appearance of a strong broad band at about  $3423 \text{ cm}^{-1}$  for stretching alcoholic (-OH) with stretching (H-bond), and also showed a weak band at about  $2902 \text{ cm}^{-1}$  due to the -OH for Carboxylic acid, the C-H  $\text{sp}^3$  and  $\text{sp}^2$  hybridization

absorption at about  $2544\text{ cm}^{-1}$ ,  $2654\text{ cm}^{-1}$  respectively. The spectrum also showed a strong band at about  $1726\text{ cm}^{-1}$  assigned to a stretching band C=O for ester group. The spectrum appearance is a weak sharp bands at about  $1597\text{ cm}^{-1}$ ,  $1581\text{ cm}^{-1}$  due to C=C for conjugated system of benzene ring and also showed a bands at about  $1284\text{--}1259\text{ cm}^{-1}$  assigned to C-O absorption band. Figure (2), showed the spectrum of  $^1\text{H}$ NMR showed, which explain the singlet signal at  $13.24\text{ ppm}$  characteristic of proton in carboxylic acid group. Furthermore, the multiples in the region  $7.53\text{--}8.10\text{ ppm}$  back to all protons in aromatic ring, the signals at  $6.27\text{--}6.46\text{ ppm}$  for four protons of methylene in the structure of co-polymer, the multiples at  $4.24\text{--}4.50\text{ ppm}$  of methyl protons, but the triplet signal in  $3.44\text{--}3.62\text{ ppm}$  due to the proton of aliphatic alcohol so this spectrum was confirmed the structure of our target polymer.

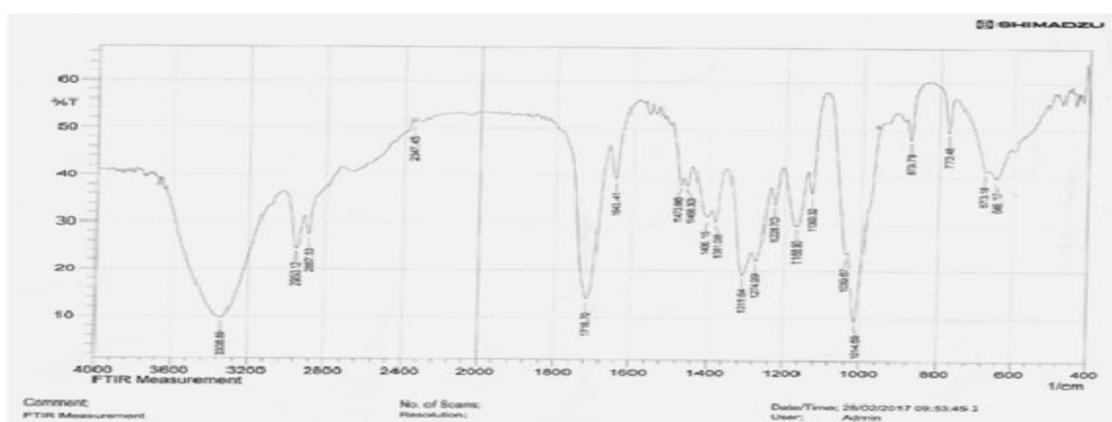


Figure (1): The FT-IR spectrum of linear co-polymer

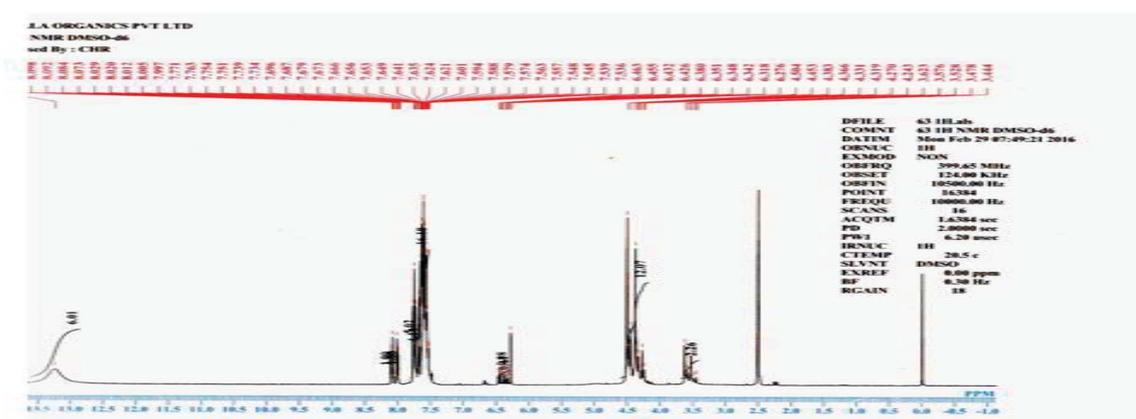


Figure (2): The  $^1\text{H}$ NMR spectrum of linear co-polymer

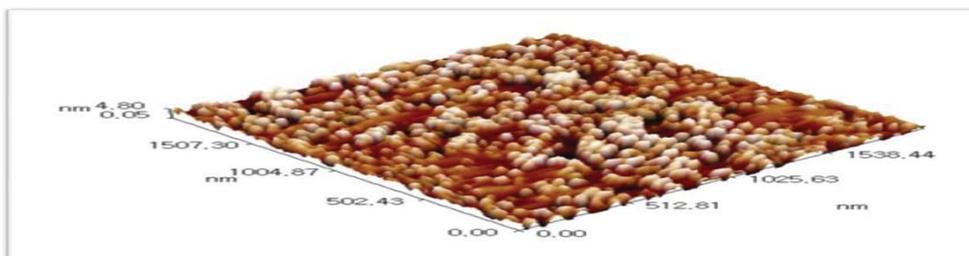
The size of particles of the linear and graft co-polymers which prepared by using solubilization process was measured by the atomic force microscope (AFM); the results showed that the co-polymers are nanoparticles co-polymers, as shown below:

Figure (3-a, b & c) shows the outer surface of the nanoparticles of linear co-polymer. The roughness of this surface and the square root square are calculated according to the coefficient:

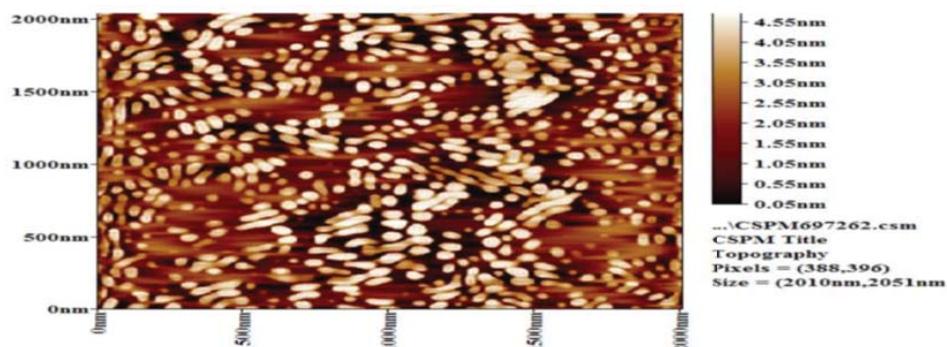
$$Rm \sqrt{\sum_{i=1}^n \frac{(Z_i - Z_{av})^2}{N}}$$

Where N, Z = the number of measured points

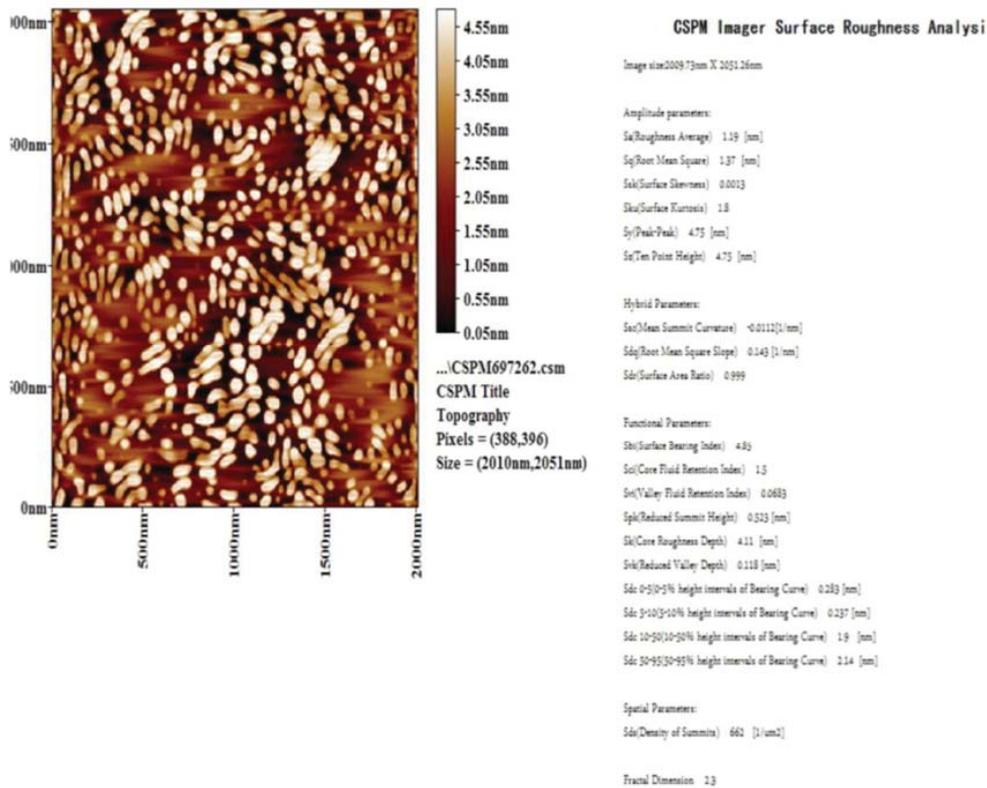
The roughness coefficient of a linear co-polymer surface was 1.19 nm and the square root square was equal to 1.37 nm. This indicates that the bold size of the nanoparticles plays an important role in the roughness of the surface, its uniform crystalline system, and the surface homogeneity. Also, the average of height of the particles was equal to 4.80 nm, as observed in figure (3- a). Table (1) represents the total rate of the particle sizes of the common linear nanoparticle and the different proportions of these volumes; The results indicate that the molecular size of the linear co-polymer nanoparticle was 94.09 nm.



**Figure (3-a): Image of Atomic Force Microscope for linear co-polymer shows 3D Image.**



**Figure (3- b): Image of Atomic Force Microscope for linear co-polymer shows 2D Image.**



**Figure (3-c): Image of Atomic Force Microscope for linear co-polymer shows 2D Image and showing all details of particles**

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

<b>Sample:1</b>			<b>Code:Sample Code</b>		
<b>Line No.:lineno</b>			<b>Grain No.:139</b>		
<b>Instrument:CSPM</b>			<b>Date:2018-04-23</b>		
<b>Avg. Diameter:94.09 nm</b>			<b>&lt;=10% Diameter:75.00 nm</b>		
<b>&lt;=50% Diameter:90.00 nm</b>			<b>&lt;=90% Diameter:115.00 nm</b>		

Diameter(nm)<	Volum e(%)	Cumulat ion(%)	Diameter(nm)<	Volum e(%)	Cumulat ion(%)	Diameter(nm)<	Volum e(%)	Cumulat ion(%)
75.00	7.19	7.19	100.00	8.63	68.35	125.00	1.44	93.53
80.00	12.95	20.14	105.00	7.19	75.54	130.00	5.76	99.28
85.00	16.55	36.69	110.00	7.19	82.73	145.00	0.72	100.00
90.00	11.51	48.20	115.00	5.04	87.77			
95.00	11.51	59.71	120.00	4.32	92.09			

## 2- Preparation of a nano graft co-polymer

About (0.25mole, 25gm) of maleic anhydride, was dissolved in 25 ml of DMSO at 40 °C, and added to the mixture (the flask contents which prepared in above).The flask was gently rise heated to 100 °C, added the drops of xylene in the form of batch (two drops in each batch), until no more water came off at 115 °C after 45 min. to prepare graft co-polymer. Leave the reaction flask to cool to the laboratory temperature, and then add the distilled water, where the suspension solution is form, then leave the suspension solution to precipitate and then filtered and washed with distilled water and leaves to dry.

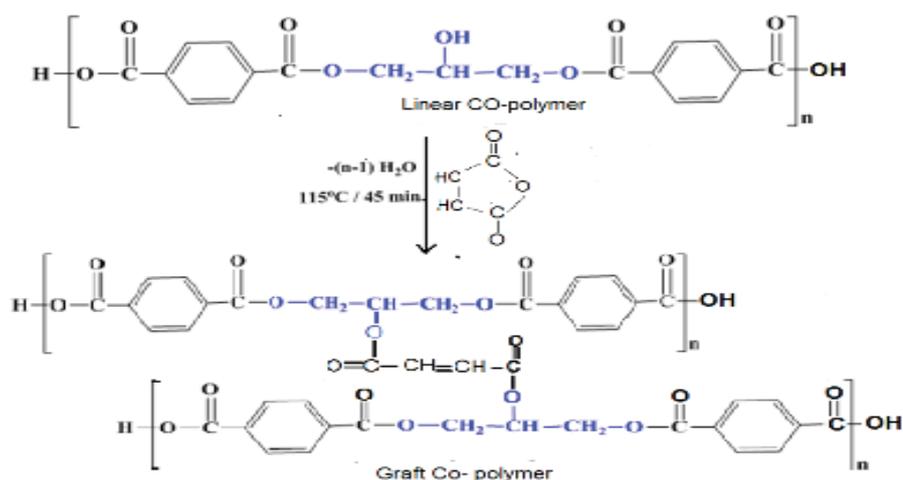
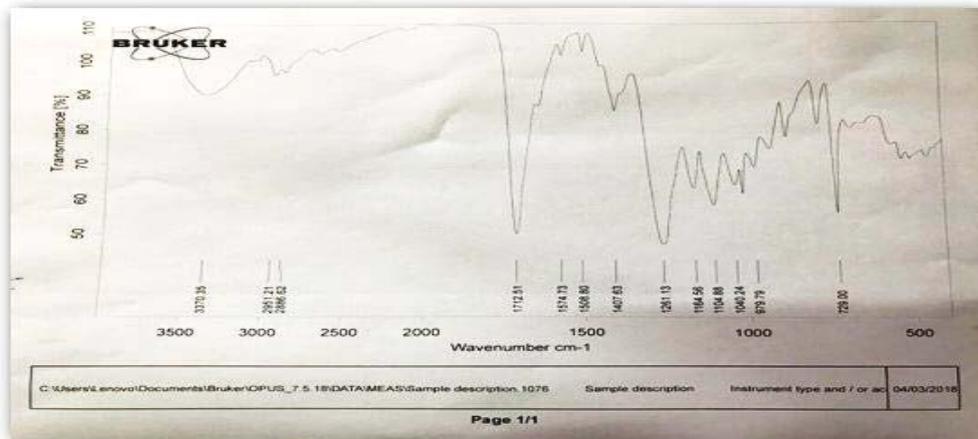
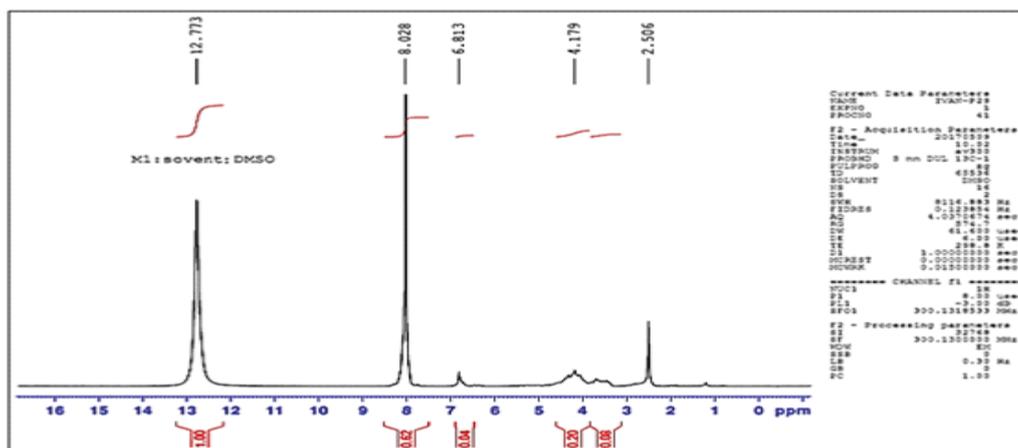


Figure (4), showed the FT – IR spectrum of the graft co-polymer, its showed the appearance of a strong broad band at  $3500 \text{ cm}^{-1}$  for stretching alcoholic(-OH) with stretching (H-bond), and the spectrum also showed the aliphatic (C-H), aromatic (=C-H) and alkenes (=C-H) at approximately at  $2880 \text{ cm}^{-1}$ ,  $3140 \text{ cm}^{-1}$  and  $3050 \text{ cm}^{-1}$  respectively, and the spectrum also showed a strong sharp band at  $1740 \text{ cm}^{-1}$  and  $1250 \text{ cm}^{-1}$  for a stretching band (C=O) ester and (C-O) ester respectively. Figure (5), showed the  $^1\text{H}$ MNR spectrum of the graft co-polymer, its showed the appearance a single signal at 2.5 ppm for DMSO , multi signal at range 3.5-4.8 ppm which can be attributed to  $[\text{CH}_2-\text{O}-\text{C}=\text{O}$  ,  $-\text{CH}=\text{CH}-]$  groups, aromatic protons signal observed as doublet signal at 6.81-8.02 ppm in addition to single signal at 12.77 ppm for carboxylic acid protons



**Figure (4): The FT-IR spectrum of the graft co-polymer**



**Figure (5): The <sup>1</sup>H NMR spectrum of the graft co-polymer**

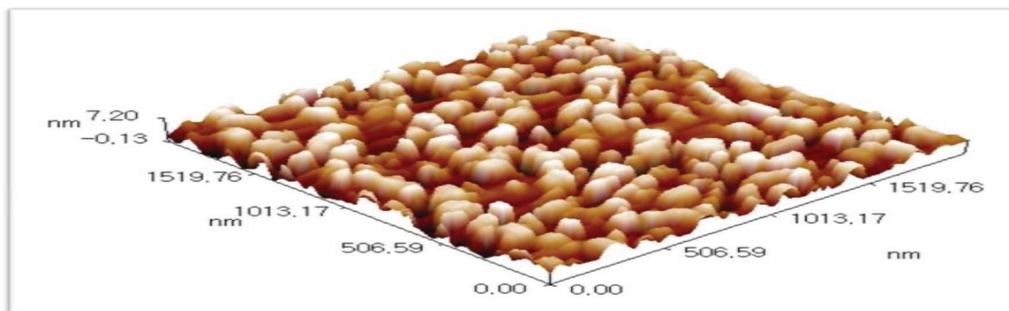
Figure (6-a, b & c) shows the outer surface of the nanoparticles of graft co-polymer. The roughness coefficient of a graft co-polymer surface was 1.68 nm and the square root square was equal to 1.96 nm. This indicates that the bold size of the nanoparticles plays an important role in the roughness of the surface, its uniform crystalline system, and the surface homogeneity, Also, the average of height of the particles was equal to 7.2 nm, as observe in Figure(6-a). Table (2) represents the total rate of the particle sizes of the graft co-polymer nanoparticle and the different proportions of these volumes; the results indicate that the molecular size of the graft co-polymer nanoparticle was 56.80nm.

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

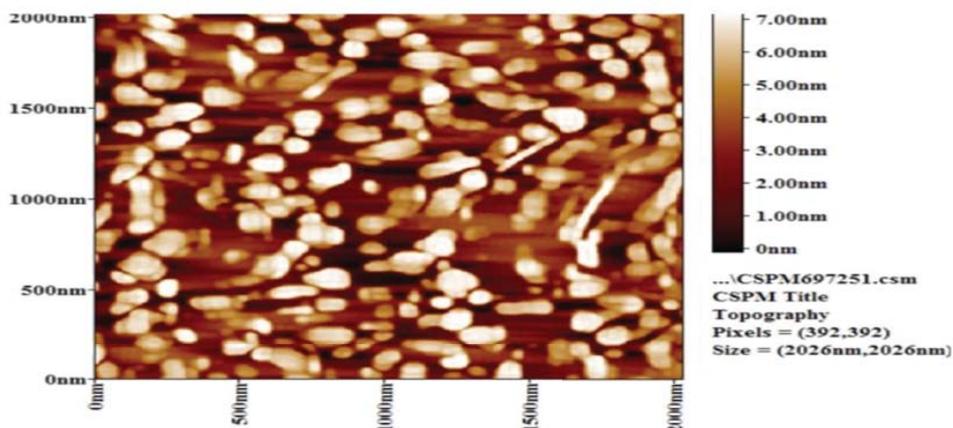
<b>Sample:M4</b>			<b>Code:Sample Code</b>		
<b>Line No.:lineno</b>			<b>Grain No.:259</b>		
<b>Instrument:CSPM</b>			<b>Date:2018-04-23</b>		
<b>Avg. Diameter:56.80 nm</b>			<b>&lt;=10% Diameter:0 nm</b>		
<b>&lt;=50% Diameter:50.00 nm</b>			<b>&lt;=90% Diameter:70.00 nm</b>		

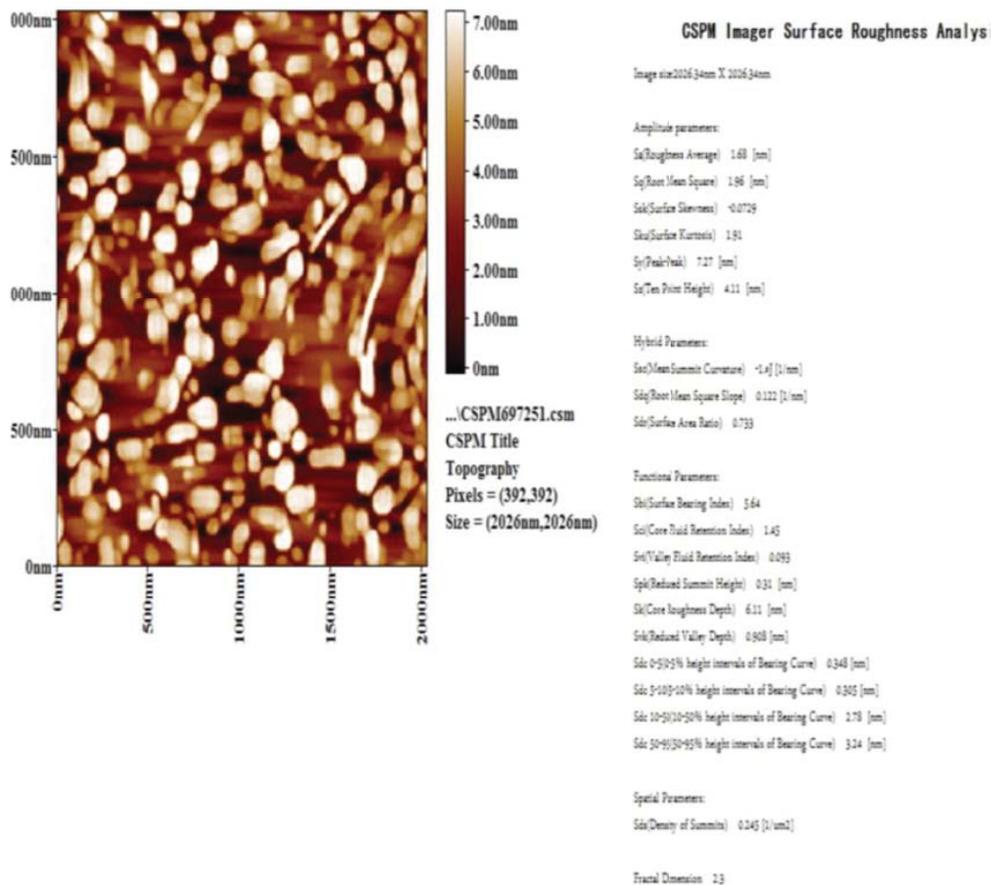
Diameter(nm)<	Volum e(%)	Cumulat ion(%)	Diameter(nm)<	Volum e(%)	Cumulat ion(%)	Diameter(nm)<	Volum e(%)	Cumulat ion(%)
50.00	26.64	26.64	65.00	11.58	81.08	80.00	3.47	99.23
55.00	26.64	53.28	70.00	8.88	89.96	95.00	0.77	100.00
60.00	16.22	69.50	75.00	5.79	95.75			



**Figure (6-a): Image of Atomic Force Microscope for graft co-polymer shows 3D Image.**



**Figure (6- b): Image of Atomic Force Microscope for graft co-polymer shows 2D Image.**



**Figure (6-c): Image of Atomic Force Microscope for graft co-polymer shows 2D Image and showing all details of particles**

### Preparation of nano-composite polymer

About 50 ml ethanol was fill in 100 ml beaker and completed the volume distilled water and added (2.0 gm) from nano graft co-polymer with (1.0 gm) of active carbon, then the mixture putted carefully with hot plate magnetic stirrer for one hrs, at 160 °C, heated was stop after 3 hrs. Leave the mixture to dry for 24 hrs. [15].

### . C- Effect of adsorption parameters

#### 1- Effect of dye concentration

About 0.05 gm from nano composite polymer added to (5,10,20,30 ,40 and 50 ml), 100ppm)from dye putted in 100ml beaker and the volume completed distilled water using water-bath shaker at 20°C with constant stirrer for 24 hrs.

#### 2- Effect of pH solution

The effect of pH solution was studied by agitating 0.05 g of nano-composite polymer and 100 mL of (GRL) dye concentration (20 ppm) using water-bath shaker at

20°C. The experiment was conducted at different pH from 3 to 11. Agitation was provided for 24 h contact time at a constant agitation speed. The pH was adjusted by adding a few drops of diluted 0.4 M NaOH or 0.4 M HCl and measured by using a pH meter.

### 3- Effect of solution temperature

The effect of solution temperature was studied by agitating of varients solution temperatures (10,20, 35, and 50°C) , mass dosage 0.05 g of nano-composite polymer and 100ml (GRL) dye concentration 20ppm using water-bath shaker. The experiment was conducted at pH 6. Agitation was provided for 24h contact time at a constant agitation speed of.

### 4-Effect the mass of nano – composite polymer

The effect of mass dosage was studied by agitating of different masses (0.01, 0.05, 0.1, 0.15, 0.2 and 0.25) g , in 100 mL of Maxilon blue (GRL) dye concentration (20 ppm) using water-bath shaker at 20 °C. The experiment was conducted at pH 6. Agitation was provided for 24h contact time at a constant agitation speed.

## Results and Discussion

### 1-Effect of adsorption parameters

**A-Effect of initial dye concentration**, the plot of the quantities of dye adsorbed ( $q_e$ ) and (R%) dye removal versus initial concentration  $C_0$  at different experimental conditions. From the Figure (7), it can be seen that the amount of dye adsorbed varies with varying initial dye concentration and increases with increase in initial dye concentration, but also the percentage of removal decreased with increasing in the dye concentrations an increasing the initial dye concentration increases the number of collisions between dye ions and the nano –composite polymer, which enhances the adsorption process. The effect of initial dye concentration on the nano–composite polymer capacity has been found to be of considerable significance for the basic dye used. [16 ]

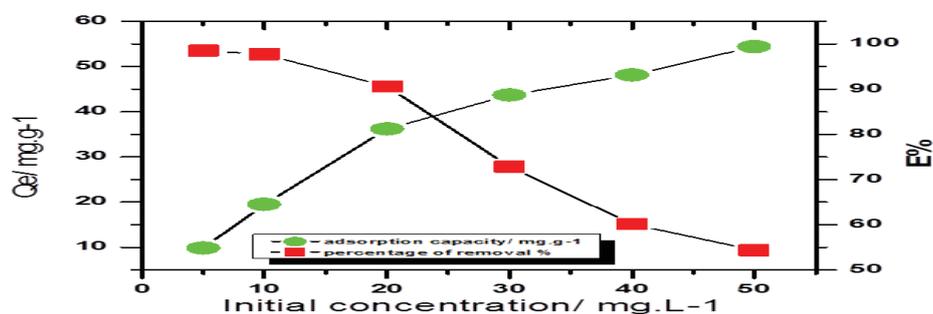


Figure (7): The plot of initial dye concentration

### B- Effect of pH

Adsorption of the dye by the nano-composite polymer is dependent upon the pH of the solution. The effect of initial pH of the dye solution on the adsorption capacity

and the initial removal percentage (R%) of the nano-composite polymer is presented [17-28 ] show in the figures (8 and 9).

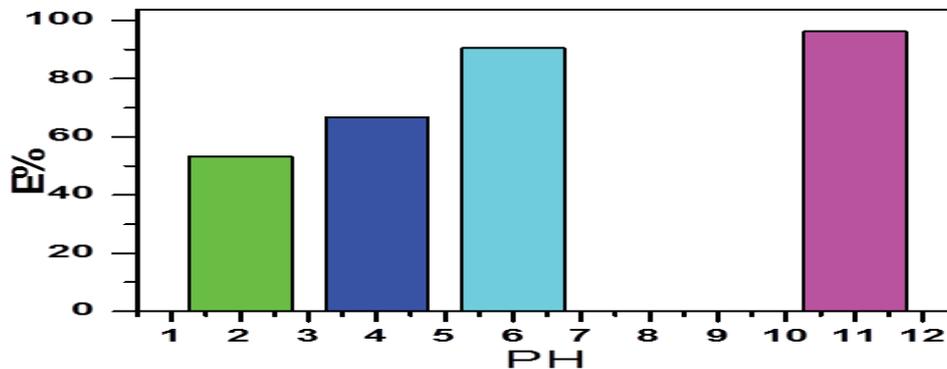


Figure (8): Effect of pH on the initial removal percentage

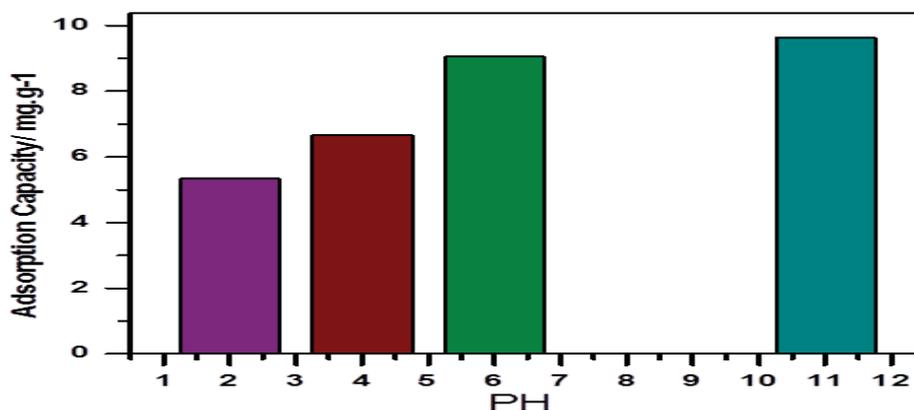


Figure (9): Effect of pH on the adsorption capacity

### C- Effect the mass of nano-composite polymer

The study was carried out to examine the effect of nano-composite polymer dose on the GRL dye removal (adsorption) at 20°C. Figure (10), exhibits that the percentage removal of dye increased with an increase in the nano-composite polymer dose (0.01–0.25g). It is apparent that by increasing the adsorbent dose the amount of adsorbed dye increases but adsorption capacity, the amount adsorbed per unit mass, decreases. It is readily understood that the number of available adsorption sites increases by increasing the adsorbent dose and it, therefore, results in an increase of the amount of adsorbed dye. The decrease in adsorption capacity with an increase in the adsorbent dose is mainly because of adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose [19].

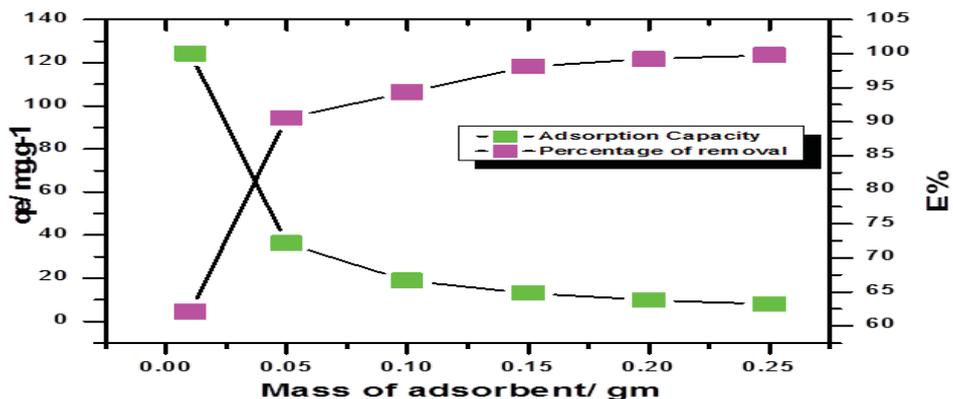


Figure (10): Effect the mass of nano-composite polymer

**D- Effect of the temperature**

The effect of solution temperature was studied by agitating of variants solution temperatures (10, 20, 35, and 50°C) mass dosage 0.05 g of nano – composite polymer and 100 mL of (GRL) dye concentration (20ppm) using water-bath shaker at 20°C. The experiment was conducted at pH=6. Agitation was provided for 24h contact time at a constant agitation speed. Temperature has a pronounced effect on the adsorption process from the change in temperature will cause changes in the equilibrium capacity of the adsorbent for adsorption of particular adsorbent. The uptake of dye decrease with the increase in temperature, indicating the exothermic nature of the adsorption reaction, while increases temperature indicated the endothermic nature of adsorption reaction, It was explained that as the temperature increased, the physical bonding between the organic compounds (including dyes) and the active sites of the adsorbent weakened. Besides a decrease in the degree of freedom of adsorbed species and a decrease in available adsorption active sites [18,29 ].

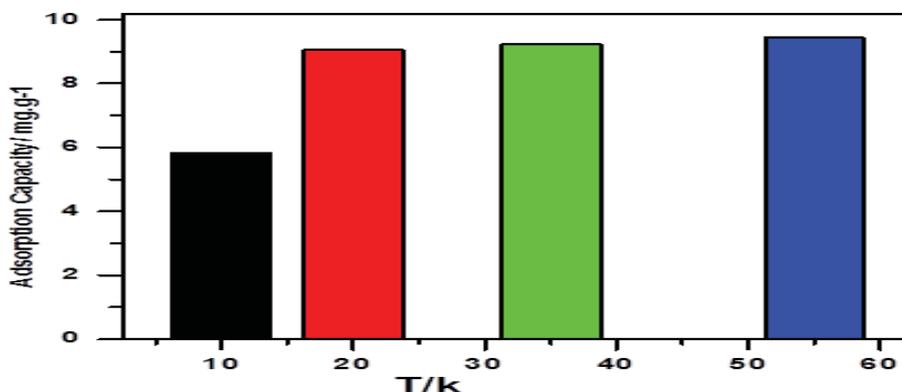
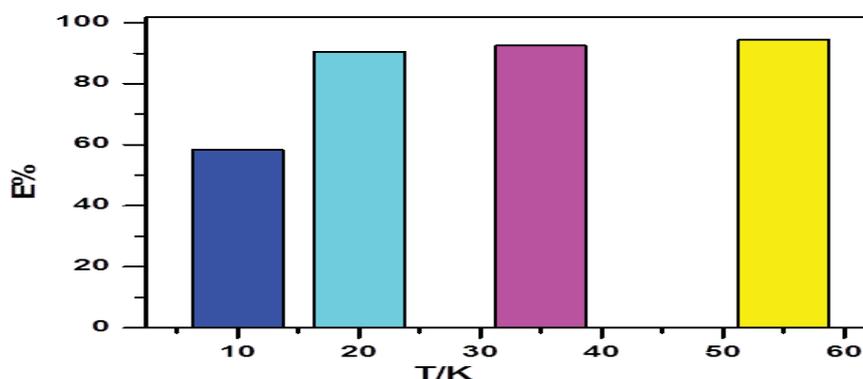


Figure (11): Effect of the temperature on adsorption capacity



**Figure (12): Effect of the temperature on the initial removal percentage**

## Conclusion

The adsorption of the GRL dye on the nano- composite polymer was studied in a batch mode operation for the parameters initial dye concentration, pH of solution, temperature, and adsorbent dosage. The results showed that adsorption of the dye increased with increase in initial dye concentrations, temperature and pH while it decreased with increase in adsorbent mass.

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