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# Removal of some dyes by adsorption method using a new nano-polymer surface

**A Thesis**

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**By**

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بسم الله الرحمن الرحيم

((وجعلنا من الماء كل شيء حي))

صدق الله العلي العظيم

(سورة الأنبياء آية 30)

## Certification

We certify that this thesis " **Removal of some dyes by adsorption method using a new nano-polymer surface**" has been prepared under my supervision at the Department of Chemistry , College of Education for Pure Sciences , University of Kerbala, in partial Fulfillment of the requirements for the degree of Master in Chemistry Sciences by the student (**Sameer Kadhim Bandar Al - Zubaidy**).

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We certify that, we read this thesis **(Removal of some dyes by adsorption method using a new nano-polymer surface)** and as examining committee examined the student (**Sameer Kadhim Bandar Al - Zubaidy**) in its content, and that in our opinion it is adequate ( **Excellence** ) with standing as a thesis for degree of master in chemistry sciences.

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I dedicated this work to my family, especially my father and mother .

**Sameer**

# DEDICATION

To the owner of the heavenly message, the symbol of knowledge and the illuminating lamp, the Prophet Mohammed, may God’s prayers and peace be upon him and his family

In front of us and our example, Imam Al-Mahdi, may God hasten his relief, and may God facilitate the way out

To whom we proudly bear his name, teach me to give without waiting, my dear father

To the symbol of love and healing balm

To the white heart (my beloved mother), may God protect her

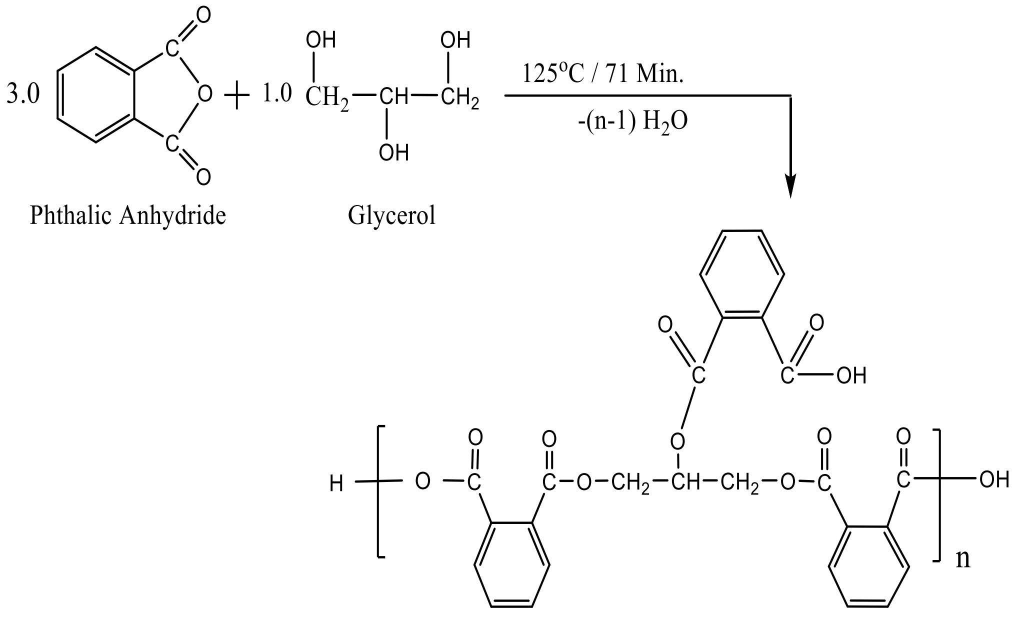
For those whom I am proud to have around me and my strength is stronger for them

To all my brothers, sisters and friends

**Sameer**

# Abstract

The grafted of processes were used to prepare the nano co-polymers is esterification process; where the method of preparing is described as shown below: The nano co-polymer was prepared from the reaction 3.0 mole of phthalic anhydride with 1.0 mole of glycerol



Nano graft co-polymers

In this thessis, a developed graft of nano co-polymer by esterifying glycerol and phthalic anhydride. X-ray diffraction analysis, differential scanning calorimetry, and atomic force microscopy, and infrared spectroscopy were used to analyze the nano polymer (DSC). It was determined whether synthetic nano-propensity polymers could remove methyl orange.,Wrights Stain and Eosin yellow 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 ,Wrights Stain and Eosin yellow from aqueous solutions.

It is evident from the drawing that the general form of adsorption isotherms is of type (S1) according to the classification of Giles). This indicates that the surface of the adsorbent material is a heterogeneous surface Also, when the covered part of the adsorbent surface increases, the adsorption temperature will decrease The increased shape of the isotherm with increasing the concentration of equilibrium confirms that the arrangement of the particles on the surface in vertical rows .

In this work, I used the Freundlich, Langmuir and Temkin equations, and applied my work to the Freundlich equation

The results showed the percentage of removal of . decreased with increasing temperature, That is, by increasing the temperature, the amount of the adsorbate material on the surface of the graft co-polymer decreases, i.e. the occurrence of an desorption process on the adsorbent surface when the temperature increases, that is, the speed of the particles diffusion on the surface of the graft co-polymer decreases, and therefore the percentage of removal will decrease when the temperature is increased.

# List of Content

# List of Figures

# List of Table

## List of Abbreviations

| **Symbol** | **Description** |
|---|---|
| DMSO | Di methyl sulfoxide |
| UV-Vis | Ultra violet-visible |
| pH | Acid value |
| IUPAC | International Union of Pure and Applied Chemistry |
| Qe | The amount of adsorbate substance |
| Ce | The concentration at equilibrium |
| C.I.No | Colour Index number |
| mg/g | Milligram per gram |
| mg/L | Milligram per liter |
| $d_{hkl}$ | Inter planer spacing between atoms |
| Nm | Nanometer |
| K | Kelvin |
| $^1$H-NMR | Proton nuclear magnetic resonance |
| FT-IR | Fourier transform infrared |
| Mw | Average weight of molecular weight |
| AFM | Atomic Force Microscope |
| Mn | Average number of molecular weight |
| ppm | Parts per million |
| $K_f$ | The adsorption amplitude |
| N | The adsorption intensity |
| DSC | Differential Scanning Calorimetry |
| TEM | Transmission electron microscopy |

# CHAPTER

# ONE

# 1. Introduction

## 1.1 polymers

A material made up of macromolecules is referred to as a polymer [1]. A macromolecule is a molecule with a high relative molecular mass that primarily consists of. the conceptual or actual numerous repetitions of units formed from molecules with low relative molecular mass [2]. The polymer, from which the term "polymer" is derived, is a big molecule made up of several repetitive subunits [3]. Both manufactured and natural polymers play a crucial role everywhere in daily life [5] due to their vast variety of characteristics [4]. Despite having a distinct definition from the current IUPAC definition, Jöns Jacob Berzelius first used the term "polymer" in 1833 [6][7]. The modern idea of polymers as covalently bonded molecular structures was first put forth by Hermann Staudinger in 1920 [8], who spent the following ten years looking for concrete proof to support this claim [9]. Polymer science has historically been primarily concerned with the products that result from covalent chemical bonds linking repeating units together; nevertheless, non-covalent connections are increasingly being given significant attention by major developing fields of study. An illustration of a natural or biological polymer is latex rubber isoprene, and an illustration of an industrial polymer is Styrofoam polystyrene. In biological contexts, all biological molecules are essentially proteins (polyamides), nucleic acids (polynucleotides), and sugars—pure polymeric molecules or molecules formed primarily of polymeric components, such as modified glycoproteins and lipoproteins that result in fatty molecules and few modifications. The polyamide for protein has a polysaccharide on its backbone [10]. Natural polymeric substances like hemp, shellac, amber, wool, silk, and natural rubber that have been used for ages are examples of the first type of polymer, which is created artificially or by humans. There are numerous additional organic polymers, including cellulose, the major ingredient in wood and paper. Polyethylene, polypropylene, polystyrene, polyvinyl chloride, synthetic rubber, phenol-formaldehyde resin (also known as bakelite), neoprene, nylon, polyacrylonitrile, polyvinyl chloride, silica, and many other synthetic polymers are on the list of materials that are almost in order of global demand. These polymers are produced in greater than 330 million tons each year (2015). [11]

### 1.1.1 Co-polymer

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. [12] Simple examples of sequentially managed polymers are mass copolymers, cyclic and co-rotating polymers.

- **Alternating copolymers** (structure 2) have monomer residues that alternate on a regular basis[13]. The equilateral copolymer of styrene and maleic anhydride produced by free radical chain growth polymerization serves as an illustration. [14] The co-growth polymer, like Nylon 66, can alternatively be thought of as a fully alternating copolymer of diamine and diacid residues, however it is frequently described as homogenous monolithic with repeating units of dimeric residues of one amine and one acid. [15]
- **Block copolymers** have extensive sequences of various monomer units[14] (structure 4). Diblock copolymers and triblock copolymers, respectively, are polymers that comprise two or three blocks of two different chemical kinds (for instance, A and B). Triblock terpolymers are polymers containing three masses, each of a different chemical type (for example, A, B, and C). [15]

- **Graft or grafted copolymers**: Chains or side branches in graft or grafted copolymers have distinct composition units or branches from the main chain. [15] Branches are added to the macromolecule's main chain (Structure 5). [14]
- **Random copolymer ….. etc**

## 1.1.2 Nanoparticles polymers

Nanoparticles with at least one dimension fewer than 100 nanometers are considered nanoparticles for the purposes of this study and application, which is known as polymer nanoscience. [16] Their physical and chemical characteristics alter as they move from being fine particles to nanoparticles.

The rise in the surface area to volume ratio and particle size are two important contributing variables. The behavior of atoms on a particle's surface area increasingly dominates that of the particle's interior due to an increase in the ratio of surface area to volume, which increases as the particle size decreases. When the particles interact with other molecules, this alters their characteristics. Because nanoparticles have a large surface area, they react more readily with other particles in a combination, increasing the mixture's strength, heat resistance, and other properties. The silicon nanoparticles are a type of nano polymer that display entirely diverse characteristics; They range in size from 40 to 100 nm, are significantly harder than silicon, and have a hardness between rubies and diamonds. [17]

Polymerization, spontaneous emulsification, solvent diffusion, and evaporation of solvents are some of the techniques utilized to create polymeric nanoparticles. There are three categories of techniques for creating polymeric nanoparticles:

1. Using techniques such solvent evaporation, nanoprecipitation, emulsification, salting out, dialysis, and supercritical fluid, nanoparticles can be created from a dispersion of premade polymers.

2. Monomer-based polymerization, such as controlled/living radical polymerization, interfacial polymerization, and emulsion, miniemulsion, and microemulsion.

3. Coacervation of hydrophilic polymers or ionic gelatin.

The selection of an appropriate technique for creating polymeric nanoparticles depends on a number of variables, including the size of the particles, the kinds of solvents and polymers employed during synthesis, the range of applications, etc. In drug delivery systems, polymeric nanoparticles can either be nanoparticles or nanocytes for controlled or sustainable release. [18]

Nanoparticles Biodegradable and biologically friendly polymers, whether synthetic or natural, make up the matrix structure of polymers. The synthetic polymers polylactide, polylactide-polyglycolide copolymers, polycaprolactones, and polyacrylates are the most often utilized. A copolymer that has been studied extensively is lactide-glycolide. Alginate, albumin, and chitosan are some of the natural polymers that have been extensively studied. Drug solubility, drug to polymer ratio, molecular weight, polymer composition, solvent, pH, homogeneity speed, and mixing time are a few formulation and process parameters that determine the release volume and coil and the stability of polymeric nanoparticles. [19]

Nanoparticles Polymers are solid colloidal molecules that are between 10 and 1000 nm in size. They are made of biodegradable polymers or copolymers that are compatible with the body because the drug can be chemically or physically bound to the surface of the carrier, physically adsorb on it, or be locked inside the carrier. Small size, biological disintegration, water solubility, toxicity, long shelf life, and stability during storage are only a few of the appealing qualities of these nanostructures. It is interesting because of these features because they can be used to transport medications, proteins, DNA, or genes to particular target tissues or organs. As a result, it is used in gene therapy, vaccines, and anti-cancer treatments, as well as for many other medicinal purposes. [20]

## 1.2 Nanotechnology

### 1.2.1 History

Although it was not well known, Norio Taniguchi coined the phrase "nanotechnology" in 1974. Use K and be inspired by Feynman's ideas. In his 1986 book "The engines of creativity: the future phase of nanotechnology," Eric Drexler coined the term "nanotechnology" and put forth the concept of a "nanoscale" that could make copies of itself and other parts of arbitrary complexity with atomic precision. Also in 1986, Drexler co-founded the Foresight Institute (to which he is no longer a member) to aid in educating the public about the ideas behind and implications of nanotechnology. [21]

Thus, the development of a conceptual framework for nanotechnology and high-definition experimental advancements that brought even more attention to the prospects for atomic control led to the creation of nanotechnology as a field in the 1980s at Drexler. Most nanotechnologies developed since the 1980s have focused on finding new techniques to create mechanical devices from a few atoms. [22]

The development of nanotechnology in modern times was spurred by two significant discoveries in the 1980s. First, the processing of individual atoms was successfully carried out in 1989 thanks to the advent of the scanning tunneling microscope in 1981, which offered an unprecedented conception of individual atoms and bonds. In 1986, Gerd Binnig and Heinrich Rohrer, who created the microscope, were awarded the Physics Nobel Prize. [23]

Second, the discovery of fullerenes in 1985 by Harry Croto, Richard Smalley, and Robert Korl, who shared the 1996 Nobel Prize in Chemistry, is noteworthy. [24] [25] Nanotechnology was not first used to describe C60. The phrase was used in relation to later research on closely comparable graphene tubes (known as carbon nanotubes and occasionally as buckyballs) that revealed possible uses for electronics and nanotechnology gadgets. The 1991 NEC Sumio Iijima, for which he was awarded the Kavli 2008 Inaugural Award in Nanoscience, is substantially responsible for the discovery of carbon nanotubes. [26]

The early 2000s saw a rise in scientific, political, and commercial interest in the area that produced both controversy and advancement. As shown by the Royal Society's study on nanotechnology, disagreements have arisen concerning the definitions and potential impacts of nanotechnologies. [27] The viability of the uses that proponents of molecular nanotechnology have envisioned has been questioned, leading to a public dispute between Drexler and Smalley in 2001 and 2003. [28]

In the interim, product marketing for innovations in nanotechnology has started. These products do not entail atomic control of the material and are restricted to bulk uses of nanomaterials. Examples include the Silver Nano platform, which uses silver nanoparticles as an antibacterial agent, sunscreens made of transparent nanoparticles, silica nanoparticles used to reinforce carbon fiber, and fabrics made of carbon nanotubes that are stain-resistant. [29] [30]

Processing matter at the atomic, molecular, and supramolecular levels is known as nanotechnology. The oldest and most thorough definition of nanotechnology [31] refers to the specific scientific objective of precisely processing atoms and molecules for the production of macroscale objects; this field is sometimes referred to as molecular nanotechnology. Later, the National Nanotechnology Initiative created a more broad definition of nanotechnology, defining it as the manipulation of materials with at least one dimension between 1 and 100 nanometers. The definition has changed from a specific technological goal to a research category that includes all types of research and techniques that address the unique properties of matter occurring below a certain size threshold in order to reflect the fact that quantum mechanical effects are significant in this range for the quantum world. Because of this, the term "nanotechnologies" is frequently used to describe a diverse spectrum of research and applications that share the property of small size. [32]

The fact that nanotechnology, as defined by size, encompasses a wide range of scientific disciplines, including surface science, organic chemistry, molecular biology, semiconductor physics, energy storage, micro-manufacturing, and molecular engineering, is quite understandable.

The development of new materials with dimensions on the nanoscale to direct control of matter on the atomic scale are only two examples of how the physics of ordinary devices have been extended to whole new ways. The effects of nanotechnology in the future are now being discussed by scientists. With a wide range of applications, including nanomedicine, nanotechnology, biomass energy production, and consumer goods, nanotechnology may be able to develop numerous new materials and gadgets. Contrarily, nanotechnology brings many of the same challenges that every new technology does, such as worries about the toxicity and environmental impact of nanomaterials, as well as potential effects on the global economy and conjectures about various apocalyptic scenarios [36]. These worries have sparked a discussion between advocacy groups. and countries on the need for a unique regulation of nanotechnology.

### 1.2.2 Fundamental concepts

The creation of molecularly level functioning systems is known as nanotechnology. Current and more complex concepts are covered in this work. In its original usage, the term alludes to the anticipated capacity to build bottom-up components using the current methodologies and tools to produce full, high-performance products. A billionth of a meter, or 10-9, makes up a nanometer (nm). For contrast, the diameter of the double helix DNA is approximately 2 nm, while the usual lengths of carbon-carbon bonds, or the distance between these atoms in a molecule, range from 0.12 to 0.15 nm. The bacteria of the genus Mycoplasma, on the other hand, are the smallest known cellular life form and measure roughly 200 nm in length. [37]

The US National Nanotechnology Initiative's definition of nanotechnology, which is utilized in the agreement, places its range between 1 and 100 nm. Because nanotechnology must construct its organs from atoms and molecules, the minimum is defined by the size of the atoms (hydrogen contains the tiniest atoms, which have a kinetic diameter of just approximately a quarter of a nanometer). Though the maximum limit is rather arbitrary, it roughly corresponds to the scale at which previously unknown phenomena in huge structures start to manifest and can be used in the nano device. [38] These novel occurrences set nanotechnology apart from microtechnologies, which are broadly used gadgets that are merely scaled-down counterparts of analogous macroscopic systems. [39]

To put this magnitude in another context, the size of a marble on earth is equivalent to one nanometer per meter. A average man's beard grows a nanometer in the time it takes to bring the blade to his face, to put it another way. [40] In nanotechnology, there are two main methods. In a "upward" approach, materials and gadgets are constructed from molecular building blocks that chemically put themselves together using molecular recognition principles. [41] The "top-down" approach involves building nanoscale items from larger entities without using atomic level control. Over the past few decades, physics disciplines including nanotechnology, nanomechanics, nanotechnology, and nanotechnology have developed to offer a basic scientific foundation for nanotechnology. [42]

### 1.2.3 Applications

According to the Emerging Nanotechnology Project, as of August 21, 2008, there were more than 800 publicly accessible nanotechnology goods that had been identified by the maker, and new items were entering the market at a rate of 3–4 each week. [30] All goods are listed in the project's publicly accessible online database. The majority of uses are restricted to negative "first generation" nanomaterials, such as titanium dioxide, which is found in sunscreen, cosmetics, surface coatings, and some food products. Carbon allotropes are also used to make gecko tape. Zinc oxide is used in sunscreen, cosmetics, surface coatings, [43] paints, and varnishes for outdoor furniture. Cerium oxide is used as a fuel catalyst. Silver is used in food packaging, textiles, disinfectants, and home appliances. [29]

Tennis balls can survive longer, golf balls can fly straighter, and even bowling balls can become more robust and have a more solid surface thanks to other applications. Nanotechnology is used in the socks and pants to make them more durable and breathable in the heat. To cure wounds more quickly, silver nanoparticles are poured into bandages. Nanotechnology has the potential to make computers and video games more affordable, quicker, and memory-rich. [45] Additionally, to construct systems for the computerization of light-based chips, such as photovoltaic chips used for quantum information processing and second information transfer. [46]

Nanotechnology may be able to make current medical applications less expensive and simpler to employ in settings like the doctor's office and home. [47] Nanomaterials are used in the production of automobiles, so future automobiles may run on fewer metals and less fuel. [48]

Currently, researchers are using nanotechnology to create diesel engines with better exhaust emissions. Currently, diesel engines in these engines use platinum as a catalyst. The catalyst is responsible for clearing the ash from the exhaust. To release oxygen, nitrogen atoms from NOx molecules are first removed using a reduction catalyst. Then, the oxidation catalyst oxidizes the hydrocarbons and carbon monoxide to produce water and carbon dioxide. [49] Both oxidation and reduction catalysts require platinum. Because it is expensive and unsustainable, using platinum is futile. The Danish business Innovations Fonden has committed DKr 15 million to the pursuit of innovative nanotechnology-based catalyst substitutes. The initiative, which was started in the fall of 2014, seeks to expand the surface area while lowering the quantity of materials needed. Its surface energy tends to decrease with organisms. For instance, two drops of water will combine to produce one drop, reducing the surface area. The efficiency of the catalyst can be improved by increasing the surface area of the catalyst that is exposed to exhaust gases. [49]

The working group's goal in this project is to develop nanoparticles that won't merge. The material is conserved each time the surface is enhanced. Therefore, the production of these nanoparticles will lower the price while increasing the effectiveness of the resulting diesel engine catalyst, which in turn results in cleaner exhaust gases. If they are successful, the team wants to utilize 25% less platinum. [50] Additionally, nanotechnology is important in the quickly developing field of tissue engineering. In order to guide a cell's differentiation to an appropriate lineage, researchers imitate nanoscale characteristics of the microenvironment when building scaffolds. [51] For instance, scientists might imitate bone resorption pits when creating scaffolds to encourage bone formation. [52]

Many researchers have been interested in nanotechnology and the preparation of nano polymers, and these polymers have been used in many applications as in some of the following studies: -

Several nano particle co-polymers (1,2,3,4 and 5) were prepared by condensation polymerization from the reaction of one mole of glycerol with (1.0, 1.5, 2.0, 2.5and 3.0) moles of phthalic anhydride at specific temperatures and times with the release of water as a byproduct was studied, and the effect of three temperatures (298, 308 and 318 K), and three different concentrations (1, 3 and 5 ppm) of nano composite copolymers were studied and it is clear that they play a very important role in the adsorption process, the experimental results showed that. The adsorption of of dyes (methylene blue and eosin yellow) on the surface of these nano composite co-polymers decreases with increasing temperature, which means that the process is a heat-emitting process, and the results obtained showed a high efficacy of the co-polymers in removing contaminants (methylene blue and eosin yellow dyes) [53].

In another study conducted by the researcher Al-Mayali [54], the study was conducted the nano particle co-polymer was synthesized using solubilization process by condensation polymerization from the reaction of 1.0 mole of Pentaerythrytol with 2.0 moles of Phthalic anhydride at constant temperature and time with releasing of water as by-product, the synthesis nano co-polymer was characterized by infrared spectroscopy (FT-IR), Proton nuclear magnetic resonance (1H-NMR) and Carbone nuclear magnetic resonance (13CNMR); On other hand, the size of the particles of the nano co-polymer was measured by atomic force microscopy technique (AFM) and X-ray diffraction analysis (XRD); the results of AFM, showed that, the particle sizes of the nano co-polymer were (97. 23nm) respectively, the results of XRD, showed that, the total average crystallites sizes were (92.63) nm; Which proved that the synthesis co-polymer is a nano-polymer. The synthesis nano-polymer was used as an absorber surface, so as to adsorb pollutants from water resulting from the process of dyeing tissues.

Three types of dyes (Malachite green and Disperse Blue and Reactive Red( dyes, which are used in dyeing tissues and are pollutants water from textile and dyeing factories, have been used to study the effectiveness of nano polymers in purifying water from industrial pollutants

The effect of three temperatures (298, 308 and 318 K) and three different concentrations (1, 3 and 5 ppm) of nano co-polymer were studied and it is apparent they play a very important role in the adsorption operation; the experimental results showed that the adsorption of (Malachite green and Reactive Red) dyes on the surface of these nano co-polymer increasing with increasing of temperature, meaning that the process is endothermic process, while the( Disperse Blue) dye the results obtained showed the adsorption decreases with increasing of temperature, meaning that the process is exothermic process ,and the results obtained showed a high effectiveness of nano co-polymer in the disposal of pollutants (Malachite green , Reactive Red and Disperse Blue) dye.

The researcher Zahraa [55], conducted an adsorption study of three types of different dyes (Orange-G), ((Reactive Yellow145)) and (Fuchsin acid), on the surface of a nano-copolymer (Nano polymer). The Nanoparticle Co-polymer was synthesized using the solubilization process by condensation polymerization from the reaction of one mole of glycerol with 1.5 mole of phthalic anhydride at 52min and 117oC with releasing water as a by-product, and then diagnosed using several techniques including (FT-IR, XRD, AFM, TEM, DSC and 1H-NMR), aseries of experiments were conducted and several experimental variables were studied, including : Surface mass, pH, Temperature effect and Adsorption Isotherms.

The values of thermodynamic functions were calculated ΔG, ΔH, ΔS, through which it was shown that the adsorption process of dyes (Orange-G, Reactive Yellow 145 and Acid Fuchsin) on the surface Nano Co-Polymer is a spontaneous and exothermic process through the negative values of ΔG and ΔH, and an increase in randomness through the positive values of entropy ΔS.

The removal of dyes (Orange-G, Reactive Yellow 145 and Acid Fuchsin) on the surface Nano Co-Polymer as an adsorbent surface at different temperatures (298K, 308K and 318K) was studied to determine the Adsorption isotherms and Thermodynamic functions.

The hypotheses isotherms of Freundlich, Temkin and Langmuir were used, in order to describe the experimental isotherms and isotherms constants, and data showed for dyes (Orange-G, Reactive Yellow 145 and Acid Fuchsin) on surface Nano Co-Polymer agrees with hypothesis isotherm the Freundlich, Temkin and Langmuir in the form of good.

## 1.3 Pollutants

As the world's population grows, there will be an exponential increase in the demand for clean water. A major challenge for the long-term sustainability of human society is the disposal of industrial effluents, which also poses environmental risks given the rapid speed of industrialization. Recycling and wastewater reclamation are crucial objectives to safeguard the world ecology and enhance environmental quality. [56–58]

### 1.3.1 Aquatic Pollution

The most crucial and necessary resource for meeting daily needs for every area of human society, including drinking, cleaning, industrial manufacturing, and agriculture irrigation, is pure water. However, the quality of natural aquatic habitats is significantly degraded by the irresponsible treatment of wastewater from homes and businesses and the wasteful disposal of pure water. Point sources and nonpoint sources are two main categories for the causes of water pollution [59]. The former one is made up of contaminants that are released into water supplies by companies, septic systems, animal feedlots, mines, the oil industry, and other sources [60]. The latter one consists of agricultural runoffs, sediment, animal wastes, and other things [61]. Due of their irregularity, nonpoint sources are more challenging to track than point sources [62].

### 1.3.2 Hazardous Pollutants

According to the classification, there are four classes that might be made up of the most frequently seen hazardous wastes that pose a threat to the world's aquatic ecosystem. The following are listed by the EPA: I toxic wastes; (ii) hazardous wastes from particular industrial sources; (iii) hazardous wastes from generic industrial operations. The EPA believes that during the previous few decades, more and more of the aforementioned contaminants have been found in rivers, lakes, and seas. We'll talk about some significant organic and inorganic wastes in water in the section that follows. [63]

### 1.3.3 Inorganic Wastes

#### 1.3.3.1 Anionic Wastes

In contaminated surface water, nitrates and phosphotes are the most common contaminants. As fertilizers for agriculture, phosphorus (P) and nitrogen (N) are essential components. Phosphorus and nitrate in the soil are greatly accumulated when large quantities of fertilizers containing P and N are applied to agricultural lands. Phosphates and nitrates may seep into ground and surface water sources, including rivers and lakes, as a result of manual irrigation and/or natural rainfall. Livestock dung is another important source of phosphate and nitrate pollutants in water systems, The health of people and other animals is in danger when nitrates are introduced into water supplies. When nitrate concentrations in water are high, it is shown to be particularly hazardous. [64,65]

Another significant family of anionic contaminants is cyanides. Both anthropogenic and natural sources can produce cyanides, which often take the form of cyanide salts like sodium and potassium cyanide or in a gaseous state as hydrogen cyanide. Inadequately treated industrial effluent, coal gasification, electroplating processes, and incomplete fuel combustion can all release cyanides into the water supply. Because the cyanide anion is known to be extremely poisonous, cyanides pose a serious hazard to human life. Humans who consume or breathe in cyanide anion risk death by having low levels of vitamin B12 in their bodies. [66]

### 1.3.3.2 Cationic Wastes

The heavy metal ions lead (pb +2) [64], mercury (Hg 2+] [65], chromium (Cr 6+) [69], nickel (Ni +3) [70], barium (Br -1], cadmium (Cd 2+) [71], cobalt (Co 3+) [72], selenium (Se 2+) [73], and vanadium (V 5+) [70], Diverse methods can be used to introduce the heavy metal ions indicated above into the aquatic system. For instance, weathering, volcanic activity, and crustal movement all result in significant volumes of heavy metal ions. Similar to current culture, fabrication of printed boards and semiconductors, metal plating and polishing, industrial dyeing processes, and other activities are the main producers of heavy metal pollution. The removal of heavy metal ion pollution from aquatic systems is essential because several heavy metal ions, such as Fe 3+, Zn 2+, Cu 2+, Mn 2+, and Co 3+, demonstrate lethal toxicity and can harm humans and animals when exposed excessively and in close proximity. [73]

### 1.3.3.3 Organic Wastes

When exposed to large concentrations of these harmful molecular contaminants, humans can develop serious illnesses. These organic compounds can be found in a variety of habitats and are derived from a wide range of commercial goods, including detergents, plastics, organic solvents, insecticides, and dyes. These organic contaminants also pose a concern to both humans and wildlife because of their long-term negative effects and chemical complexity. Particularly, thousands of persistent organic pollutants (POPs) are a class of compounds made up of a wide range of hazardous, bio accumulative, and susceptible to long-range transport organic substances [75–78]. According to other reports, POPs primarily differ in the amount of chlorine substitutions and have extended half-lives in the environment, lingering in particular in soils, sediments, and air. They are discharged into the environment by agricultural activities, landfill effluents, urban and industrial waste, and other means, and they experience a variety of reactions that confirm their ubiquity. [79]

Most aliphatic organic compounds are surface runoffs, and metropolitan areas tend to have higher concentrations. In addition, the byproducts of oil combustion and petroleum oils are primarily aliphatic substances. Alkenes, alkynes, dichlorodifluoromethane, 1,2-dichloroethane, 2,propanol, and tetramethylammonium ions are only a few of the aliphatic organic substances that have been identified as harmful pollutants in aquatic environments, primarily from surface runoffs. Another class of organic compounds, known as polycyclic aromatic hydrocarbons (PAH), are released into the atmosphere when wood, carbon, and oil are burned insufficiently. They are recognized as a priority pollutant by the EPA [80]. Polychlorinated biphenyls (PCBs) are widely used in a variety of industrial processes, electrical transformers, capacitors, carbonless copy paper, and polymers, which increases their environmental permeability.

Surfactants are one of the most adaptable classes of organic substances used in commercial, domestic, personal care, and pharmaceutical goods [81]. They have the power to change the physicochemical state of the natural habitat since they can exist in anionic, cationic, nonionic, and amphoteric forms. They can create compounds in water at high quantities that kill microorganisms. Pesticides, which come in a variety of chemical structures and are employed in both agricultural and non-agricultural applications such herbicides, insecticides, fungicides, and germicides, are another category of organics. Dye is a colored chemical that binds strongly to the substrate it is applied on. Numerous substrates, including textiles, leather, plastic, and paper, are dyed. According to their use, chemical makeup, application, or type of chromophore they contain, dyes can be categorized into a variety of groups [82].

Byproducts of numerous industrial processes, including the production of plastics, polymer precursors, photographic developers, dyes, pharmaceuticals, and pulp and paper sector, include phenol and phenolic compounds [83]. Additionally, insufficient mineralization of the phenolic compounds results in the production of naturally occurring, organic byproducts such lignins, tannins, and humic substances, all of which are common in our environment. The easy donation of free electrons that results in the formation of phenoxy radicals and intermediates is primarily responsible for the toxicity of phenols and phenol derivatives. These phenoxy radicals can enter the cell and harm the membranes of the mitochondria, the nucleus, and the endoplasmic reticulum as well as their constituent enzymes and nucleic acids. Additionally, phenol exposure might harm skin by reacting with amino acids in the epidermis [86].

## 1.4 Adsorption

Adsorption is the adhesion of atoms, ions, or molecules from a surface-dissolved gas, liquid, or solid. On the adsorbent surface, a layer of adsorbents is produced by this process. This process is distinct from absorption, which occurs when a liquid or solid (the absorbent) dissolves or penetrates a liquid or solid (the absorbate). [85]

Adsorption is a product of surface energy, just as surface tension. In bulk materials, other atoms in the substance fulfill all of the ionic, covalent, or mineral bonding requirements for the constituent atoms of the substance. Adsorbents can be drawn to the atoms on the adsorbent surface because they are somewhat unsurrounded by other adsorbent atoms. The specifics of the species involved will determine the type of the binding, however the adsorption process is typically categorized as either chemical absorption or physisorption (weak van der Waals force property) (the covalent bonding property). Additionally, electrostatic attraction can be to blame. [85]

Adsorption of gases and solutes is usually described by isotherms, that is, the amount of adsorption on the adsorbent as a function of pressure (if the adsorbent is a gas) or concentration (of solvents in the liquid phase), are typically used to describe the adsorption of gases and solutes. To enable comparison of various materials, the adsorbed quantity is almost always rounded by the adsorbent mass. There have been 15 distinct heat models created thus far. [87]

Industrial dyes are soluble in water and are used to color paper, skin, hair, food, cosmetics, and textiles, among other things, in many fields of modern technology. Due to its toxicity, the removal of color from home industrial or liquid waste has received considerable attention in recent years [88]. Prior to the 19th century, natural sources, particularly those from plants or animals, were used to extract compounds having coloring qualities. At the start of the 20th century, however, synthetic materials nearly entirely supplanted natural dyes [89]. Today, hundreds of novel colored compounds enter the market each year, with the exception of a few inorganic dyes, and are developing into a variety of varied uses [90].

According to increasingly severe international requirements, textile and tanning industries are among the biggest water users that produce significant pollution in wastewater that is loaded with various contaminants like dyes, etc. [91]. In actuality, a variety of conventional wastewater treatment techniques, including oxidation and sedimentation, have been employed. Even though they appear to be efficient, because to technical limitations, high exploitation costs, or potential limitations, they are only able to treat small amounts of liquid waste. [92]

Adsorption to remove contaminants of all types (organic and inorganic) from the fluid phases is one of the techniques discussed in wastewater treatment that has drawn the interest of many researchers in recent decades. [93]

The interaction between an adsorbent and an adsorbate is described using adsorption isotherms, which are frequently used to estimate the concentration of a particular adsorbent pollutant. A comparison of linearity and nonlinearity, the former of which is frequently used to more accurately determine isotherm (which is used to avoid errors affecting R2 during linearity) [94]

## 1.5 Types of Adsorption

There are two types of adsorption: chemical and physical. Physical adsorption, also known as physisorption, is reversible since weak forces are involved. Low temperatures favor physical adsorption to take place. It is exothermic and has an adsorption heat that is comparable to the latent heat of condensation since it is quite similar to a condensation process [95]. Chemical adsorption, also known as chemisorption's, is crucial for gas phase catalysis but is typically irrelevant for liquid-solid adsorption at room temperature. Chemisorption is a process that takes place at high temperatures with a high activation energy, strong bonds, and is irreversible. In chemical sorption, the heat of adsorption is frequently high and is comparable to the heat produced during a chemical reaction[95]. The distinctions between physical adsorption and chemical adsorption .

**Table (1-1): Characteristics of Physisorption and Chemisorption**

| No. | Physisorption | Chemisorption |
|---|---|---|
| **1** | Nature of the forces is vander Waales forces. | Nature of forces is chemical bonds. |
| **2** | Heat of adsorption less than 40kj mol$^{-1}$ | Heat of adsorption more than 40kJmol-1 |
| **3** | No electron transferred or shared between the adsorbed species and the adsorbent surface. | Electron transferred or shared between the adsorbed species and the adsorbent surface. |
| **4** | Takes place without needing of activation energy. | Activation energy may be needed. |
| **5** | The process is non specific. | The process known by its specify. |
| **6** | Multi layer adsorption may occur because the forces act as great distances. | Activation lead to a monolayer, may befollowed by incorporation. |
| **7** | Adsorption is appreciable only at temperatures below the boiling point of the adsorbate. | Adsorption can occur at high temperatures. |
| **8** | . The process is reversible; the adsorbed layer canbremoved by evacuating or warming to moderate temperature. | The process can be irreversible which may lead to a chemical reaction. |
| **9** | Temperature of occurrence depend on boiling point of the adsobate and is usually low. | Temperature of occurrence depend onactivation energy and is usually high |

## 1.6 Adsorption Isotherms

The relationship between the concentration of the adsorbent (Ce) in the solution and the adsorption capacity of the adsorbent (Qe) at equilibrium at constant temperature is called the adsorption isotherm. And his group, depending on the shape and shape of the resulting curve, into four main classes bearing the symbols are S, L, H, C. These symbols represent the primary sections of the isotherms, which included the main classes of secondary classes in the form of numbers 1, 2, 3, 4, and max. As shown in Figure (1-5) [96].

1- Class S: When the particles adsorbed on the adsorbent surface are oriented vertically or diagonally, in addition to the fact that the solvent may suffer severe adsorption on the surface, the isotherm curve takes the shape of (S shape).

2- Class L: If the particles are directed horizontally onto the surface layer of the adsorbent material, the adsorption is single-layer, and it is specific to the Lankmuir isotherms.

3- Class H: This class occurs in high adsorption affinity. This isotherm is often formed in very dilute solutions as well as when adsorption of very large molecules such as polymers.

4- Class C: This class indicated the presence of the Partition constant between the adsorbent material on one side and the solution with the adsorbent surface on the other, in addition to a high probability of chemical adsorption.

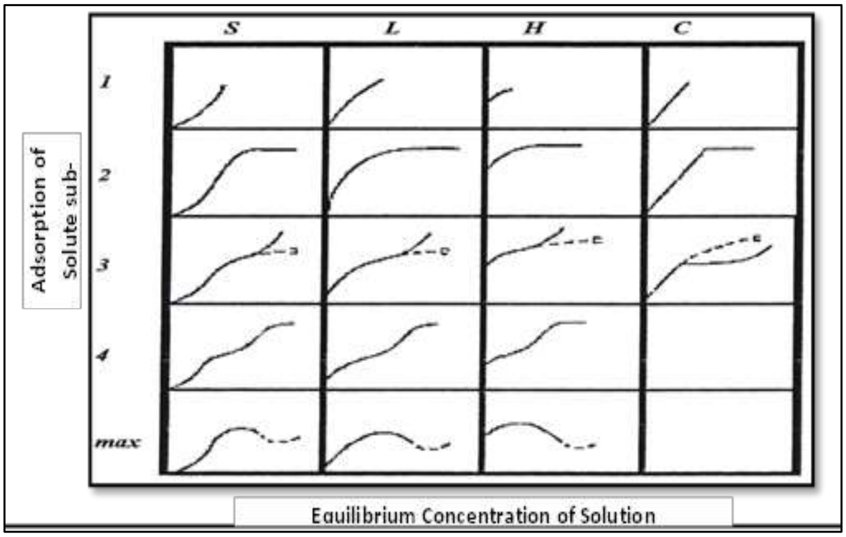


**Figure (1-1) Classification (Giles) of adsorption isotherms [97].**

## 1.7 Theories of Adsorption

Several hypotheses, theories and various forms have been proposed to describe the adsorption process and the resulting form of isotherm as shown in Table (1-2).

**Table (1-2) adsorption hypotheses and theories**

| Isotherm | Type of Adsorption | Equation | |
|---|---|---|---|
| | | Nonlinear | Plot |
| Langmuir [98] | Physical and chemical | $Q_e = \frac{abC_e}{1 + bC_e}$ | $\frac{C_e}{Q_e}\ Vs\ C_e$ |
| Freundlich [99] | Physical and chemical | $Q_e = K_f\, C_e{}^{1/n}$ | $logQ_e\ Vs\ logC_e$ |
| Temkin [100] | Chemical adsorption | $Q_e = \frac{RT}{b} LnA_T C_e$ | $Q_e\ vs\ LnC_e$ |
| Redlich-Peterson [101] | Physical and chemical | $Q_e = \frac{K_R C_e}{1 + a_R C_e^{g}}$ | $Ln\left(K_R \frac{C_e}{Q_e} - 1\right) vs\ LnC_e$ |
| Toth [102] | Multimolecular Physical | $Q_e = \frac{K_T C_e}{(a_T + C_e)^{\frac{1}{t}}}$ | $Ln\left(\frac{Q_e}{K_T}\right) vs\ LnC_e$ |

### 1.8 Langmuir Adsorption Equations

The studies indicated that the mathematical equations that explained the adsorption processes differed in the adsorption of gases from the adsorption of liquids. The Lankmire equation was developed as a basis for explaining the adsorption of gases on the surfaces of solid materials, and this equation was also applied to the adsorption of solutes in the liquid phase on the surfaces of solid materials, especially most of the pollutants dissolved in water such as dyes. This led to a wide spread of the equation after it was developed by (Irving Langmuir) in (1918) when describing the adsorption of gas molecules on a flat solid surface, and Lankmayr assumed that adsorption occurs for one molecular layer on the surface of the adsorbent material, and also ruled out the occurrence of interactions between the adsorbed particles in the low coverage of the surface. Where the amount of the adsorbent material increases rapidly at the beginning of adsorption and then reaches the stage of stability due to the desorption process, as the general Lankmayr equation is based on a number of basic assumptions, namely [98]:

1. All adsorption sites are equal and constant, and the energy distribution on the surface is uniform when the surface of the adsorbent is homogenous.

2. The lack of interaction of the adsorbed molecules with each other.

3. Most adsorption is obtained by the same mechanism.

4. In the case of maximum adsorption, a thin film is formed where the adsorbed molecules are not placed on other previously adsorbed molecules. But only on the free surfaces of the adsorbent.

Rarely are all four of these hypotheses true for many reasons. Perhaps there are defects on the adsorbent surface and its inhomogeneity, or perhaps some of the adsorbed molecules are inactive, and the adsorption mechanism of the first particles does not have to be the same for the subsequent ones. Most likely is the fourth condition because most of the particles will adsorb to the thinner layers. Langmuir isothermal is the first choice for most adsorption models, and it has many applications in surface kinetics. Equation (1-4) represents the Lancomeyer equation for adsorption from the solution and (1-5) is the linear Lancomeyer equation for adsorption [103].

$$Q_e = \frac{abC_e}{1+bCe} \qquad (1\text{-}4)$$ [58]

$$\frac{C_e}{x/m} = \frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{a} \qquad (1\text{-}5)$$ [58]

whereas :

Qe: the adsorption weight capacity in units (g-1.mg).

Ce: the concentration of the solute (adsorbed) at equilibrium in units ((mg.L-1).

a: The maximum adsorption capacity when the adsorption surface is completely saturated in units (mg.g-1).

b : Lankmeier constant related to adsorption energy or equilibrium constant as indicated in equation (1-4)

When Ce/Qe is plotted against Ce, the slope is 1/a and its intercept is 1/ab, as in Figure (1-6).

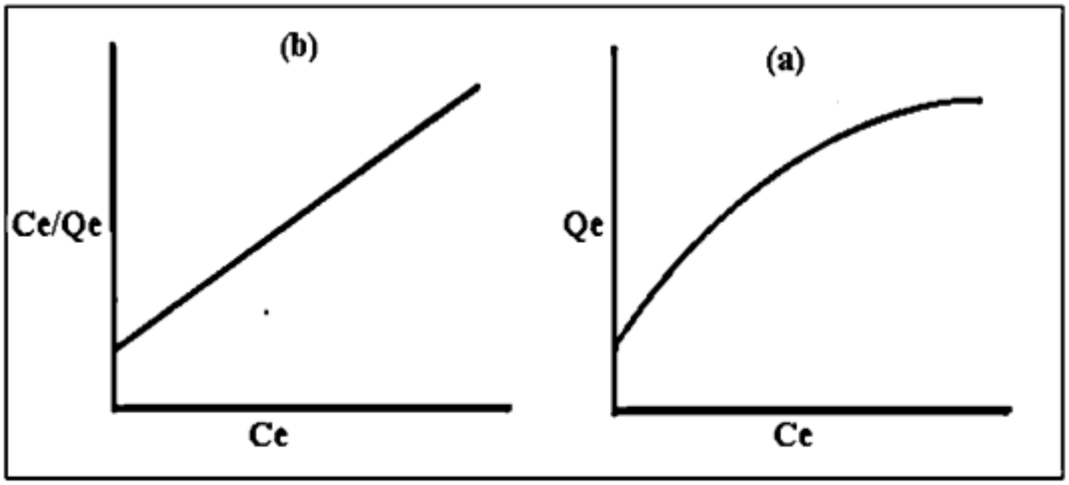


**Figure (1-2) a- Lancomyer isotherm equation, b- linear Lancomeyer isotherm equation.**

## 1.9 Freundlich Adsorption Equation

In (1926 AD), the German scientist (Freundlich) assumed that adsorption changes logarithmically with pressure. The Freindlich equation is one of the most important equations that have been successfully used in the case of adsorption from the solution when the surfaces are mostly heterogeneous, meaning that the changes in the potential energy are irregular due to the occurrence of adsorption sites at different levels of energy. Also, adsorption may occur in multiple layers that led to a change in the adsorption isotherm. This change is explained by Frendlich's equation. It is the change in the amount of the adsorbed substance (the adsorption capacity) per unit area or the mass of the adsorbent with the equilibrium concentration (Ce), and its mathematical formula is as in the equation (1-6) [104].

$$Q_e = K_f \, C_e^{1/n} \qquad (1\text{-}6)$$

By taking the logarithm equation (1-6)

$$logQ_e = logK_f + \frac{1}{n} logC_e \qquad (1\text{-}7)$$

Where kf and n are the empirical Frendlich constants, where n is a measure of the intensity of adsorption, while kf is a measure of the amount of adsorption that can be obtained from drawing the relationship between (log Qe) versus (logCe) its slope (1/n) and its intercept (kf log), the values of which depend These constants depend on the nature of the adsorbent surface, the adsorbent material, and the temperature. Frendlich's equation differed from Lankemeier's equation in its conformity with physical adsorption when it is several layers, adding heterogeneous surfaces of materials, as in Figure (1-7).

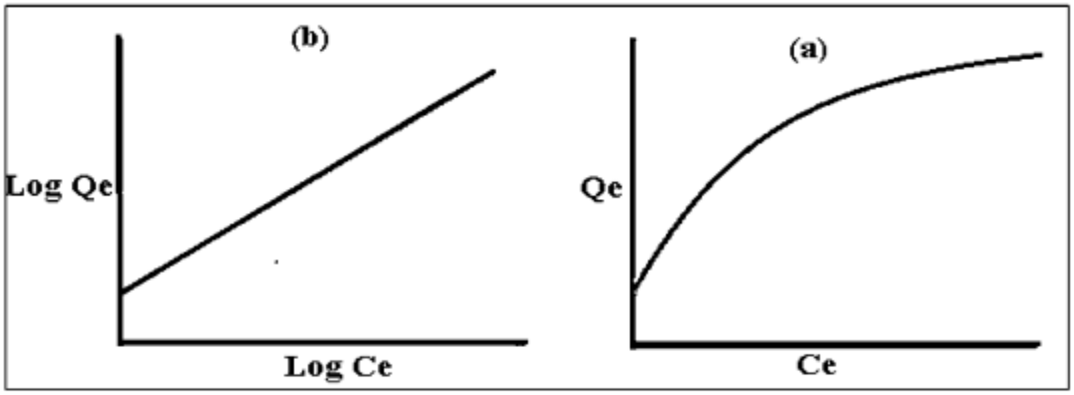


**Figure (1-3 a- Freundlich isotherm equation, b- Linear Frenlich isotherm equation.**

## 1.10 Temkin Adsorption Equation

The scientist Temkin suggested a linear decrease in the temperature associated with the adsorption process for all molecules in the layer with the surface covering due to the interactions between the adsorbate and the adsorbent surface), and the temkin isotherm can be represented by nonlinear equations (1-8) and linear (1-9). the following two [105]:

$$Q_e = B.LnA_T C_e \tag{1-8}$$

$$Q_e = BLnA_T + BLnC_e \tag{1-9}$$

whereas :-

AT: is the adsorption equilibrium constant (AT) representing the maximum adsorption energy.

B: isotherm constant enabled which is equal to RT/b.

R: represents the general constant for gases (J.mol-1.K-18.314).

T: the absolute temperature, K.

b: enthalpy of adsorption (J.mol-1).

The values of AT and B can be found by plotting the linear equation (1-9) between Qe versus LnCe where the slope of equation B is equal to while the cut-off of the equation is the value of BLnAT as in Figure (1-8).

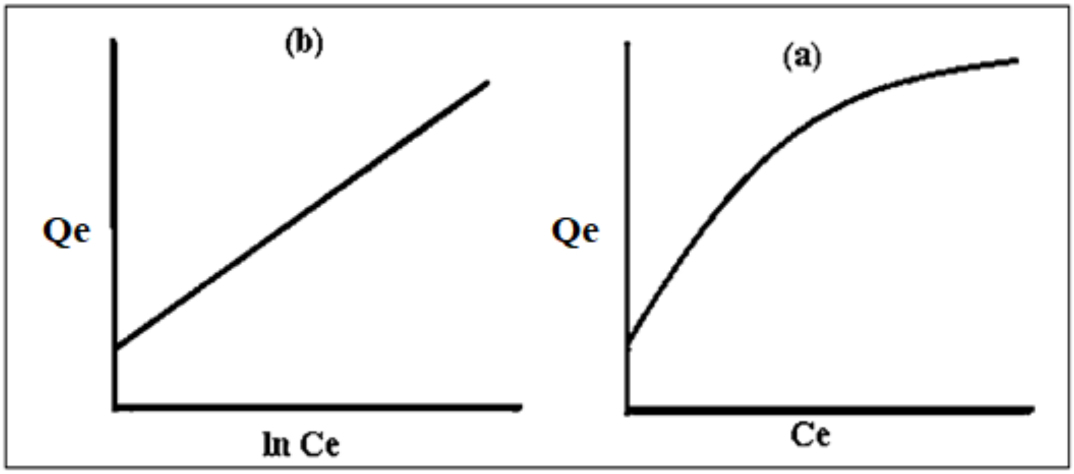


**Figure (1-4) a- temkim equation Isotherm enables linear equation, b- temkin Isotherm enables linear equation.**

## 1.7 Pollution by Dyes

Dyes can interact in some way with the substance being dyed to produce vibrant colors. Generally, dyes are used to color clothes and to make different cell and tissue types more noticeable. Additionally, dyes can be eliminated from their aqueous solutions in a number of methods and are regarded as a typical form of water contaminant. The adsorption approach is one of the most crucial of these techniques [96].Dyes are widely used in the textile, paper, plastic, food and cosmetic industries. Waste from these industries can affect our atmosphere causing pollution. The level of pollutants even at low concentration is very visible and affects aquatic life. Hence, pollution from pigments is not only a serious public health concern, but also many serious environmental problems due to its persistence in nature and insoluble propertie [97]. Chemists found a relationship between the color of a substance and its composition. In the year (1868 AD), the scientist (Eraeb) and his colleagues explained that the presence of unsaturated groups in the molecule is a major factor in the emergence of color, Witt, explained about the presence of certain functional groups in the molecule. The compound that makes it colored. They are called chromophores, they mean color bearing groups, they include -C=C-, -C=S, -C=O, -N=O, $-NO_2$, -N=N-. There are groups that increase the intensity of the color carried by the chromophore group, and these groups are called auxiliary groups or auxochromes, that is, color tonics ]98[. In our study, dyes can be classified into several types according to their chemical composition. As shown in Table (1-3) [99]

**Table (1-3): Classification of dyes**

| Applications | Example | The type of dye |
|---|---|---|
| Wool, silk, polyurethane fiber, nylon. | Methyl orange, Methyl red , RBB and Congo red | Acidic dyes |
| Pharmaceutical polyesters, cotton, paper. | Aniline yellow, Butter yellow, ,Azure C and Malachite green | Basil dyes |
| Cotton, wool, silk, nylon | Martius yellow and Congo red | Direct dyes |
| Cotton, wool, silk | Procion dye (2,4,6-tri chloro 1,3,5-triazine),<br>Reactive Red dye. | Reactive dyes |
| Wool, a coloring agent in food | Indigo ,Benzanthro and Tyrian purple | Oily dyes |
| Polyesters and Polyamides | Disperse Blue Dye | Disperse Dye |

## 1.8 Aim of the Study

The work can be summarized as follows:

1- Synthesis of nano co-polymer by esterification process. and its characterization using spectra FT-IR, $^1$H-NMR, DSC, AFM, XRD and TEM

2- The use of the prepared nano co-polymer in removing pollution from aqueous solutions of some types of dyes

# CHAPTER

# TWO

# Materials & Methods

## 2.1 Chemical and Techniques

### 2.1.1 Chemicals

The following Table (2-1) shows all solid and liquid chemical materials used in this study .

**Table (2-1): Chemical material, purity and companies supply**

| Materials | Purities | Company |
|---|---|---|
| phthalic anhydride | 99% | BHD |
| Glycerol | 99.5% | ALPHA |
| Dimethylsulfoxide (DMSO) | 99.5% | CDH |
| methyl orange dye | 99% | MERCK |
| Wrights Stain dye | 98% | MERCK |
| Eosin yellow dye | 98% | MERCK |

### 2.1.2 Techniques and Instruments

1. Fourier Transformer Infra-Red Spectroscopy (FT-IR) spectra in range 400-4000 $cm^{-1}$ has been used by potassium bromide disc on FT-IR instrument Bruker spectrophotometer /USA, Department of Chemistry / College of Sciences / University of Babylon.

2. $^1$H-NMR Spectroscopy, Bruker Bio Spin 400 MHz spectrometer Ghazi Osman Pasha University / Turkey

3. Atomic Force Microscope (AFM), Oxford, USA / Department of Chemistry/ College of Sciences / Baghdad University

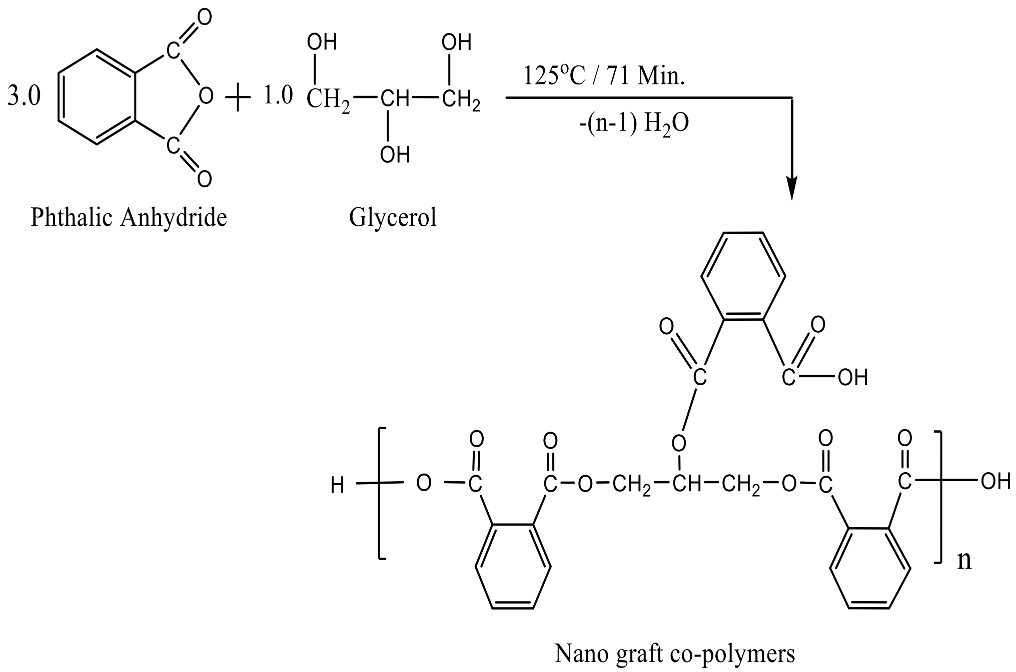
4. Differential scanning calorimetry (DSC), Shimadzu, Japan / University of Babylon / College of Materials Engineering

5. X-Ray Diffraction (XRD), Rigaku Ultima iv, Japan, Berta laboratory for laboratory investigations, Iran.

### 2.2 Synthesis of nanoparticles co-polymers

The processes were used to prepare the nano co-polymers is esterification process; where the method of preparing is described as shown below:

In 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 $C^o$ until clear liquor is formed and added (1.0 mole, 92 g) of glycerol to the solution. The mixture warmed carefully to 100 $C^o$ then 15 mL of xylene was added carefully to the reaction beaker, in the form of batch (three drops in each batch), withdrawal of water formed by the esterification process, and the beaker was gently heated. Heating was stopped after (71min, at 125 $C^o$ ), 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 filtrated and wash with distilled water and leave to dry,



**The general reaction of synthesis of nano graft co-polymer**

## 2.3 Preparation of Dyes Solutions

Dye solutions (Eosin yellow, Wrights Stain and methyl orange ) were prepared using the following general method:

The standard solution of the dye prepared by dissolving (0.5 g) of the dye in a certain amount of distilled water and then complete it to (1000 mL) to prepare a concentration (500 ppm) of this solution. From this concentrated solution, the diluted solutions were prepared in concentrations (1, 3, 5and 7 ppm) by taking the appropriate volume of the concentrated solution and then dilute with (100 mL) distilled water.

## 2.4 Determination of Calibration Curve

The Calibration curve that represented the relationship between absorbance and concentration was determined by prepared three concentrations (1, 3,5 and 7ppm) of the three types of dyes (Eosin yellow, Wrights Stain and methyl orange ) for solutions used in the study, the absorbance of these concentrations was measured at the maximum wavelength ($\lambda_{max}$ = λmax = 520 nm) for the Eosin yellow dye as shown in Figure (2-1 a), after which the calibration curve between absorption and concentration is drawn as in Figure (2-1 b) and at the maximum wavelength ($\lambda_{max}$ = 424 nm) for the Wrights Stain dye as shown in Figure (2-2 a), after which the calibration curve between absorption and concentration is drawn as in Figure (2-2b) ,and at the maximum wavelength ($\lambda_{max}$ = 464 nm) for the methyl orange dye as shown in Figure (2-3a), after which the calibration curve between absorption and concentration is drawn as in Figure (2-3b).

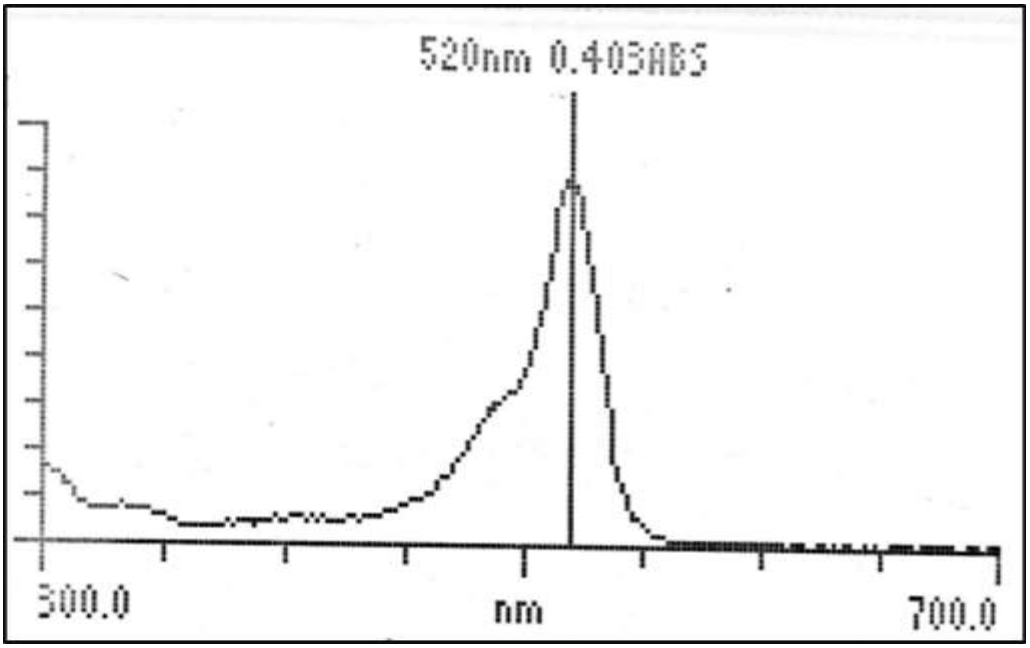


**Figure (2-1 a): The maximum wavelength (λ max ) for the (Eosin yellows dys)**

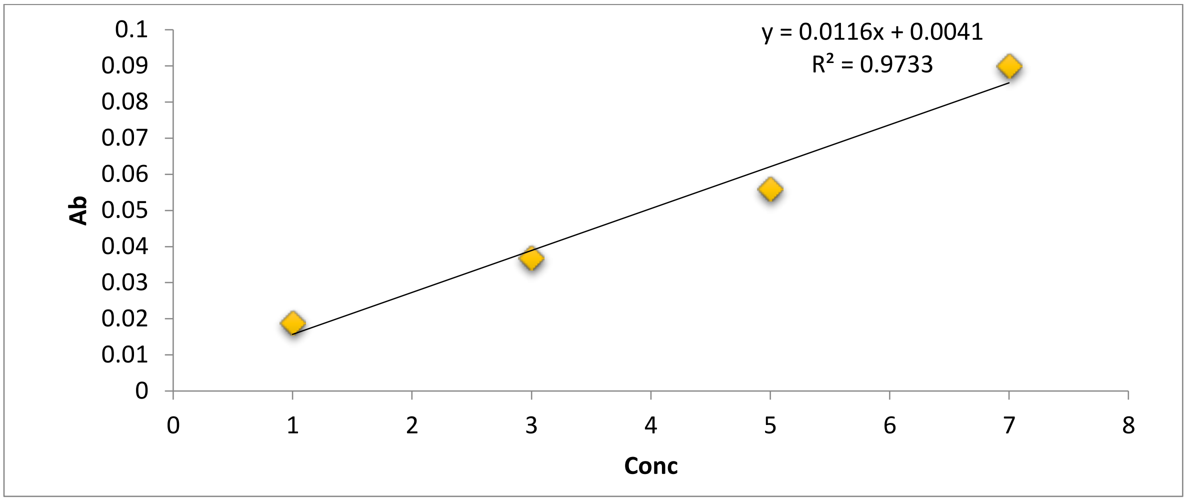


**Figure (2-1 b): The calibration curve between absorption and concentration of Eosin yellow**

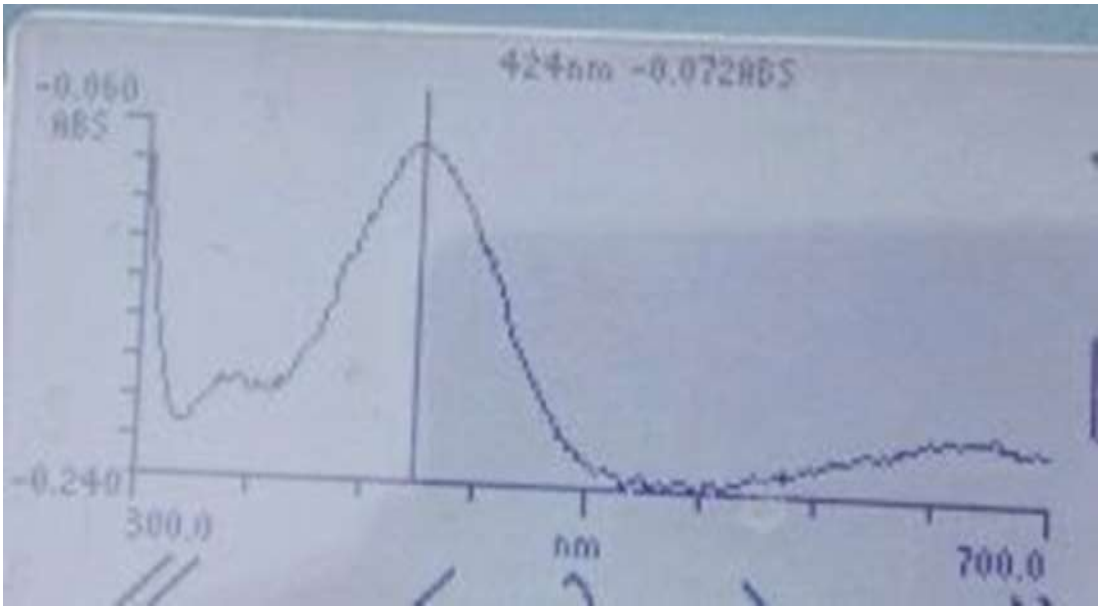


**Figure (2-2 a): The maximum wavelength (λ max ) for the Wrights Stain dye**

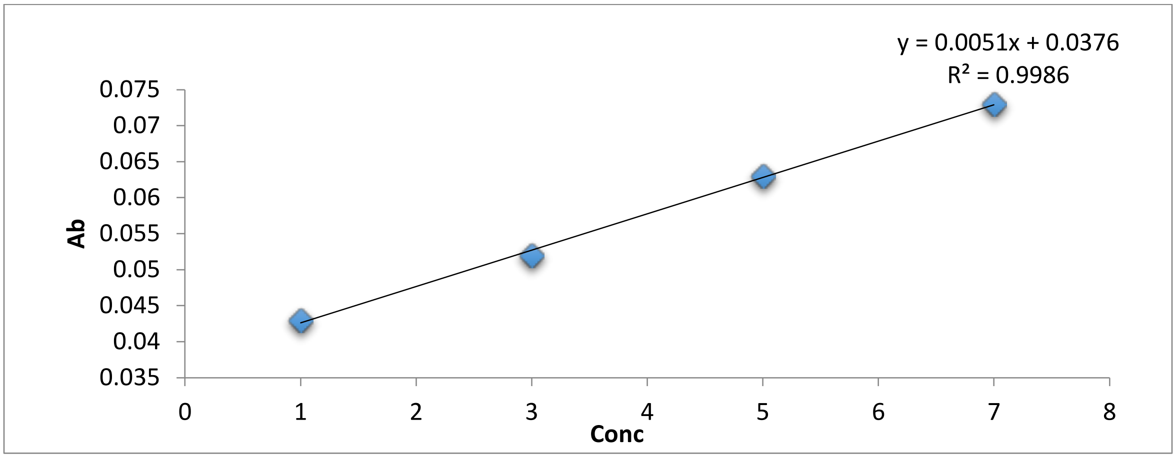


**Figure (2-2 b): The calibration curve between absorption and concentration of Wrights Stain dye**

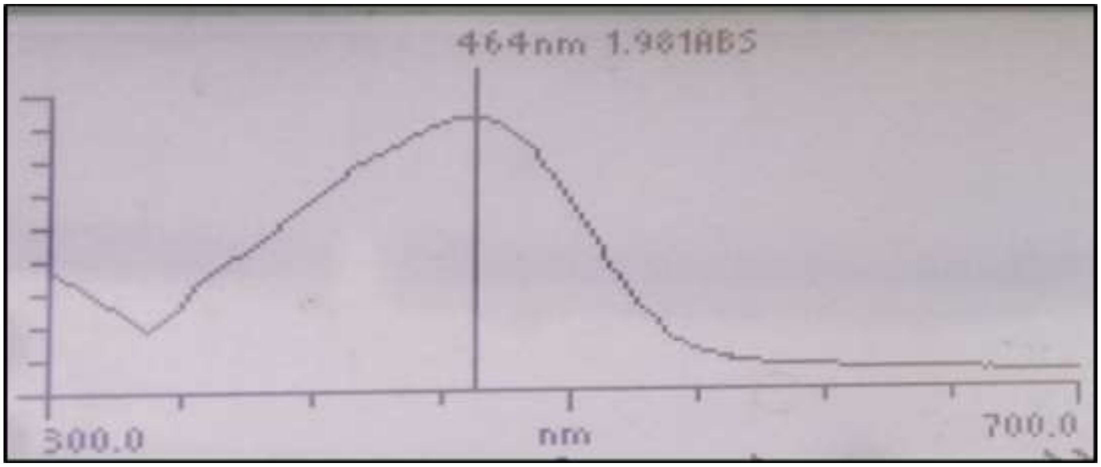


**Figure (2-3 a): The maximum wavelength (λ max ) for the methyl orange dye**

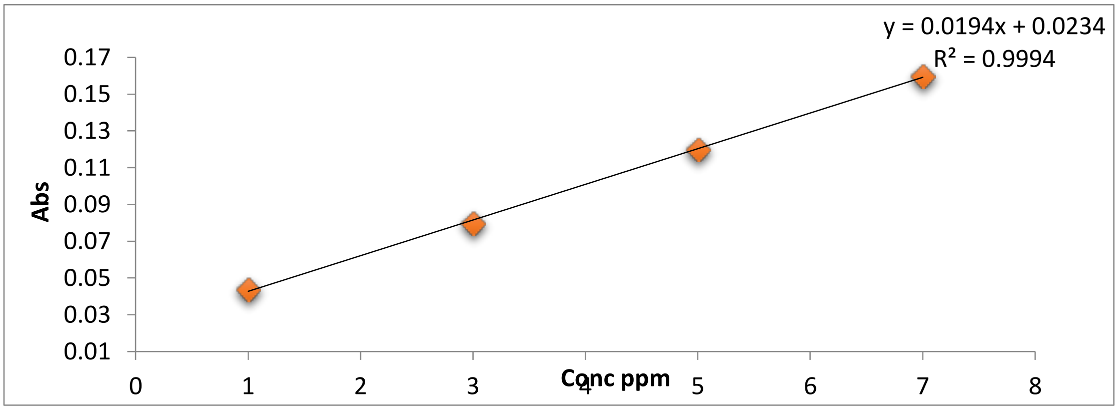


**Figure (2-3b): The calibration curve orange dye between absorption and concentration of methyl**

## 2.5 Determination of Equilibrium Factors

To determine the weight of the adsorbent material that is given the highest amount of adsorption, different weights were taken from the adsorption surface nano- copolymer within the range (0.01,0.012,0.013,0.014,0.015 and 0.016g) and placed in contact with 15ml from the solution of the adsorbent (Eosin yellow, Wrights Stain and methyl orange ) dyes and by concentrating 7ppm of volumetric flask and the absorbance of it was measured after the of 60 min, from placing in the vibrator has a temperature 298k and the surface weight was chosen, which gave the lowest absorbency.

As for determining the time required for the equilibrium to occur between the adsorbent surface nano co-polymer and the adsorbent material (Eosin yellow, Wrights Stain and methyl orange ) dyes. 18 volumetric flask were taken and placed in it 15ml of 7ppm concentrations of each dye in contact with the predetermined weight (nano co-polymer) was placed in the water bath shaker at constant temperature of 298K , then samples were drawn from it at successive times and the absorbance was measured for as in the Table (2-2).

**Table (2-2): shows the weight and equilibrium time for each dye.**

| The name of the dye | Wt (g) | Time(min) |
|---|---|---|
| **Eosin yellow** | 0.018 | 20 |
| **Wrights Stain** | 0.02 | 30 |
| **methyl orange** | 0.016 | 25 |

## 2.6 Determination of Adsorption Isotherms

For the purpose of finding adsorption isotherms, four solutions were prepared from each polymer and with concentrations of (1,35, and 7 ppm) of same dyes, then 15 ml of each concentration of dye was taken and placed in volumetric flasks in contact with the specified predetermined weight of the adsorbent surface (nano co-polymer), after these flasks were placed in shaking device with a temperature of 298K and after reaching the specified and the predetermined equilibrium time for each dye ,then the solutions were filtered and the samples were analyzed using UV.-Vis. spectroscopy, and determined the concentration of each solution at equilibrium $C_e$ (mg/L) of the calibration curves and then determined the amount of the adsorbate substance $Q_e$ (mg/g) under the following relationship ]124[.

$Q_e = (C_o-C_e) .V_{sol} / Wt$…………………(2-1)

**Were as**

Qe: the amount of adsorbate (mg/g).

$C_o$: the initial concentration of the adsorbate (mg/L).

Ce: the residual concentration of the adsorbate at equilibrium (mg/L).

Vsol: the total volume of the adsorbate solution (L).

wt: weight of the adsorbent (g).

## 2.7 Effect of Temperature on Adsorption

For the purpose of studying the effect of temperature on adsorption, the adsorption isotherm was studied for each dye [Eosin yellow, Wrights Stain and methyl orange] at a temperature (298-308-318 K).

# CHAPTER

# THREE

# 3. Results and Discussions

## 3.1: Synthesis and characterization of nano co-polymer

The nano co-polymer was created by esterifying three moles of phthalic anhydride with one mole of glycerol, and it was then characterized using several methods (FT-IR, $^1$H-NMR, AFM and XRD and DSC) ,

Figure (3-1) showed the FT-IR spectrum, which appeared as a very weak broad band at (3093 cm$^{-1}$) attributed to the bond (O-H) carboxylic and H-bond, and showed stretching bands at (3067 cm$^{-1}$ and 2887 cm$^{-1}$) attributed to the bond (C-H) aromatic and an asymmetric (C-H) aliphatic bond, as well as a strong stretching band at (1757 cm$^{-1}$) attributed to the ester bond (C=O). Moreover, stretching bands at (1402, 1468, and 1595 cm$^{-1}$ assigned to (C=C) aromatic, a very sharp peak at (1107 cm$^{-1}$) attributed to the bond (C-O) ester, and bands at (709 and 903 cm$^{-1}$) attributed to di substitution of aromatic ring.

Figure (3-2) shows $^1$H-NMR spectrum and which explains the singlet signal of the distinctive proton in the carboxylic acid group at 13.04 ppm, Additionally, the signals at 4.26- 4.28 ppm for four methylene protons in the co-polymer structure, the multiple at 4.15 ppm of methyl protons, and the multiple in the region 7.55–7.68 ppm attributed to all protons in the aromatic ring, but the aliphatic alcohol signal has vanished indicating the formation of a graft co-polymer.

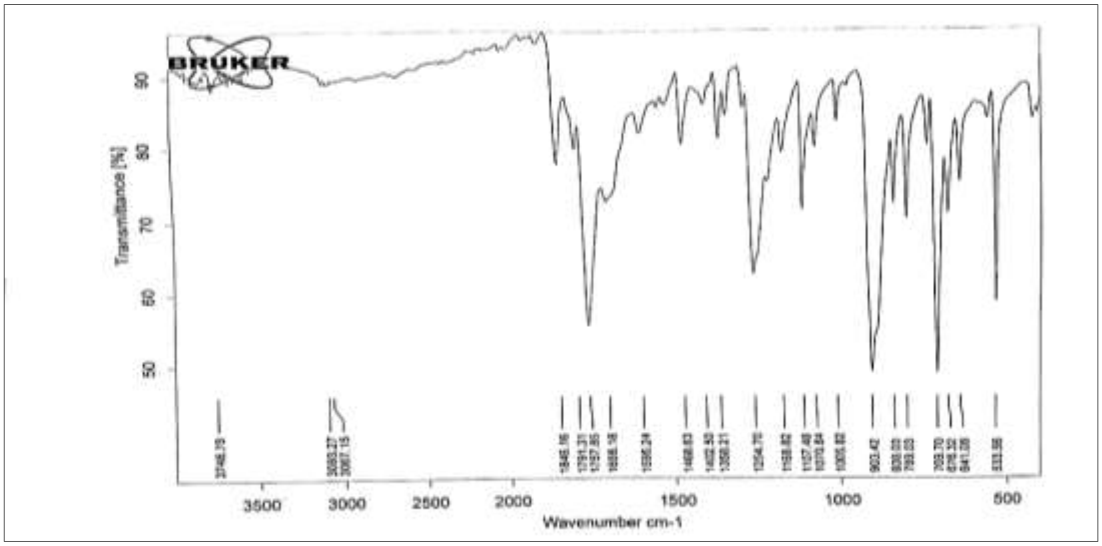


**Figure (3-1): FT-IR of nano co-polymer**

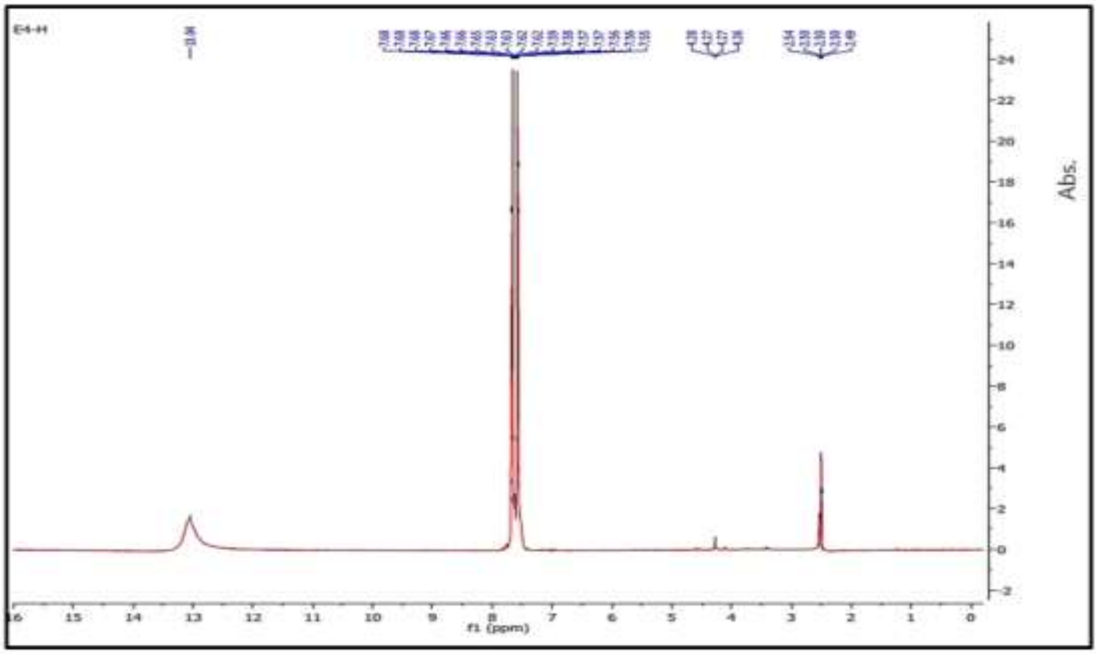


**Figure (3-2): $^1$H-NMR spectrum of nano co-polymer**

Figure (3-3 a, b and c) shows the outer surface of the nanoparticles of co-polymer. The roughness coefficient of co-polymer surface was 5.08 nm and the square root square was equivalent to 5.94 nm. This indicates that the bold size of the nanoparticles affects 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 Figure (3-3 a). Table (3-13) represents the total rate of the particle sizes of the nano co-polymer and the different proportions of these volumes; the results indicate that the molecular size of the co-polymer nanoparticle was 68.62 nm and the distribution of the varied ratios of co-polymer nanoparticle particle sizes is shown in Figures (3-4).

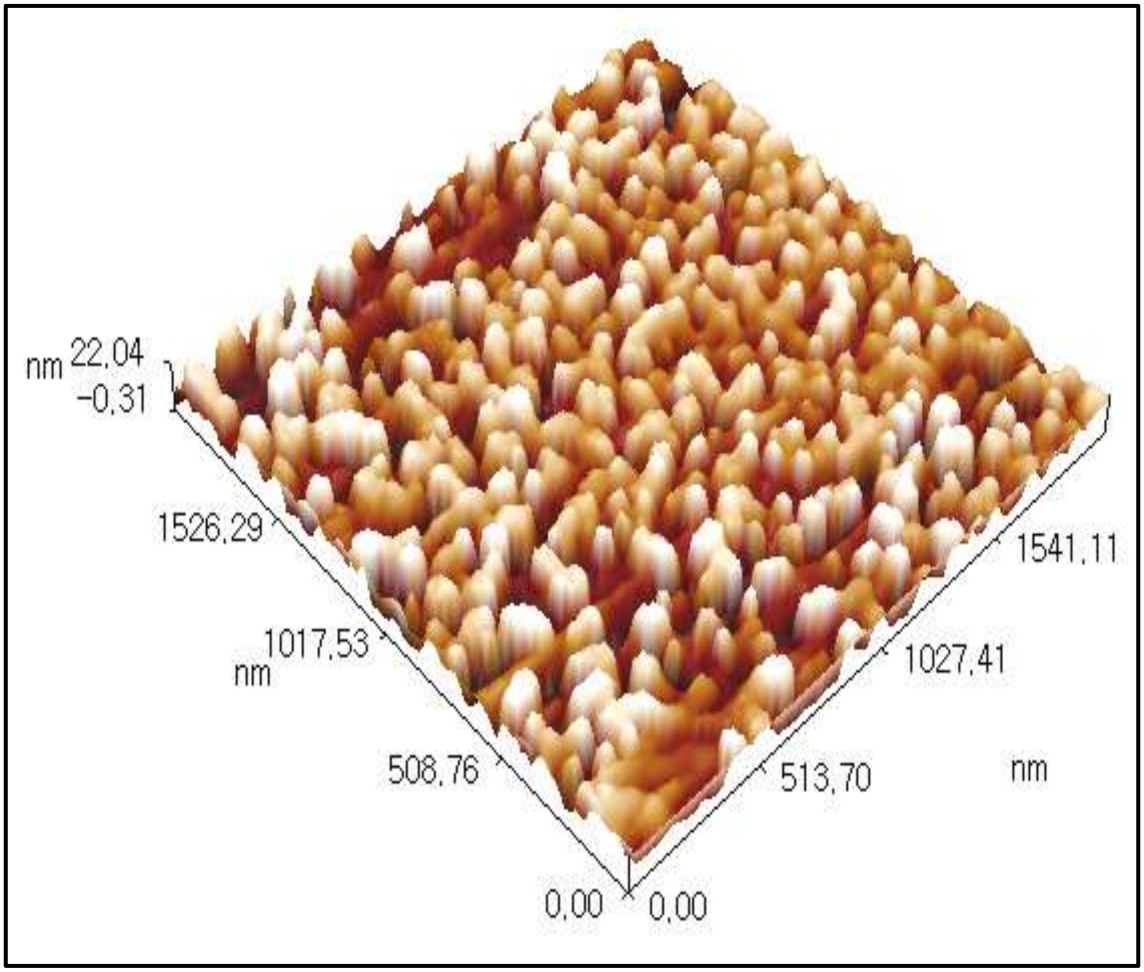


Figure (3-3 a): Image of Atomic Force Microscope for nano co-polymer shows 3D Image

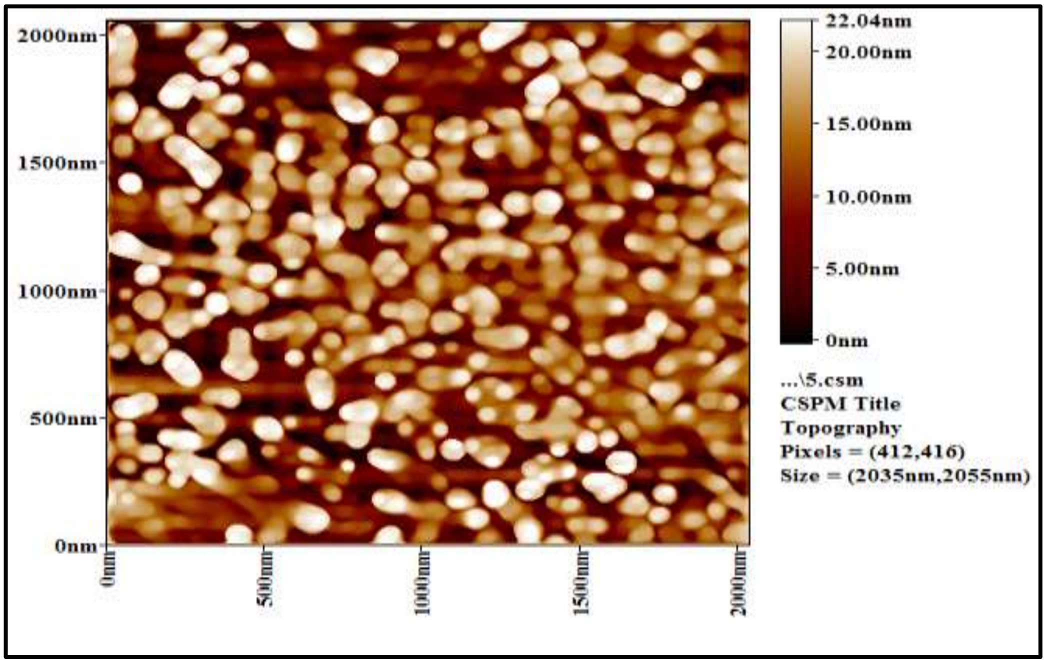


Figure (3-3 b): Image of Atomic Force Microscope for nano co-polymer shows 2D Image

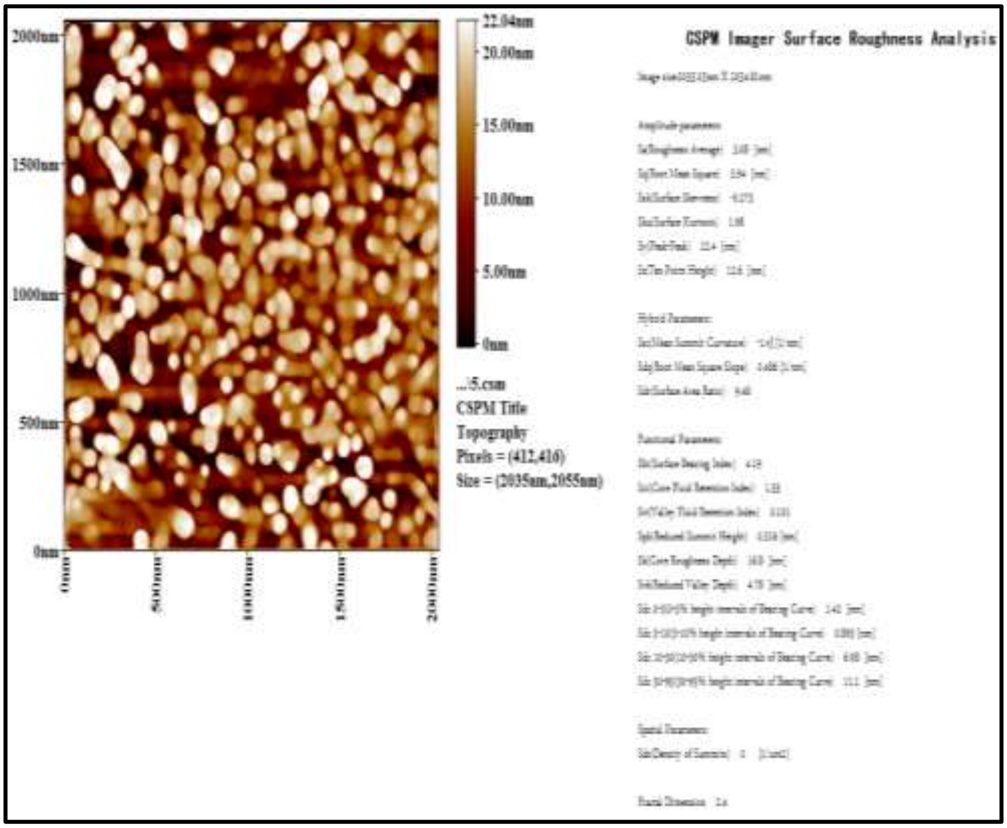


Figure (3-3 c): Image of Atomic Force Microscope for nano co-polymer shows 2D Image and showing all details of particles

**Table (3-1): 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:** 2022-06-24 |

| | |
|---|---|
| **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 (%) |
|---|---|---|---|---|---|---|---|---|
| 45.00 | 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 | | | |

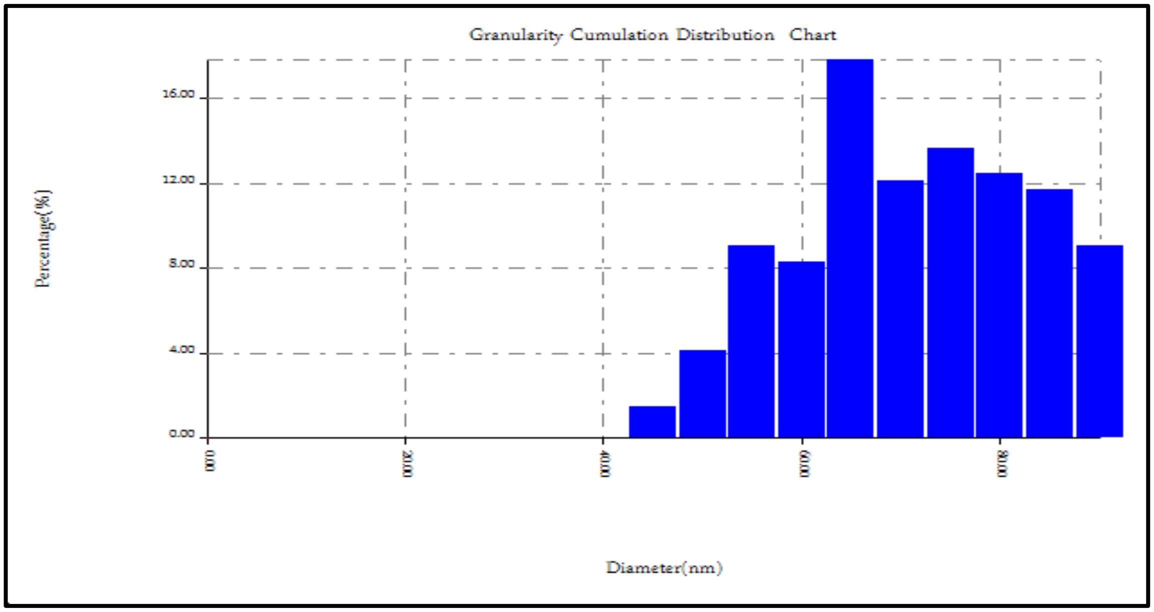


**Figure (3-4): Distribution of the different proportions of particle sizes of the nano co-polymer**

The x-ray diffraction (XRD) in the nanoparticles co-polymer in Figure (3-5) exhibits peaks at 2 values of (15.4°, 18.5°, 21.2°, 22.2°, 26.9°, and 30.5°). These peaks demonstrated that a crystalline molecule with fewer amorphous carbon atoms had created the new co-polymer. the average inters planer spacing (dhkl) between atoms utilizing origin software was 0.415 nm According to Bragg's Law:

$$n\lambda = 2d\sin\theta \text{ ……… Bragg's Law}$$

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

$$D = \frac{k\lambda}{\beta cos\theta} \text{ ……..... Scherrer's equation}$$

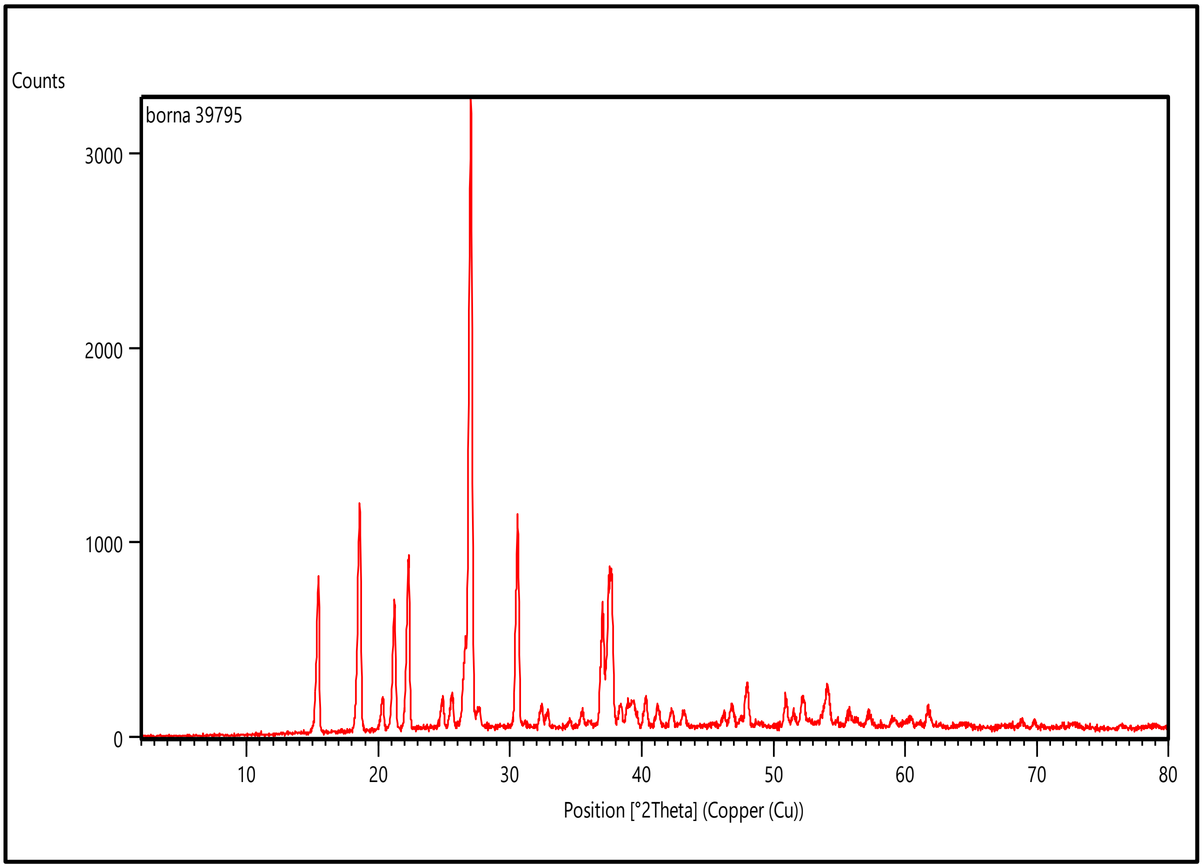


Figure (3-5): X-ray diffraction in the nanoparticles co-polymer

**Table (3-2) the proportions crystallites sizes and the distances between atoms (d-spacing) in the nano co-polymer**

| 2 θ | θ | FWHM | D nm | d $_{hkl}$ nm | D (Av.) nm | d $_{hkl}$ (Av.) nm |
|---|---|---|---|---|---|---|
| 15.41888 | 7.70944 | 0.10308071 | 77.77159 | 0.57421 | **68.4874** | **0.4152** |
| 18.56158 | 9.28079 | 0.12176233 | 66.10961 | 0.477637 | | |
| 21.20363 | 10.60181 | 0.11615246 | 69.58317 | 0.418681 | | |
| 22.26382 | 11.13191 | 0.11743049 | 68.94823 | 0.398978 | | |
| 26.9992 | 13.4996 | 0.13275784 | 61.54072 | 0.32998 | | |
| 30.55913 | 15.27956 | 0.12296861 | 66.97155 | 0.292302 | | |

Figure (3–8 ) shows The DSC thermograms for the nano co-polymer. The first thermal transition at the peak, which is 48.68 C$^{o}$, represents the glass transition temperature (Tg), the second transition at the peak, which is 134.10 C$^{o}$, represents the crystallization temperature (Tc), and the third and fourth transitions at the peaks, which are 197.60 and 302.19 C$^{o}$, respectively, represents the melting temperature (Tm) .

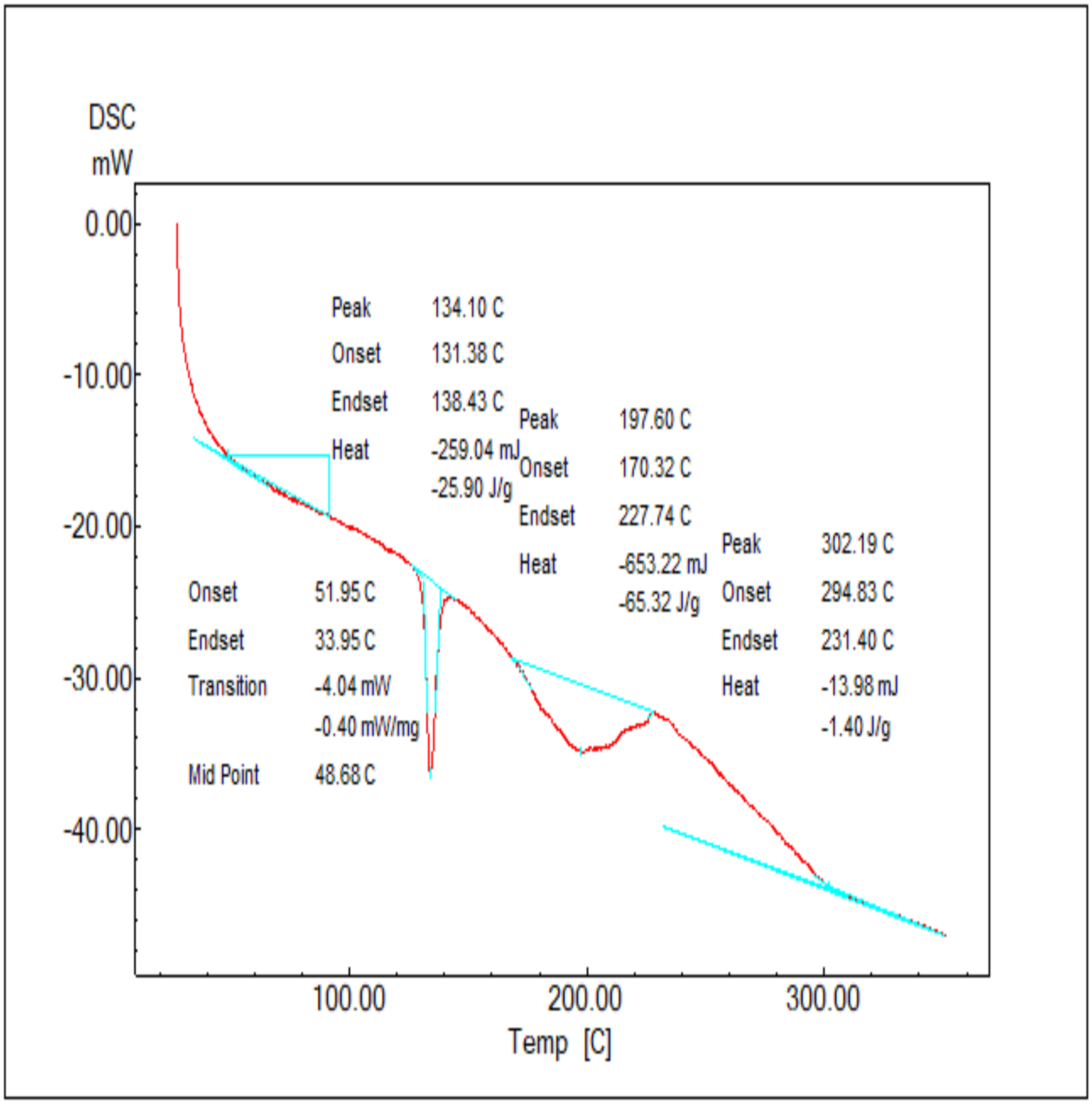


**Figure (3-8): DSC thermo grams of nano co-polymer**

## 3.2 Removal of pollutants

The pollutants were removed by using the adsorption process, where nano co-polymer were used as adsorbent surfaces with Eosin yellow, Wrights Stain and methyl orangedyes) as adsorbate materials (pollutants).

## 3.3 Adsorption isotherm on the surface of nano co-polymer

The adsorption of Eosin yellow, Wrights Stain and methyl orange dyes were studied on the nano co-polymer, where adsorption isotherms were obtained at a temperature of 298K as shown in Table (3-4), (3-5) and (3-6) for all dyes respectively and Figure (3-9) , (3-10) and (3-11) for Eosin yellow, Wrights Stain and methyl orangedyes

It is evident from the drawing that the general form of adsorption isotherms is of type (S1) according to the classification of Giles). This indicates that the surface of the adsorbent material is a heterogeneous surface [106]. Also, when the covered part of the adsorbent surface increases, the adsorption temperature will decrease [103]. The increased shape of the isotherm with increasing the concentration of equilibrium confirms that the arrangement of the particles on the surface in vertical rows .Hydrogen bonding[110].

The dyes adsorption data were treated according to the following linear formula of the following logarithmic Ferndelsh equation:-

$\text{Log } Qe = \text{Log } Kf + 1 / n \text{ Log } Ce$ ……….(1-3).

Ce : Concentration of the adsorbate at equilibrium (mg/L).

Qe : Quantity of the adsorbate material at equilibrium (mg/g).

$K_f$, n: are isotherm constants indicate the capacity and intensity of adsorption respectively.

Tables (3-7),(3-8) and (3-9) and figures (3- 12), (3-13) and ( 3-14) show the extent to which the adsorption of Eosin yellow, Wrights Stain and methyl orange dyes correspond to the Freundlich equation, and when drawing the relationship between

Log Qe versus Log Ce we get straight lines as shown in table (3-7),(3-8) and (3-9), and figures (3-12), (3-13) and(3-14) for all the pigments on the stirrupsre spectively.

**Table (3-4): adsorption of Eosin yellow, on the surface of the nano co-polymer at a temperature of 298K.**

| Temp | Con.(ppm) | $C_e$ (mg/L) | Qe (mg/g) |
|---|---|---|---|
| | **1** | **0.1637** | **0.6969** |
| | **3** | **0.3362** | **2.2198** |
| | **5** | **0.4224** | **3.1846** |
| | **7** | **0.5086** | **5.4095** |

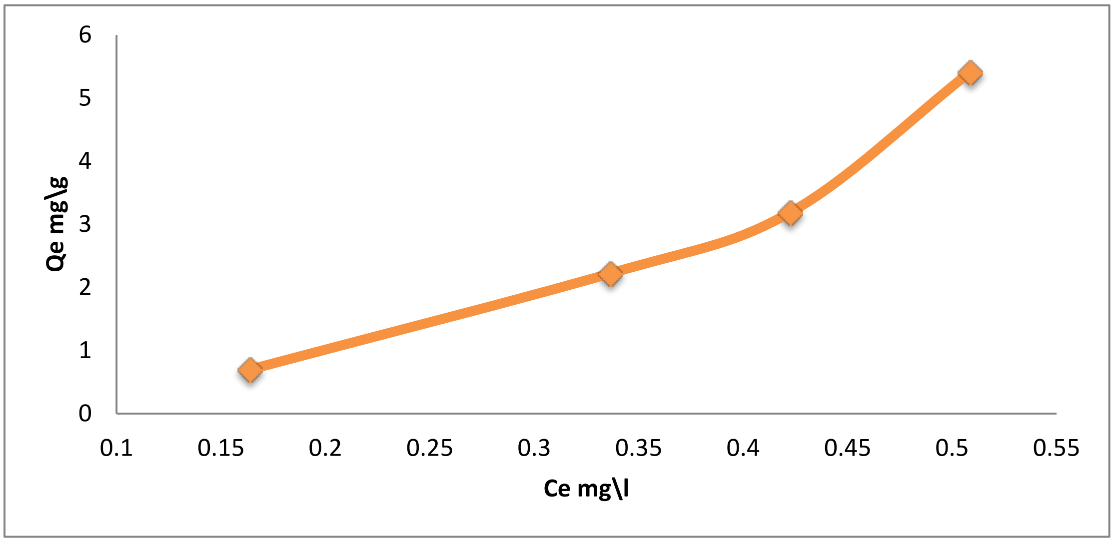


**Figure (3-9): Adsorption isotherm Eosin yellow, dye on the surface of graft co-polymer**

**Table (3-5): Adsorption of Wrights Stain dye on the surface of nano co-polymer at 298K .**

| Temp | Con.(ppm) | $C_e$ (mg/L) | $Q_e$ (mg/g) |
|---|---|---|---|
| | 1 | 0.1413 | 0.6440 |
| | 3 | 0.3043 | 2.0217 |
| | 5 | 0.3586 | 3.4810 |
| | 7 | 0.4130 | 4.9402 |

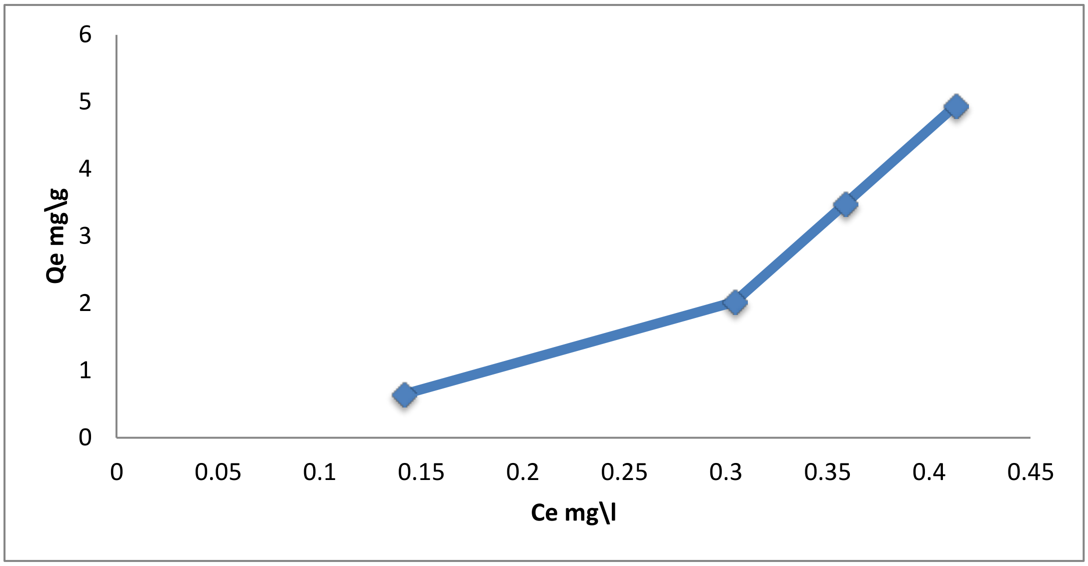


**Figure (3-10): Adsorption isotherm Wrights Stain dye on the surface of graft co-polymer.**

**Table (3-6): Adsorption of methyl orange dye 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 |

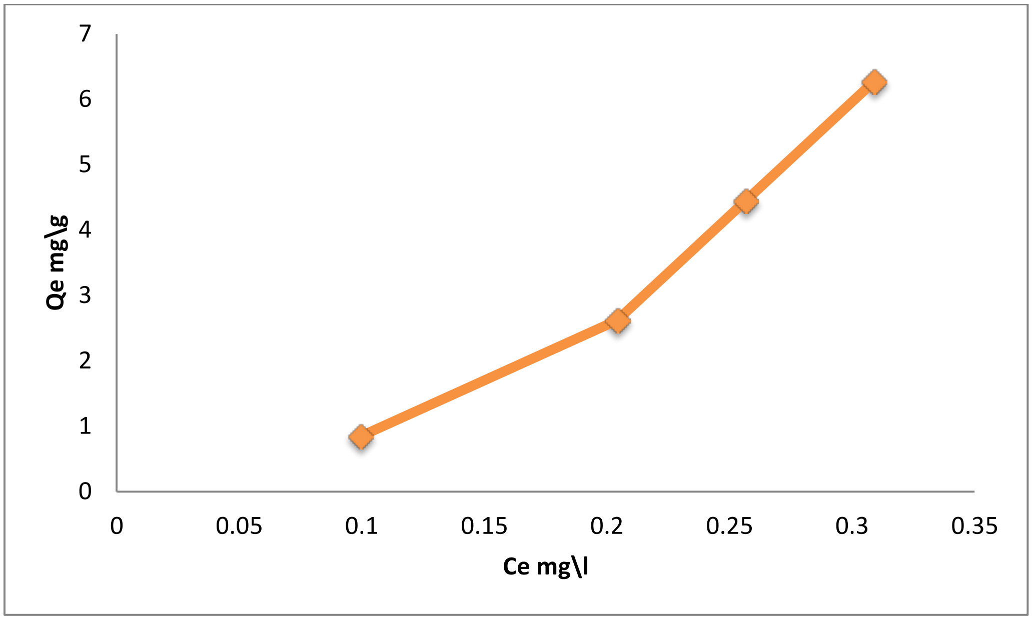


**Figure (3-11): Adsorption isotherm methyl orange dye on the surface of graft co-polymer.**

**Table (3-7): Adsorption of Eosin yellow, dye on the surface of graft co-polymer.at 298K,308K and 318K (by applying Freundlich equation).**

| **Conc.(ppm)** | **298K** | | **308K** | | **318K** | |
|---|---|---|---|---|---|---|
| | -LogC$_e$ | LogQe | -LogC$_e$ | LogQe | -LogC$_e$ | Log Q$_e$ |
| **1** | 0.7859 | -0.1568 | 0.602 | -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 | 0.115 | 0.5474 |
| **7** | 0.2936 | 0.7331 | 0.1668 | 0.7214 | 0.0688 | 0.7094 |

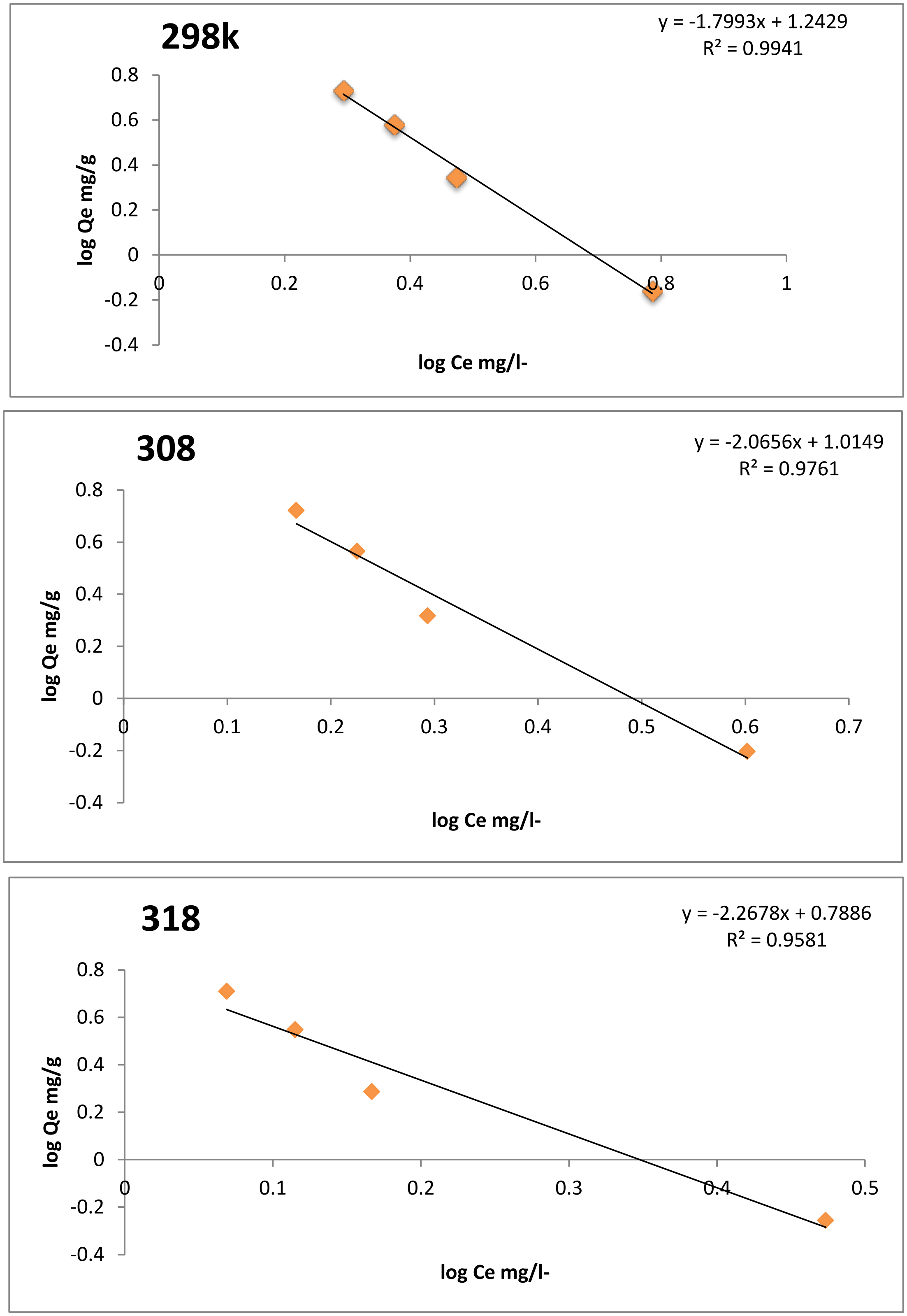
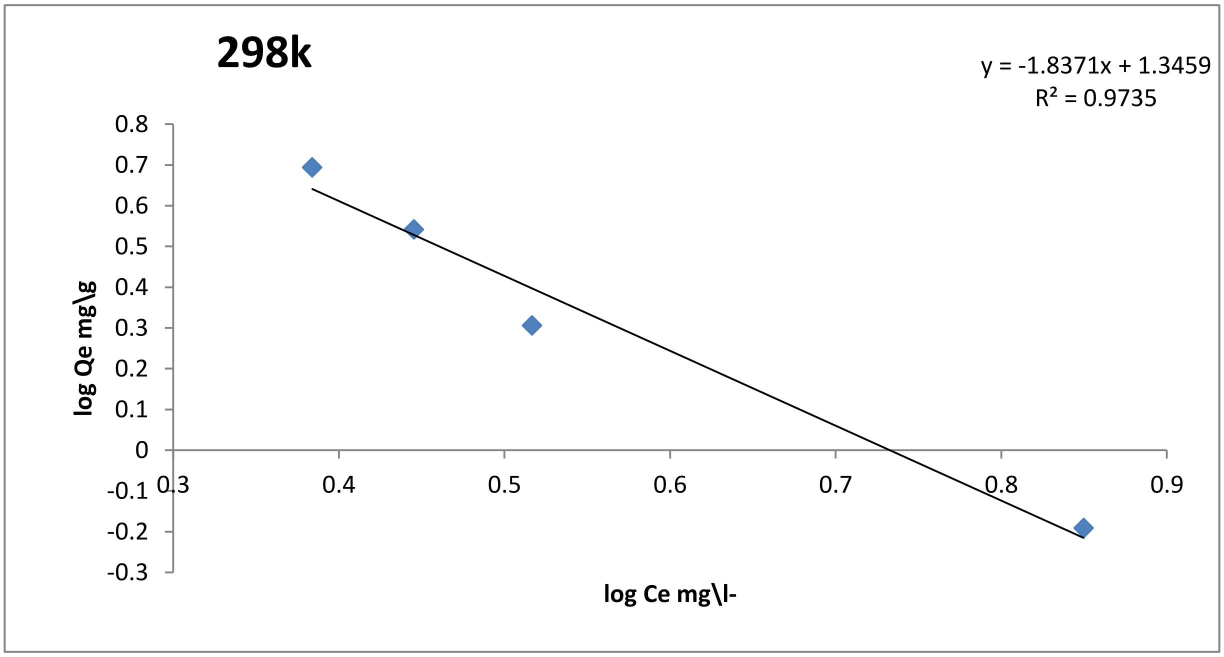
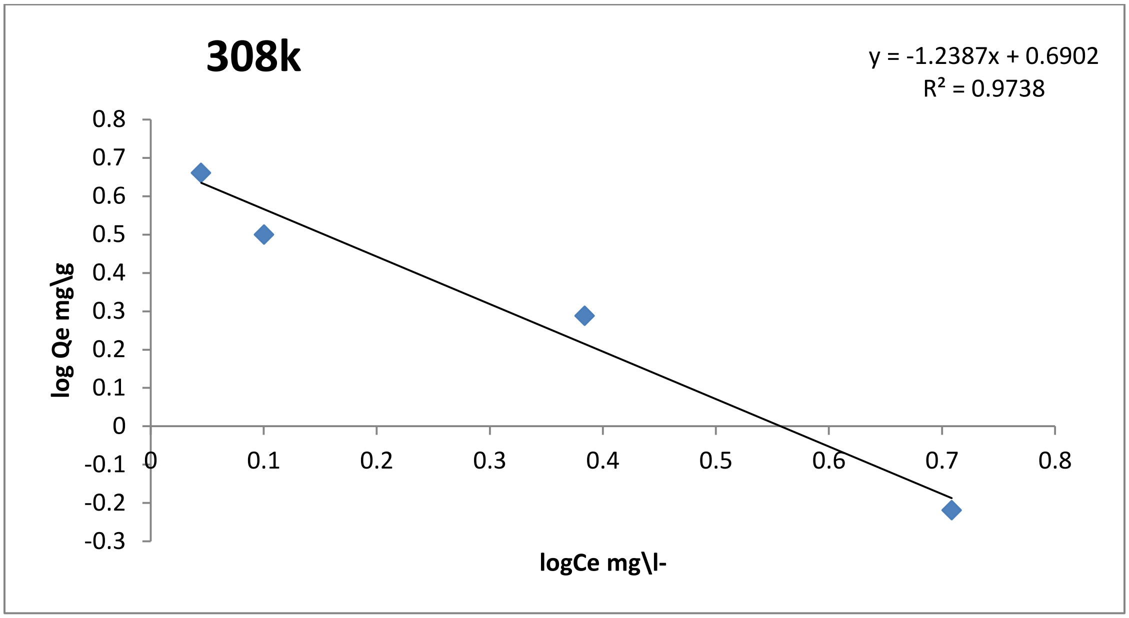


**Figure (3-12): Apply Freundlich equation on adsorption of Eosin yellow, dye on the surface of graft co-polymer at 298K,308K and318K.**

**Table (3-8): Adsorption of Wrights Stain dye on the surface of graft co-polymer at 298K,308K and 318K (by applying Freundlich equation)**

| Conc .(ppm) | 298k | | 308k | | 318k | |
|---|---|---|---|---|---|---|
| | -LogCe | LogQe | -LogCe | LogQe | -LogCe | LogQe |
| **1** | 0.8498 | -0.1911 | 0.7086 | -0.2194 | 0.602 | -0.2498 |
| **3** | 0.5166 | 0.3057 | 0.384 | 0.2878 | 0.1644 | 0.2396 |
| **5** | 0.4453 | 0.5417 | 0.1005 | 0.4989 | 0.0447 | 0.4876 |
| **7** | 0.384 | 0.6937 | 0.0447 | 0.6602 | 0.0193 | 0.6563 |





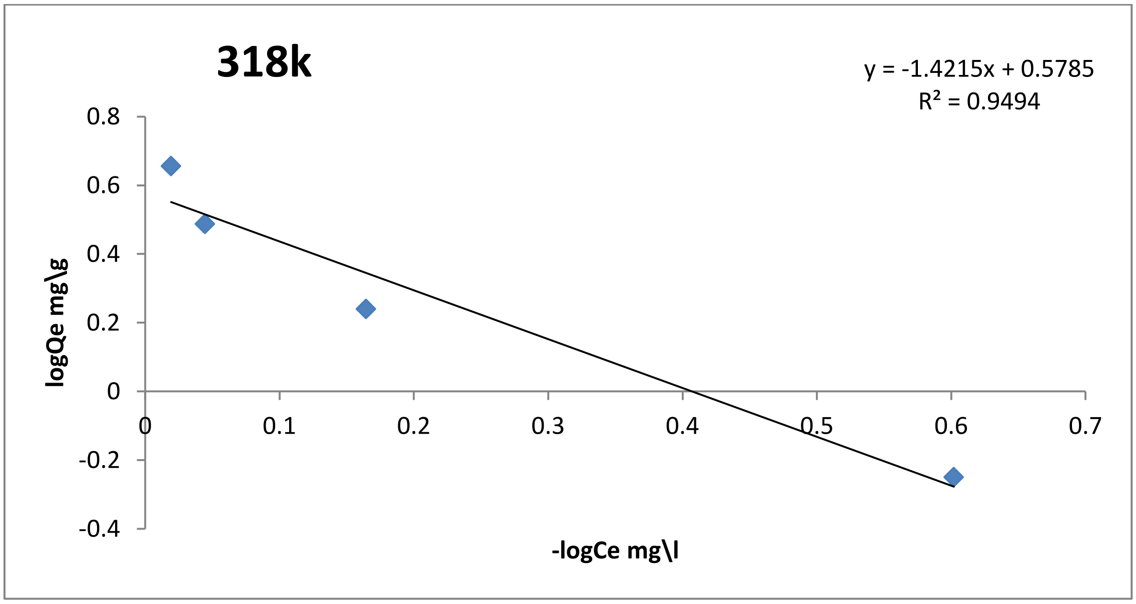
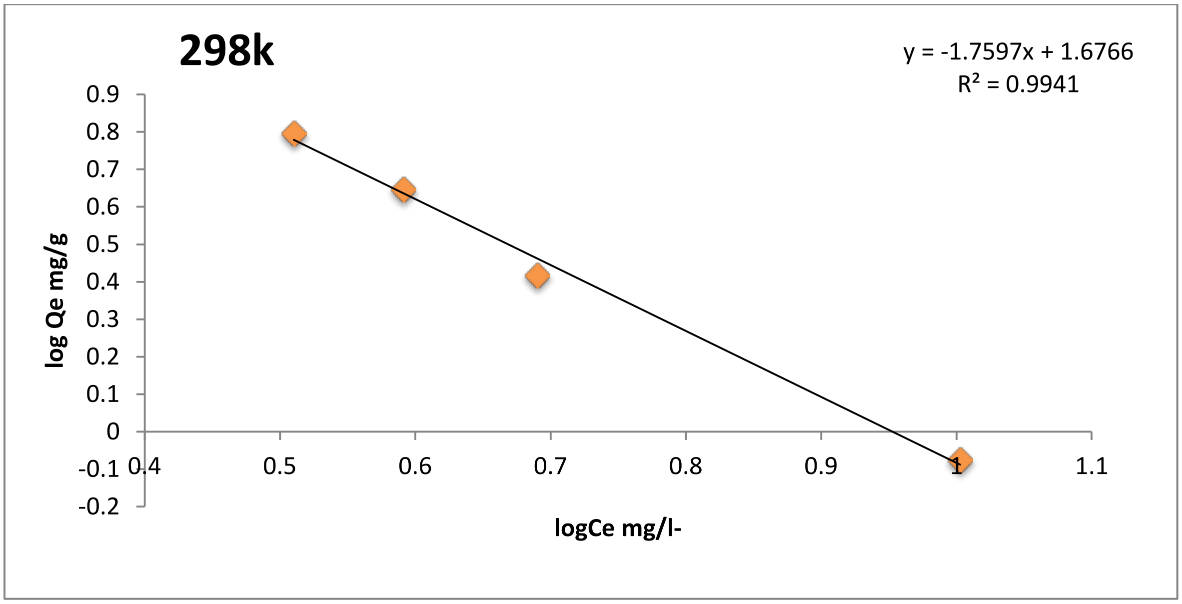


**Table (3-13): Adsorption of Wrights Stain dye on the surface of graft co-polymer at 298K,308K and 318K (by applying Freundlich equation)**

**Table (3-9): Adsorption methyl orange on the surface of nano co-polymer at 298K,308K and 318K (by applying Freundlich equation).**

| Conc.(ppm) | T298 | | T308 | | 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 |



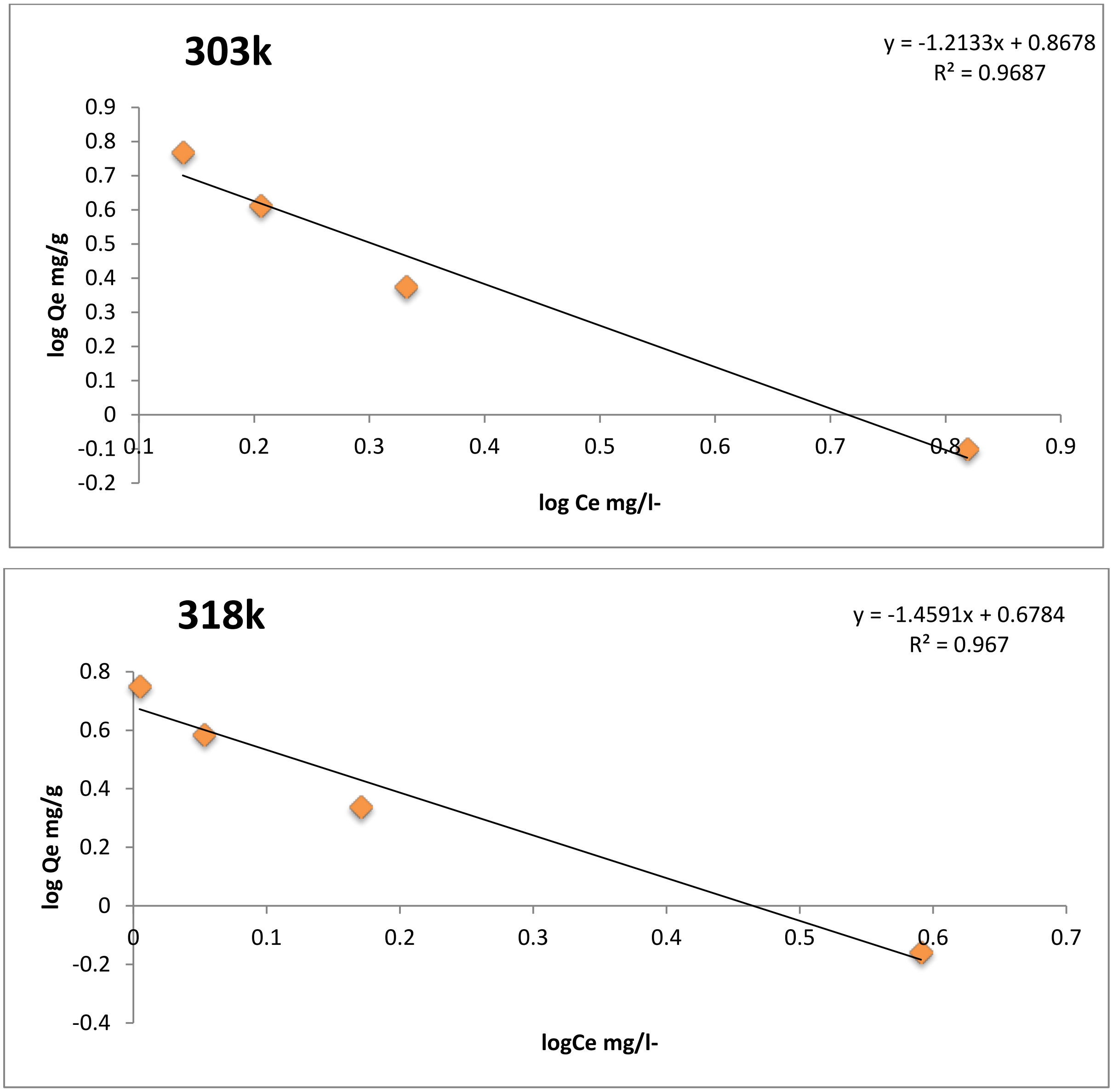


**Figure (3-14): Apply Freundlich equation on adsorption of methyl orange dye on the surface of graft co-polymer at 298K,308K and 318K.**

The adsorption data for Eosin yellow, Wrights Stain and methyl orange dyes were processed according to the linear relationship of the Langmuir equation as shown in table (3-10),(3-11) and (3-12) for all dyes respectively, and when drawing the relationship between ($C_e$ / $Q_e$) versus Ce We obtain a linear relationship as shown in figure (3-15),(3-16) and (3-17) according to the following equation [ 111] .

$Ce / Q_e = 1 / a + (b / a) Ce$…………….(3-2).

where as:

Qe: Adsorption capacity at equilibrium (mg / g).

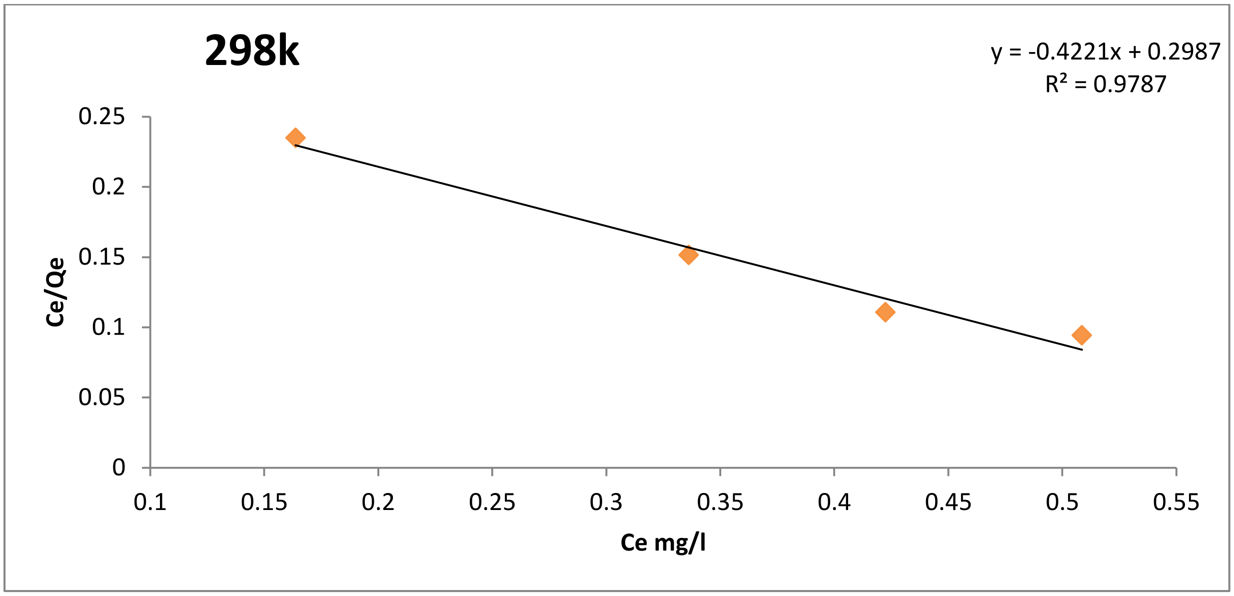
Ce: Concentration of solute at equilibrium in units (mg / L).

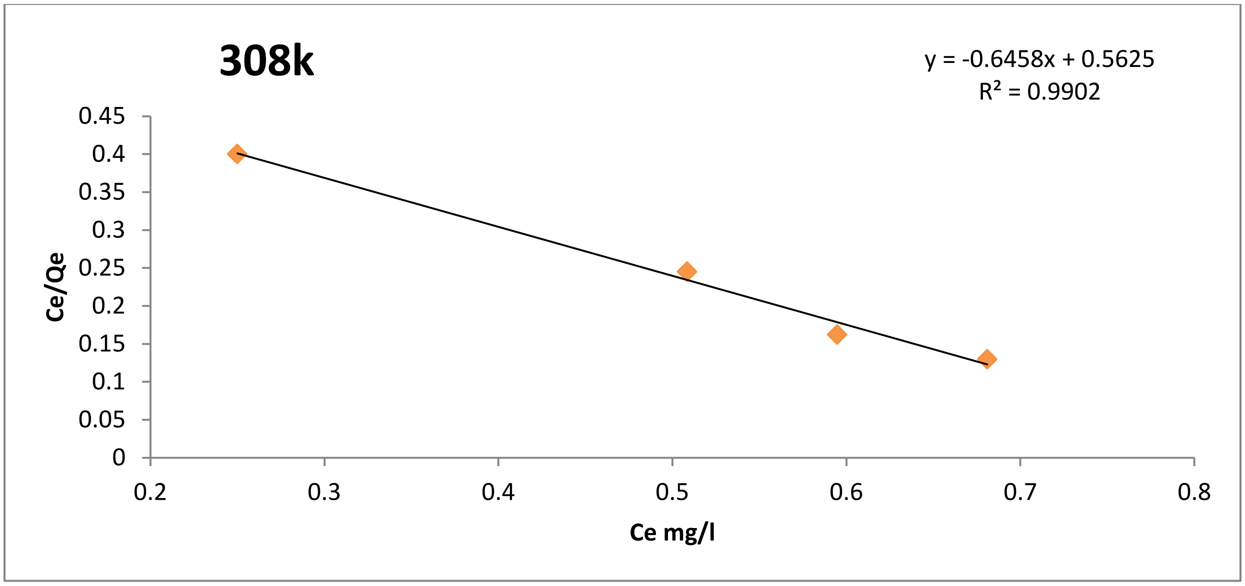
a: Proportionality constant (is the theoretical maximum adsorption capacity(mg/g)).

b: Langmuir adsorption constant (L /mg)

**Table (3-10): Adsorption of Eosin yellow dye on the surface of nano copolymer at 298K,308K and 318K (by applying Langmuir equation).**

| **Conc PPm** | **T298** | | **T308** | | **T318** | |
|---|---|---|---|---|---|---|
| | Ce | $C_e/Q_e$ | Ce | $C_e/Q_e$ | Ce | $C_e/Q_e$ |
| **1** | 0.1637 | 0.2348 | 0.25 | 0.4 | 0.3362 | 0.6078 |
| **3** | 0.3362 | 0.1514 | 0.5086 | 0.2449 | 0.681 | 0.3523 |
| **5** | 0.4224 | 0.1107 | 0.5948 | 0.1620 | 0.7672 | 0.2175 |
| **7** | 0.5086 | 0.0941 | 0.681 | 0.1293 | 0.8534 | 0.1666 |


298k
y = -0.4221x + 0.2987
R² = 0.9787
Ce/Qe
0.25
0.2
0.15
0.1
0.05
0
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
Ce mg/l


308k
y = -0.6458x + 0.5625
R² = 0.9902
Ce/Qe
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Ce mg/l

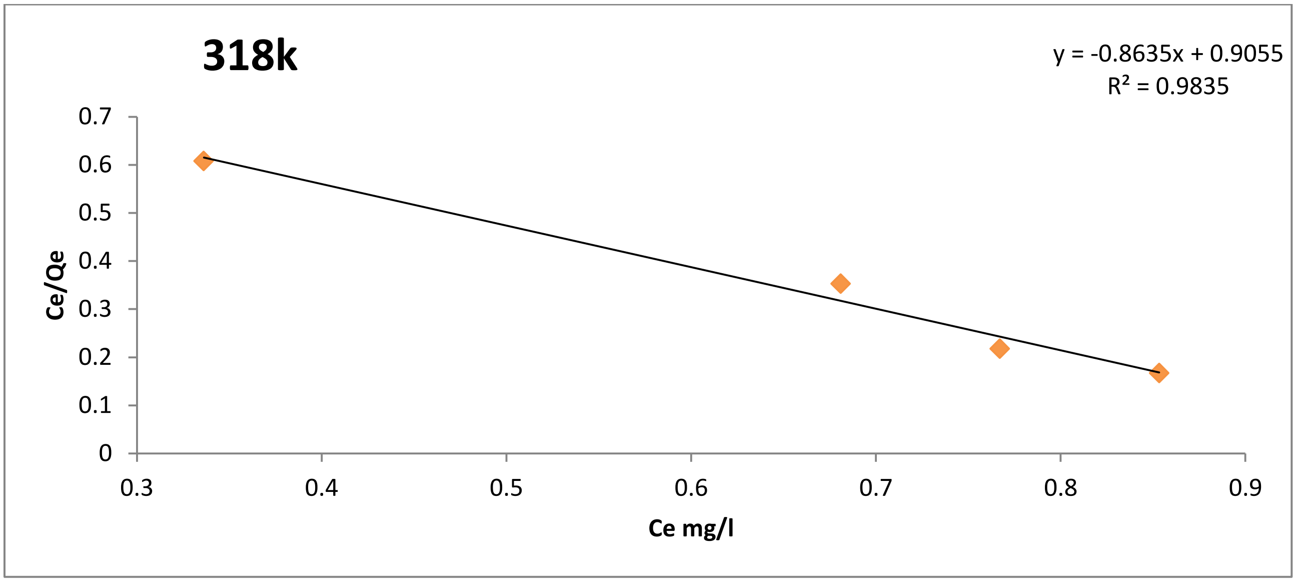
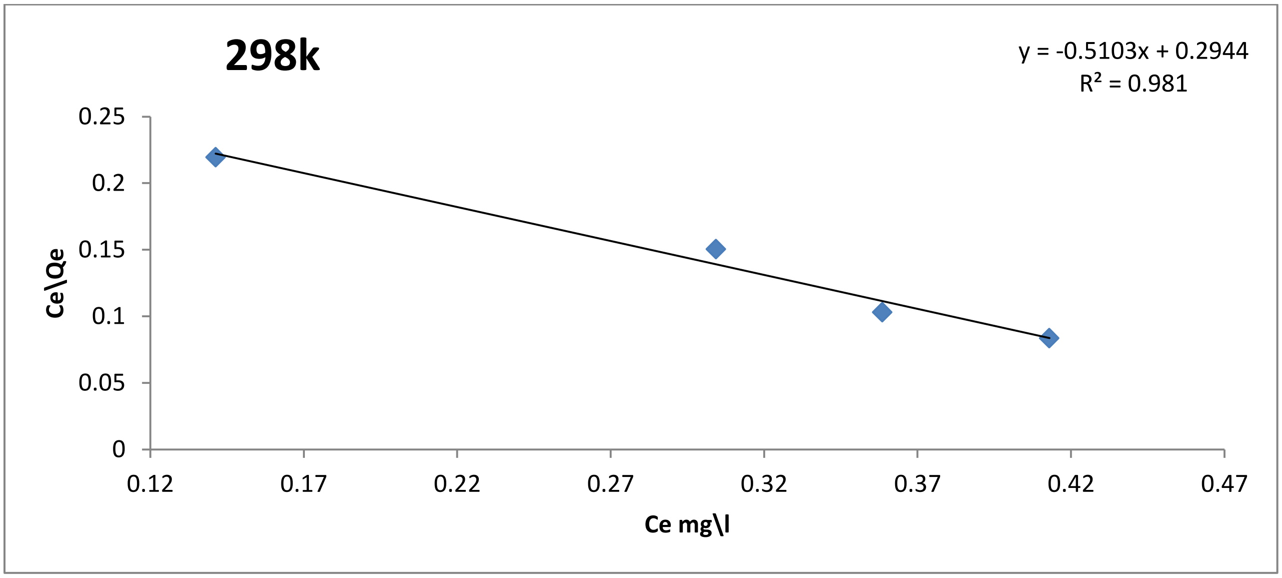
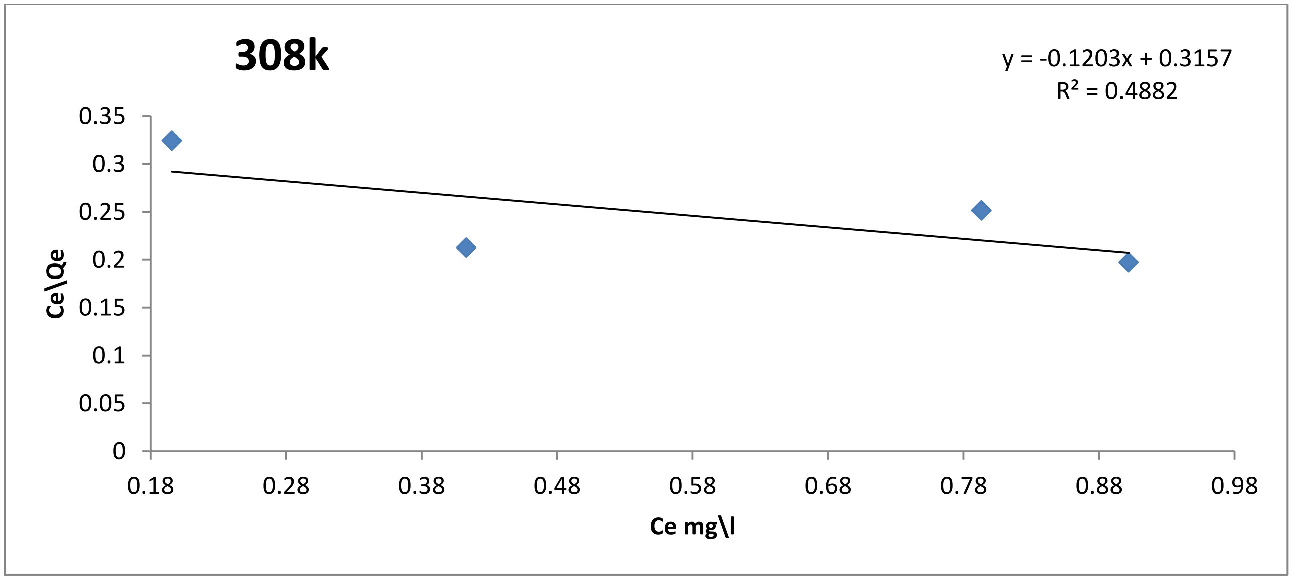


**Figure (3-15): Apply Langmuir equation on adsorption of Eosin yellow dye on the surface of graft co-polymer at298k,308k and 318K**

**Table (3-11): Adsorption of Wrights Stain dye on the surface of graft co-polymer at 298K,308K and 318K (by applying Langmuir equation)**

| **Conc PPm** | **T298** | | **T308** | | **T318** | |
|---|---|---|---|---|---|---|
| | Ce | Ce/Qe | Ce | Ce/Qe | Ce | Ce/Qe |
| **1** | 0.1413 | 0.2194 | 0.1956 | 0.3242 | 0.25 | 0.4444 |
| **3** | 0.3043 | 0.1505 | 0.513 | 0.2128 | 0.6847 | 0.3943 |
| **5** | 0.3586 | 0.1030 | 0.6934 | 0.2514 | 0.9021 | 0.2935 |
| **7** | 0.413 | 0.0835 | 0.9021 | 0.1972 | 0.9565 | 0.2110 |


298k
y = -0.5103x + 0.2944
R² = 0.981
0.25
0.2
0.15
0.1
0.05
0
Ce\Qe
0.12
0.17
0.22
0.27
0.32
0.37
0.42
0.47
Ce mg\l


308k
y = -0.1203x + 0.3157
R² = 0.4882
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Ce\Qe
0.18
0.28
0.38
0.48
0.58
0.68
0.78
0.88
0.98
Ce mg\l

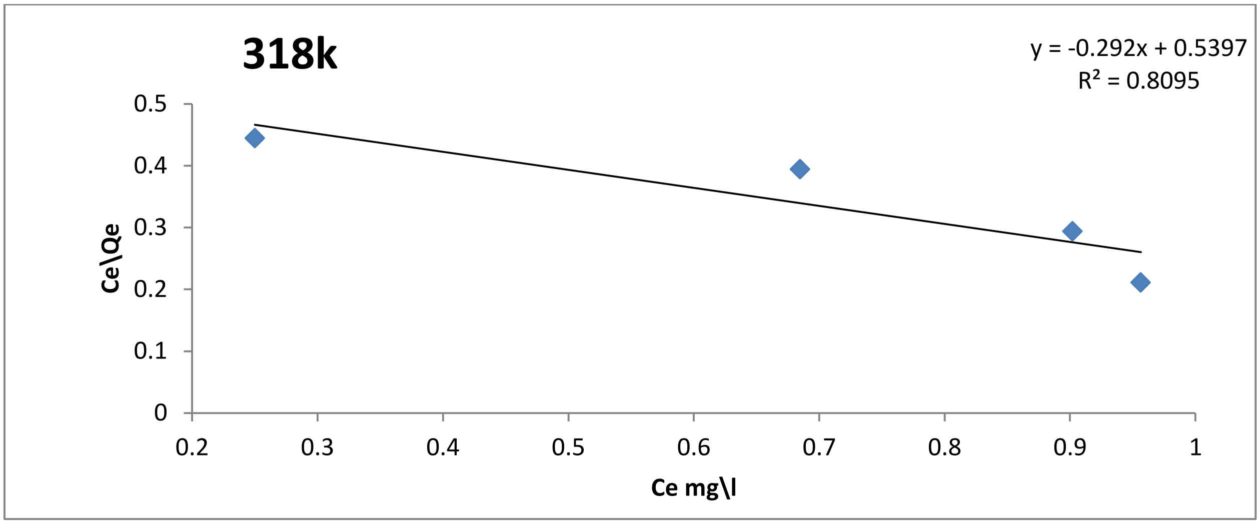
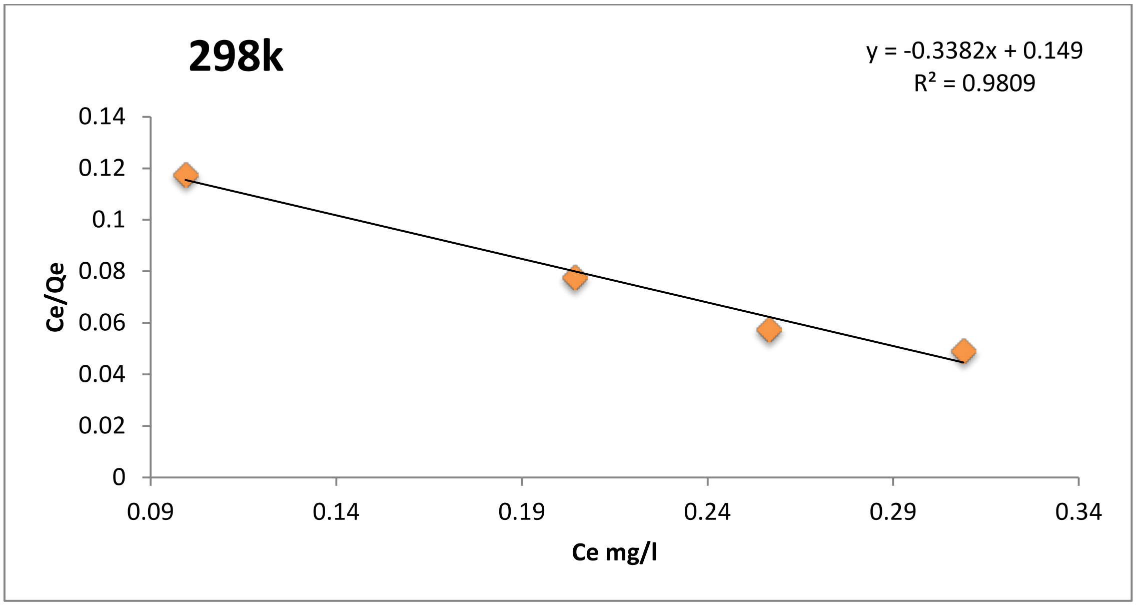
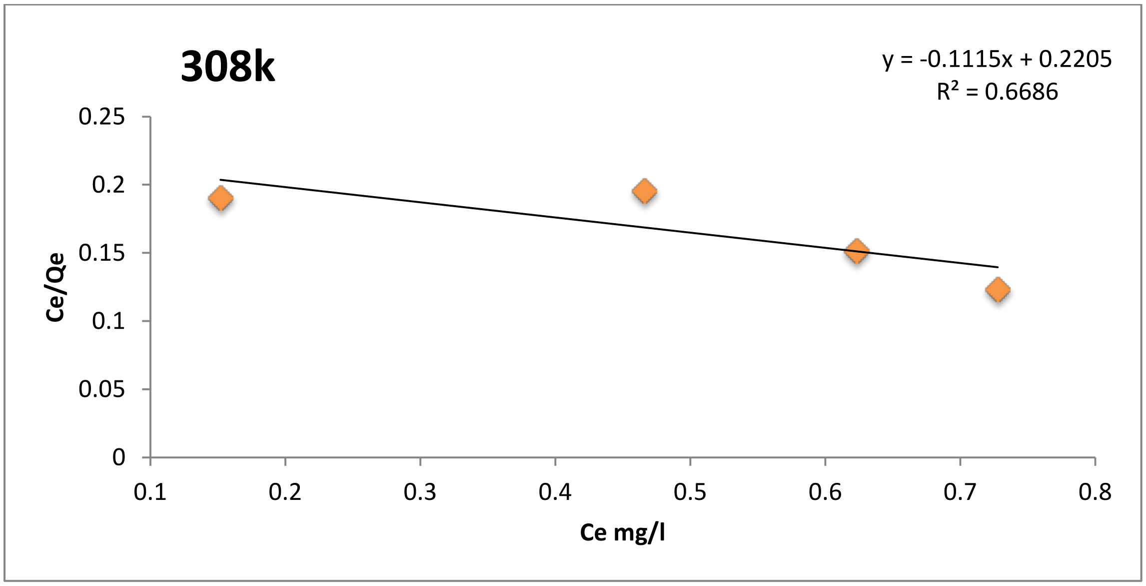


**Figure (3-16): Apply Langmuir equation on adsorption of Wrights Stain dye on the surface of graft co-polymer at298K,308K and 318K**

**Table (3-12): Adsorption of methyl orange dye on the surface of graft co-polymer at 298K,308K and 318K (by applying Langmuir equation)**

| **Conc PPm** | **T298** | | **T308** | | **T318** | |
|---|---|---|---|---|---|---|
| | Ce | Ce/Qe | Ce | Ce/Qe | Ce | Ce/Qe |
| **1** | 0.0994 | 0.1177 | 0.1818 | 0.1909 | 0.2565 | 0.3680 |
| **3** | 0.2041 | 0.0778 | 0.4659 | 0.1961 | 0.6753 | 0.3098 |
| **5** | 0.2565 | 0.0576 | 0.623 | 0.1518 | 0.8848 | 0.2293 |
| **7** | 0.3089 | 0.0492 | 0.7277 | 0.1237 | 0.9895 | 4.5747 |


298k
y = -0.3382x + 0.149
R² = 0.9809
Ce/Qe
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0.09
0.14
0.19
0.24
0.29
0.34
Ce mg/l


308k
y = -0.1115x + 0.2205
R² = 0.6686
Ce/Qe
0.25
0.2
0.15
0.1
0.05
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Ce mg/l

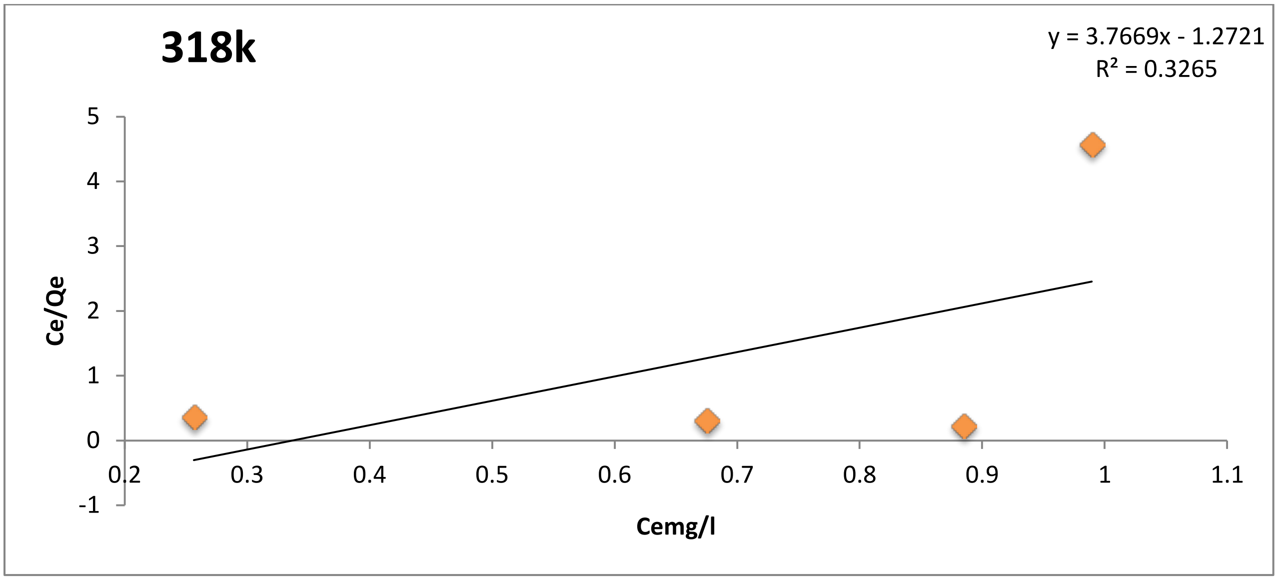


**Figure (3-17): Apply Langmuir equation on adsorption of methyl orange dye on the surface of graft co-polymer at298K,308K and 318K**

The adsorption data for Eosin yellow, Wrights Stain and methyl orange dyes were processed according to the linear relationship of the equation Temkin as shown in table (3-13),(3-14) and (3-15) for all dyes respectively and when drawing the relationship between ($Q_e$) values versus ($LnC_e$) We obtain a linear relationship as shown in figure (3-18),(3-19) and(3-20) according to the following equation[ 109] .

$Q_e$=B $LnA_T$+B $LnC_e$…………..(3-3).

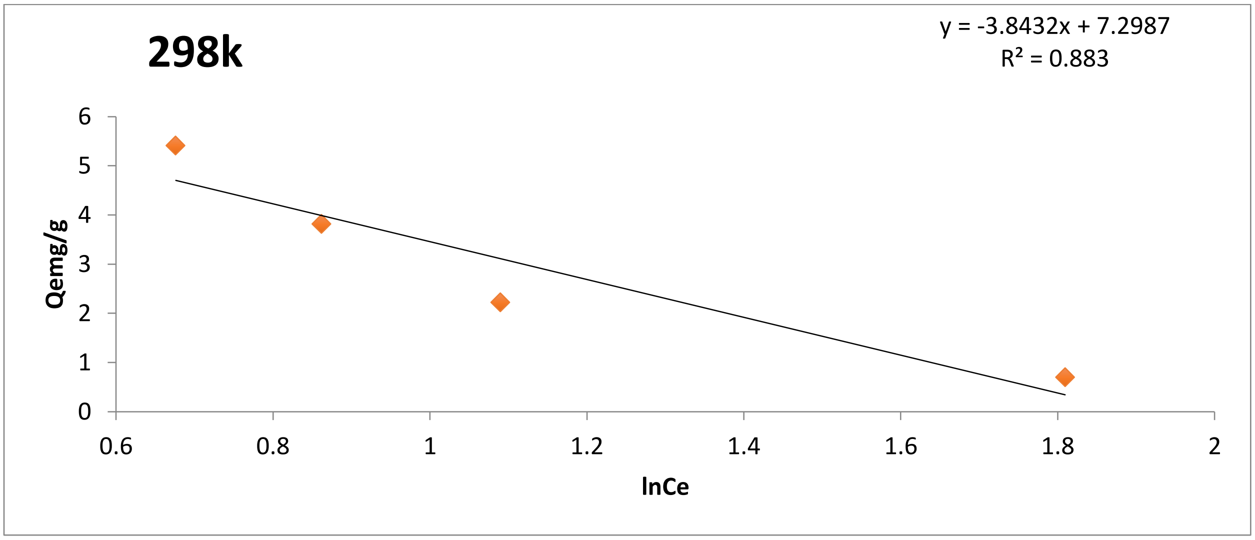
Qe: Adsorption capacity at equilibrium (mg / g).

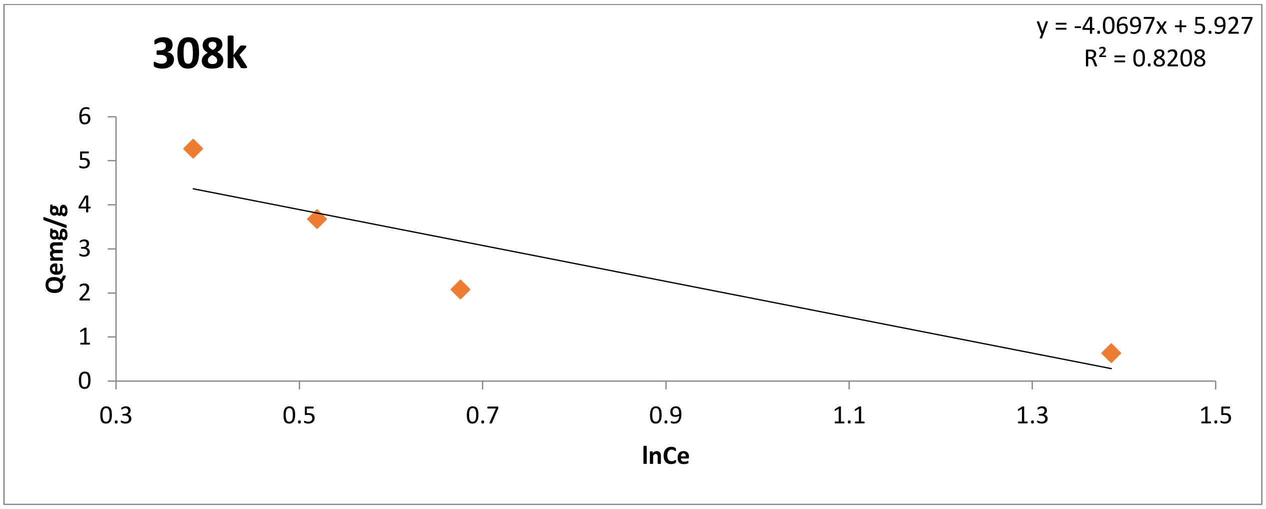
Ce: Concentration of solute at equilibrium in units (mg / L).

($A_T$,B) are Temkin constants: $A_T$ indicate equilibrium binding constant that corresponding to the maximum binding energy, while (B) is related to the heat of sorption.

**Table (3-13): Adsorption of Eosin yellow dye on the surface of graft co-polymer at 298K,308K and 318K (by applying Temkin equation)**

| Conc | 298K | | 308K | | 318K | |
|---|---|---|---|---|---|---|
| PPm | -LnCe | Qe | -LnCe | Qe | -LnCe | Qe |
| 1 | 1.8097 | 0.6969 | 1.3862 | 0.625 | 1.09 | 0.5531 |
| 3 | 1.09 | 2.2198 | 0.676 | 2.0761 | 0.3841 | 1.9325 |
| 5 | 0.8618 | 3.8146 | 0.5195 | 3.671 | 0.265 | 3.5273 |
| 7 | 0.676 | 5.4095 | 0.3841 | 5.2658 | 0.1585 | 5.1221 |





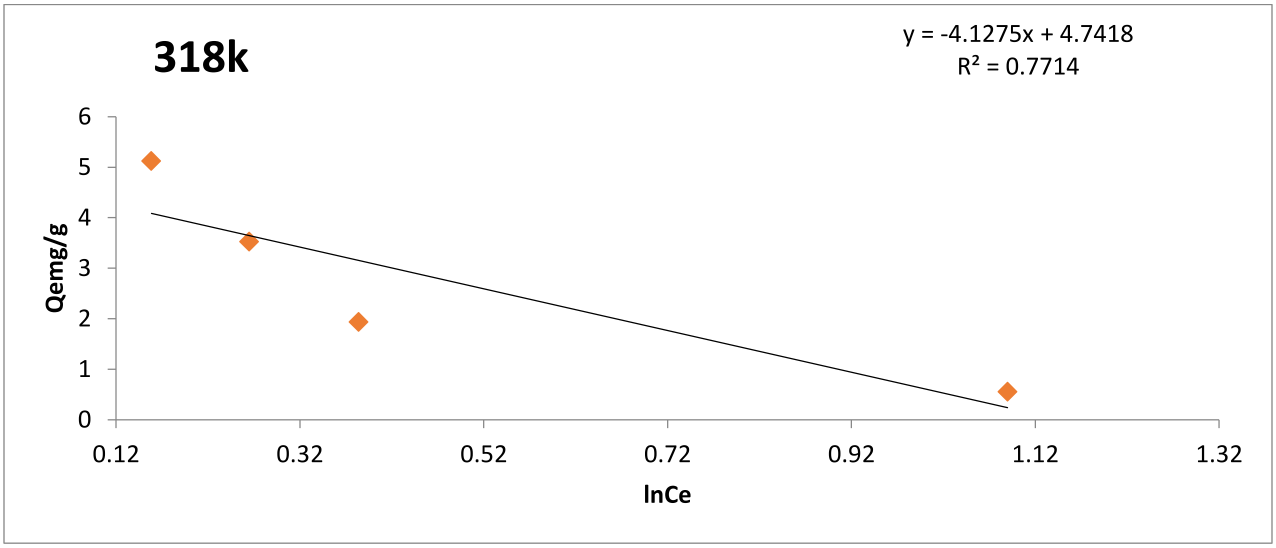
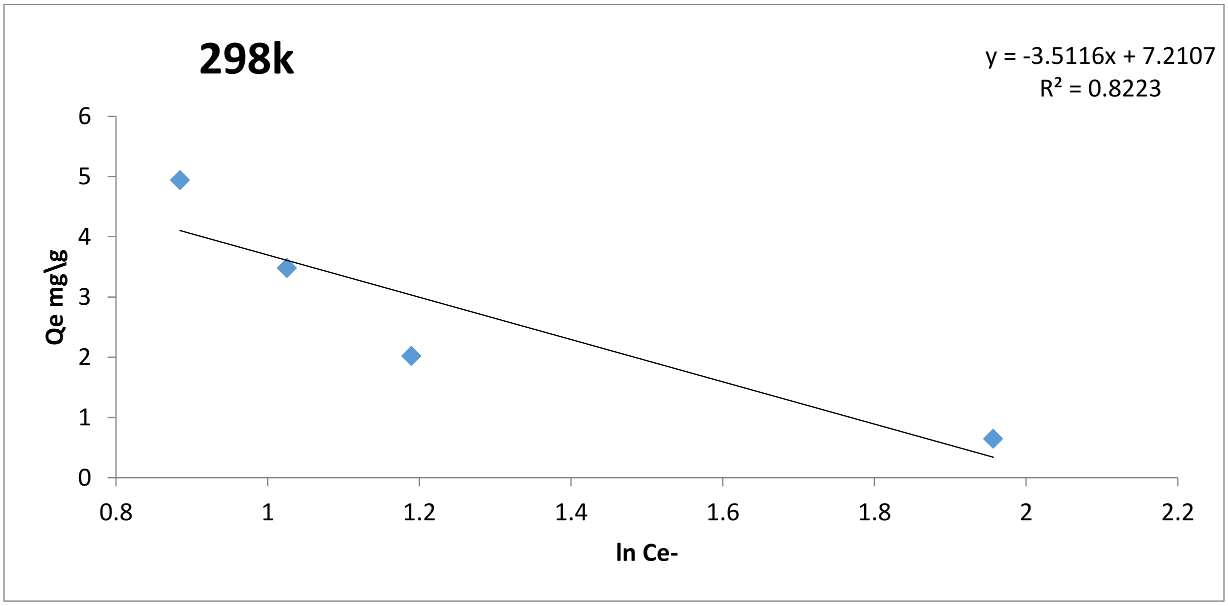
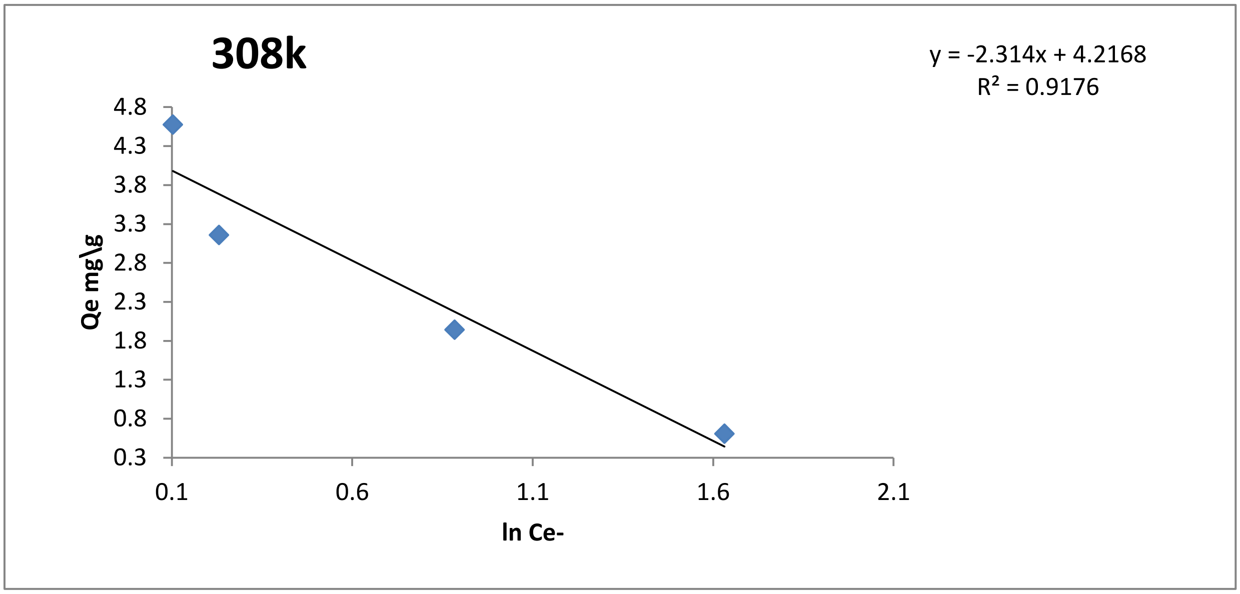


**Figure (3-18): Apply Temkin equation on adsorption of Eosin yellow dye on the surface of graft co-polymer at 298K,308K and 318K**

**Table (3-14): Adsorption of Wrights Stain dye on he surface of graft co-polymer at 298K,308K and 318K (by applying Temkin equation)**

| Conc. Ppm | 298K | | 308K | | 318K | |
|---|---|---|---|---|---|---|
| | -LnCe | Qe | -LnCe | Qe | -LnCe | Qe |
| **1** | 1.9568 | 0.6440 | 1.6316 | 0.6033 | 1.3862 | 0.5625 |
| **3** | 1.1897 | 2.0217 | 0.8843 | 1.9402 | 0.3787 | 1.7364 |
| **5** | 1.0255 | 3.4810 | 0.2314 | 3.1549 | 0.103 | 3.0734 |
| **7** | 0.8843 | 4.9402 | 0.103 | 4.5734 | 0.0444 | 4.5326 |





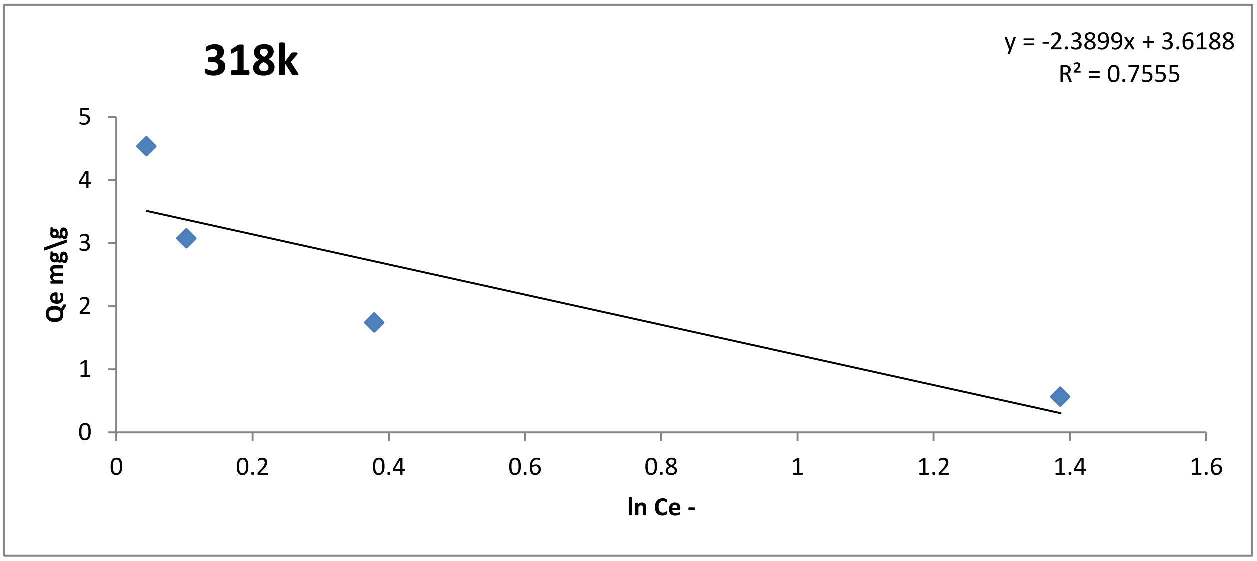
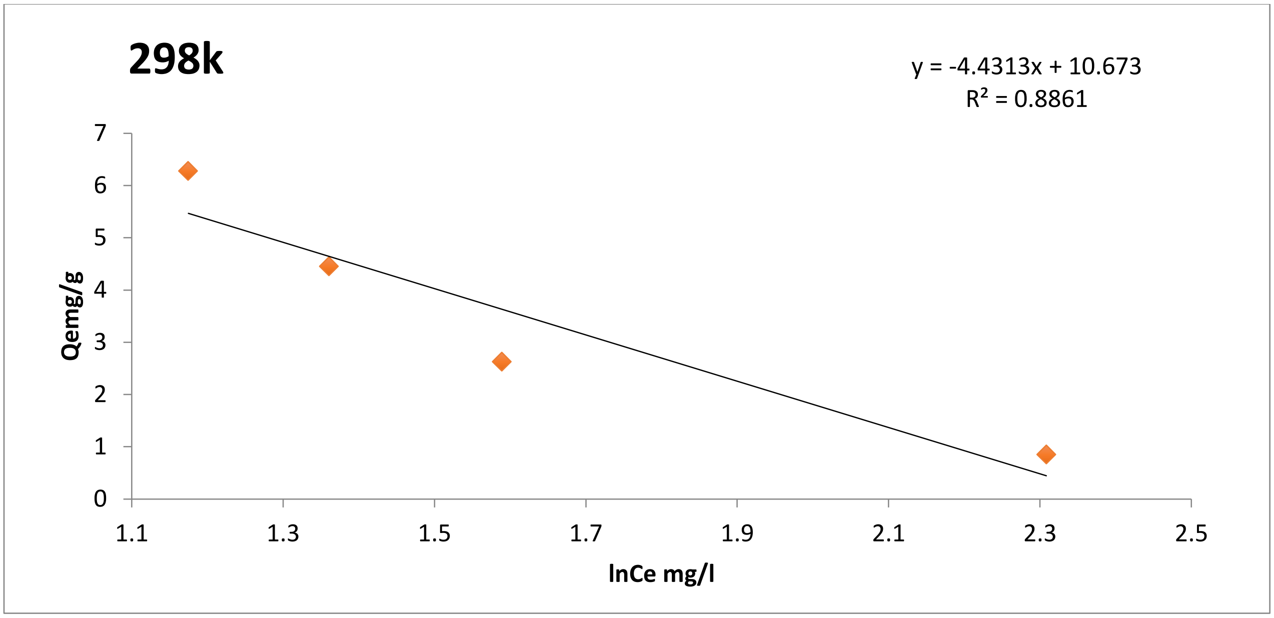
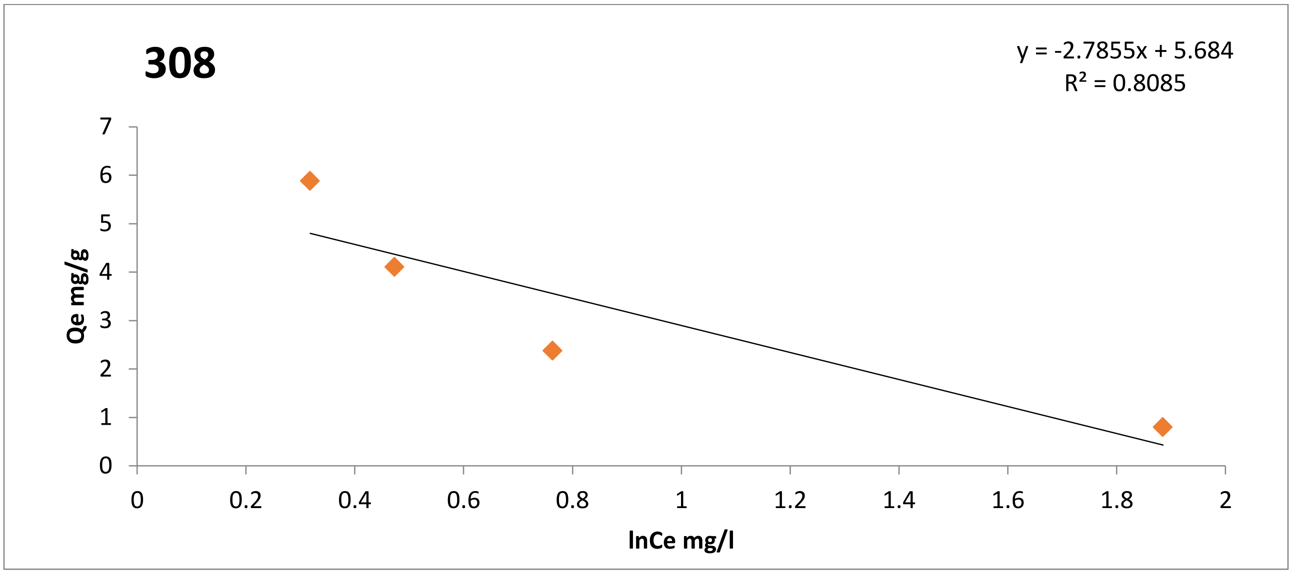


**Figure (3-19): Apply Temkin equation on adsorption of Wrights Stain dye on the surface of graft co-polymer at 298K,308K and 318K**

**Table (3-15): Adsorption of methyl orange dye on the surface of nano co-polymer at 298K,308K and 318K (by applying Temkin equation)**

| Conc. | 298K | | 308K | | 318K | |
|---|---|---|---|---|---|---|
| | -LnCe | Qe | -LnCe | Qe | -LnCe | Qe |
| 1 | 2.3086 | 0.8443 | 1.8851 | 0.7951 | 1.3606 | 0.6970 |
| 3 | 1.5891 | 2.6211 | 0.7637 | 2.3757 | 0.3925 | 2.1794 |
| 5 | 1.3606 | 4.4470 | 0.4732 | 4.1034 | 0.1223 | 3.858 |
| 7 | 1.1747 | 6.2729 | 0.3178 | 5.8802 | 0.0105 | 5.6348 |





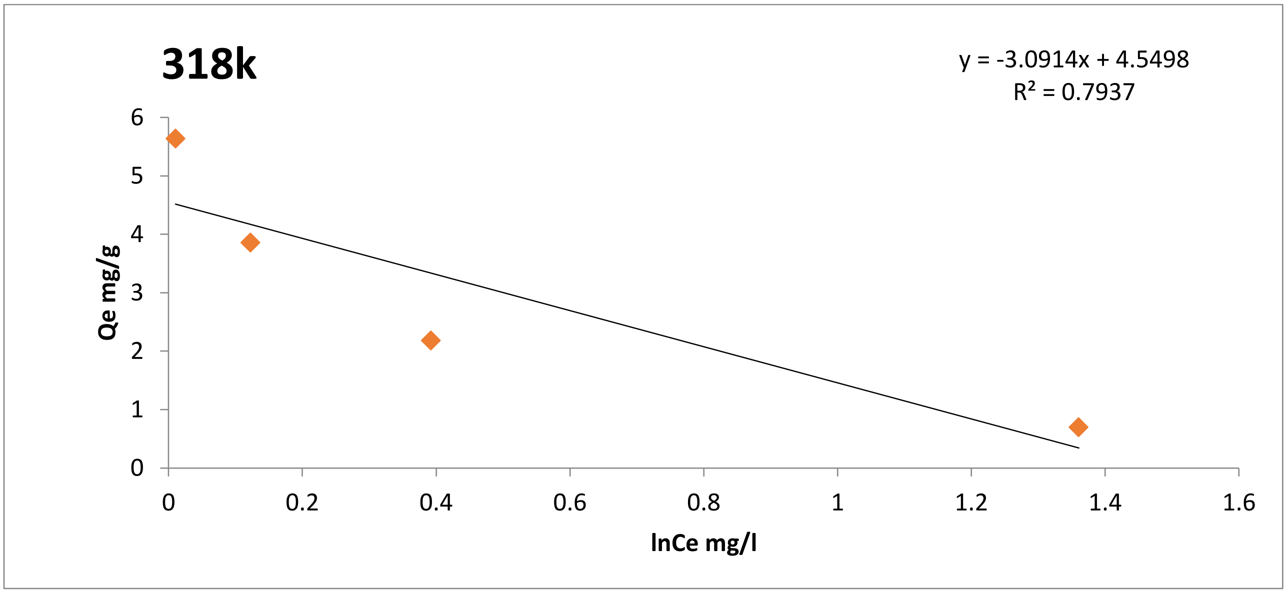


**Figure (3-20): Apply Temkin equation on adsorption of methyl orange dye on the surface of graft co-polymer at 298K,308 K and 318K**

The experimental Friendlash, Langmuir and Temkin constants and the correlation coefficient were calculated from the data of these lines for Eosin yellow, Wrights Stain and methyl orange table (3-16).

**Table (3-16): shows the values of the Friendelch , Langmuir and Temkin constants via the adsorption of Eosin yellow, Wrights Stain and methyl orange dye on the surface of the graft co-polymer**

| | **Eosin yellow** | | | **Wrights Stain** | | | **methyl orange** | | |
|---|---|---|---|---|---|---|---|---|---|
| **Friendiash Transaction** | | | | | | | | | |
| **T(K)** | **-N** | **$K_f$** | **$R^2$** | **-N** | **$K_f$** | **$R^2$** | **-N** | **$K_f$** | **$R^2$** |
| 298 | 0.9941 | 17.49444 | 0.9941 | 0.55577 | 22.17686 | 0.9735 | 0.56828 | 47.48946 | 0.9941 |
| 308 | 0.9761 | 10.34904 | 0.9761 | 0.48412 | 4.900044 | 0.9738 | 0.81433 | 7.91225 | 0.9687 |
| 318 | 0.9681 | 6.146105 | 0.9581 | 0.44096 | 3.788785 | 0.9494 | 0.67385 | 5.136887 | 0.967 |
| **Langmuir Transaction** | | | | | | | | | |
| **T(K)** | **-a** | **-b** | **$R^2$** | **-a** | **-b** | **$R^2$** | **-a** | **-b** | **$R^2$** |
| 298 | -2.3691 | -1.41312 | 0.9787 | -1.95963 | -1.73336 | 0.981 | -2.9568 | -2.2698 | 0.9809 |
| 308 | -1.5484 | -1.14809 | 0.9902 | -8.31255 | -0.38106 | 0.4882 | -8.9686 | -0.50567 | 0.6686 |
| 318 | -1.1580 | -0.95362 | 0.9835 | -3.42466 | -0.54104 | 0.8095 | -3.0627 | -0.25666 | 0.3265 |
| **Temkin Transaction** | | | | | | | | | |
| **T (K)** | **-B** | **$A_T$** | **$R^2$** | **-B** | **$A_T$** | **$R^2$** | **-B** | **$-A_T$** | **$R^2$** |
| 298 | 0.3453 | 3.3608 | 0.883 | 0.7015 | 4.1652 | 0.8223 | 0.6689 | 3.0288 | 0.8861 |
| 308 | 0.5261 | 3.4360 | 0.8208 | 0.4720 | 4.6604 | 0.9176 | 0.5391 | 3.4993 | 0.8085 |
| 318 | 0.7221 | 3.3827 | 0.7714 | 0.3667 | 4.2320 | 0.7555 | 0.4346 | 2.6401 | 0.7937 |

Table (3-16) shows that the values of the constant $K_f$ in the Frendelsch equation are an approximate indicator of adsorption capacity, and n indicates the intensity of adsorption, which are constants that include all the factors affecting the adsorption process.

The values of the constant,a of the Langmuir equation, represent a constant related to the maximum adsorption capacity, and the higher the value of the adsorption capacity the better. The values of the constant b are related to the adsorption energy. ($A_T$,B) are Temkin constants: AT indicate equilibrium binding constant that corresponding to the maximum binding energy, while (B) is related to the heat of sorption.

## 3.4 The effect of temperature on adsorption on the surface of the nano co-polymer

The effect of temperature on adsorption of Eosin yellow, Wrights Stain and methyl orange dyes dye on the surface of the graft co-polymer was studied, and within the experimental heat range (298,308,318 K) [113] , as shown in table (3-17), (3-18) and (3-19) and figure (3-21),(3-22) and (3-23) for Eosin yellow, Wrights Stain and methyl orange dyes respectively, which show adsorption isotherms assigned at these temperatures.

The adsorption of the Eosin yellow, Wrights Stain and methyl orangedyes dye results on the surface of the nano co-polymer showed that it decreased with increasing temperature, meaning that the process is of the exothermic process [111] Any physical adsorption (need slow temperatures) .

**Table (3-17): Effect of temperature on adsorption of Eosin yellow dye**

| Conc(ppm) | 298k | | 308k | | 318k | |
|---|---|---|---|---|---|---|
| | Ce mg/L | Qe mg/g | Ce mg/L | Qe mg/g | Ce mg/L | Qe mg/g |
| **1** | 0.1637 | 0.6969 | 0.25 | 0.625 | 0.3362 | 0.5531 |
| **3** | 0.3362 | 2.2198 | 0.5086 | 2.0761 | 0.681 | 1.9325 |
| **5** | 0.4224 | 3.8146 | 0.5948 | 3.671 | 0.7672 | 3.5273 |
| **7** | 0.5086 | 5.4095 | 0.681 | 5.2658 | 0.8534 | 5.1221 |

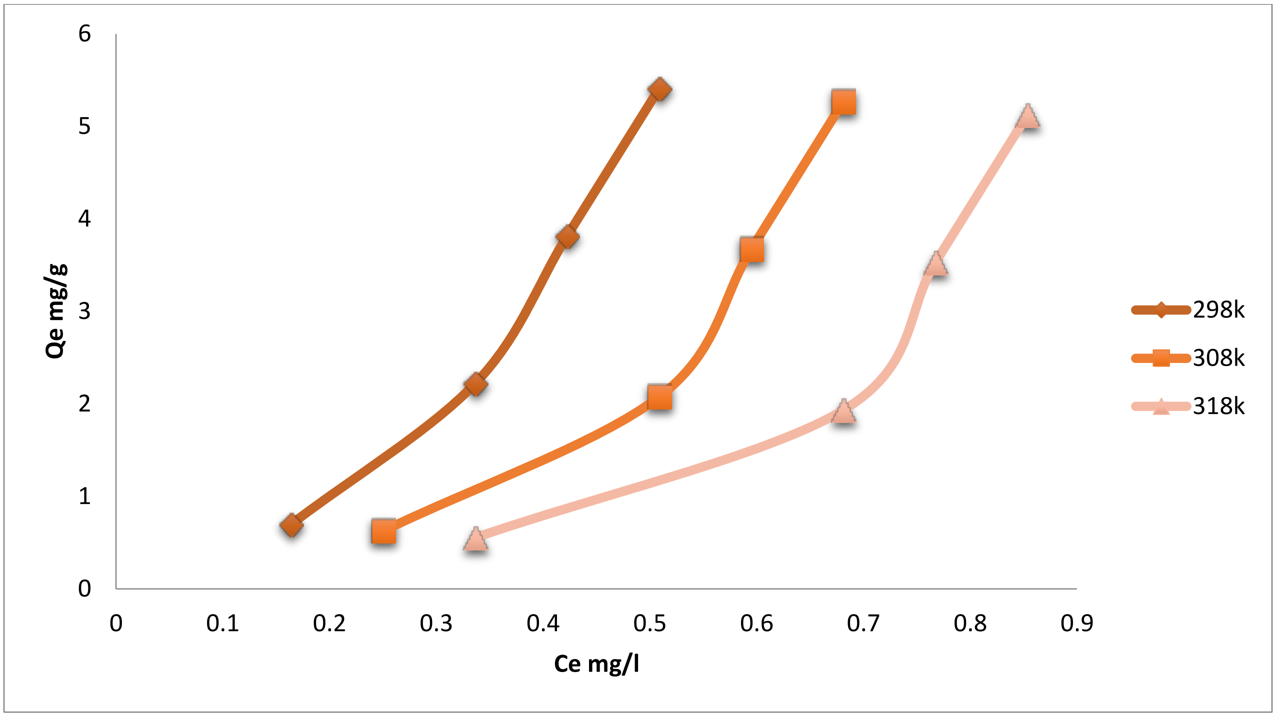


**Figure (3-21): Effect of temperature on adsorption of graft co-polymer at (1, 3 ,5and 7ppm) of Eosin yellow**

**Table (3-18): Effect of temperature on adsorption of Wrights Stain**

| Conc(ppm) | 298k | | 308k | | 318k | |
|---|---|---|---|---|---|---|
| | Ce mg/L | Qe mg/g | Ce mg/L | Qe mg/g | Ce mg/L | Qe mg/g |
| **1** | 0.1413 | 0.6440 | 0.1956 | 0.6033 | 0.25 | 0.5625 |
| **3** | 0.3043 | 2.0217 | 0.513 | 1.9402 | 0.6847 | 1.7364 |
| **5** | 0.3586 | 3.4810 | 0.6934 | 3.1549 | 0.9021 | 3.0734 |
| **7** | 0.413 | 4.9402 | 0.9021 | 4.5734 | 0.9565 | 4.5326 |

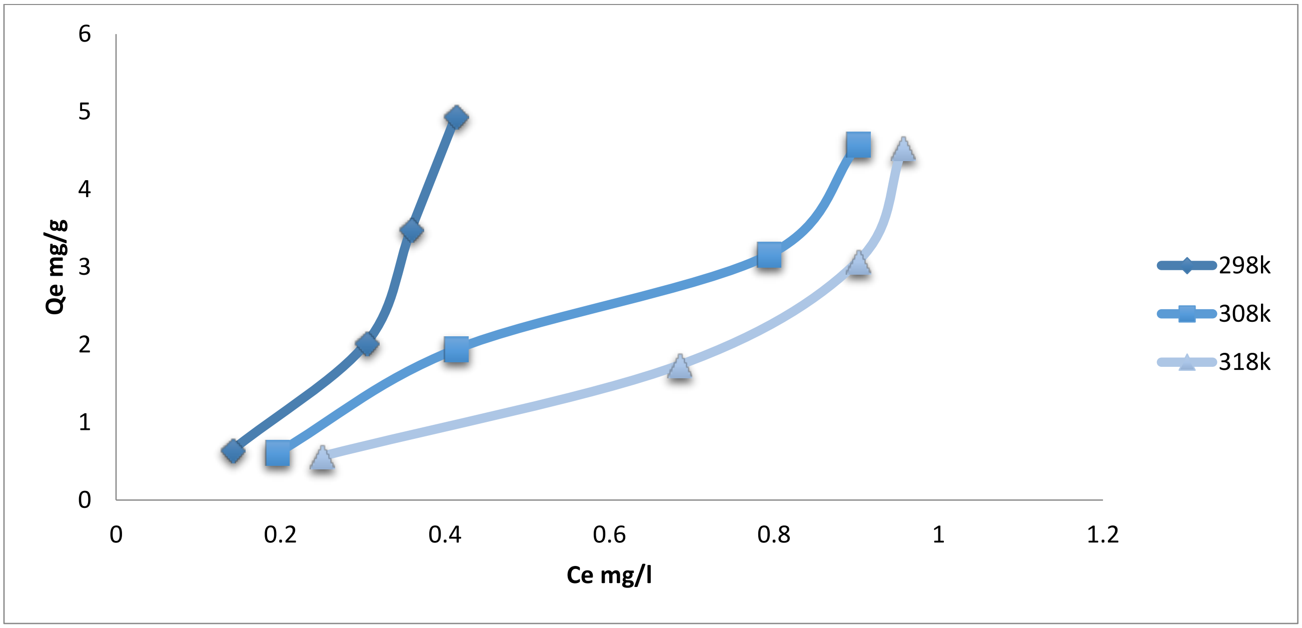


**Figure (3-22): Effect of temperature on adsorption of graft co-polymer at (1, 3 ,5and 7ppm) of Wrights Stain.dye**

**Table (3-19): Effect of temperature on adsorption of methyl orange dye**

| 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 | 0.1818 | 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 |

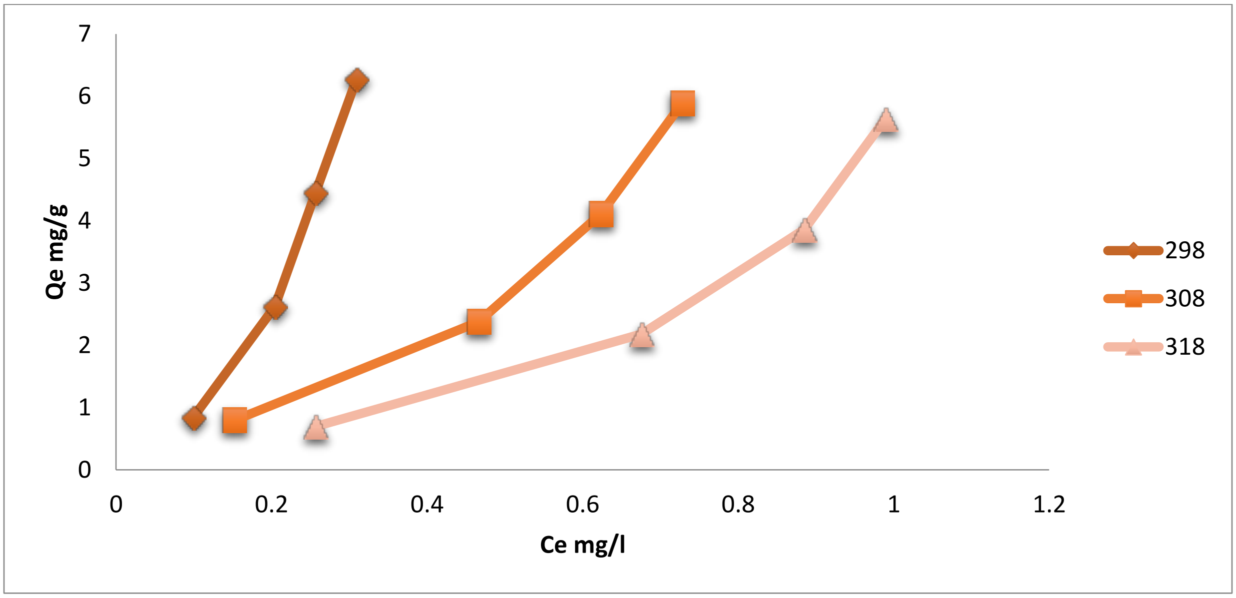


**Figure (3-23): Effect of temperature on adsorption of graft co-polymer at (1, 3 ,5 and 7ppm) of methyl orange dye**

The results showed the percentage of removal of . decreased with increasing temperature, That is, by increasing the temperature, the amount of the adsorbate

material on the surface of the graft co-polymer decreases, i.e. the occurrence of an desorption process on the adsorbent surface when the temperature increases, that is, the speed of the particles diffusion on the surface of the graft co-polymer decreases, and therefore the percentage of removal will decrease when
the temperature is increased. as shown in table (3-20) and (3-21) (3-22)for Eosin yellow, Wrights Stain and methyl orangedyes respectively.

**(3-20) :shows the percentage of Eosin yellow removal due to the effect of temperature.**

| T(K) | Conc. ( ppm) | Re%= $\frac{C_o - Ce}{C_o}$ X 100% |
|---|---|---|
| **298** | **1** | 83.63 |
| | **3** | 88.7933 |
| | **5** | 91.552 |
| | **7** | 92.7342 |
| **308** | **1** | 75 |
| | **3** | 83.0466 |
| | **5** | 88.104 |
| | **7** | 90.2714 |
| **318** | **1** | 66.38 |
| | **3** | 77.3 |
| | **5** | 84.656 |
| | **7** | 87.8085 |

**Table (3-21) :shows the percentage of Wrights Stain removal due to the effect of temperature**

| T(K) | Conc. ( ppm) | Re%=$\frac{C_o - Ce}{C_o}$ X 100% |
|---|---|---|
| 298 | 1 | 85.87 |
| | 3 | 89.8566 |
| | 5 | 92.828 |
| | 7 | 94.1 |
| 308 | 1 | 80.44 |
| | 3 | 82.9 |
| | 5 | 86.132 |
| | 7 | 87.1128 |
| 318 | 1 | 75 |
| | 3 | 77.1766 |
| | 5 | 81.958 |
| | 7 | 86.3357 |

**Table (3-22) shows the percentage of, methyl orange dyes removal due to the effect of temperature**

| TK | Conc.<br>( ppm) | X 100% Re%=$\frac{C_o - Ce}{C_o}$ |
|---|---|---|
| 298 | 1 | 90.06 |
| | 3 | 93.1966 |
| | 5 | 94.87 |
| | 7 | 95.5871 |
| 308 | 1 | 81.82 |
| | 3 | 84.47 |
| | 5 | 87.54 |
| | 7 | 89.6042 |
| 318 | 1 | 74.35 |
| | 3 | 77.49 |
| | 5 | 82.304 |
| | 7 | 85.8642 |

## 3-5 Calculate the thermodynamic values of ΔH, ΔS, ΔG.

The thermodynamic values represented by the values of ΔS, ΔG, ΔH, were calculated, where the value of ΔH was calculated by drawing the relationship between Log Xm (versus the reciprocal of temperature (1 / T) and its value is shown in tables (3-23),(3-24)and (3-25) for Eosin yellow, Wrights Stain and methyl orange dyes dye on the surface of the graft co-polymer respectively, based on the Vant-Hoff-Arrhenius Equation [112]

$\text{Log } X_m = (-\Delta H / 2.303RT) + \text{Cons}$……(3-5)

Represent:-

Log Xm: Logarithm of greatest adsorbed quantity (mg / g)

R: general constant for gases.(80314 $\text{Jmol}^{-1}$)

T: temperature (K).

Cons. : Constant of the van der Hoff equation.

A linear relationship was obtained and from the slope of this relationship, as in figures (3-24), (3-25) and (3-26) the value of ΔH, was calculated, and the slope is equal to:

$\text{Slope} = -\Delta H / 2.303R$

The value of change in free energy (ΔG) was calculated from the following equation.

$\Delta G = - R\, T\, \text{Ln}\, (Q_e / C_e)$ ………(3-6)

When applying the Gibbs equation [113] . the values of the change are obtained by entropy) S (Δ whose value is listed in table ,(3-25) for the, Eosin yellow, Wrights Stain and methyl orange dyes ,respectively, and the equation is:

**$\Delta G = \Delta H - T\Delta S$ …………(3-7)**

**Table (3-23): shows the values of 1 / T, Log Xm of Eosin yellow on the surface of the graft co-polymer within the experimental heat range (298,308,318 K)**

| Temp(K) | Xm (mg/g) | K -1 1/T×10-3 | LogXm |
|---|---|---|---|
| **298** | 5.4095 | 3.3557 | 0.7331 |
| **308** | 5.2658 | 3.2467 | 0.7214 |
| **318** | 5.1221 | 3.1446 | 0.7094 |

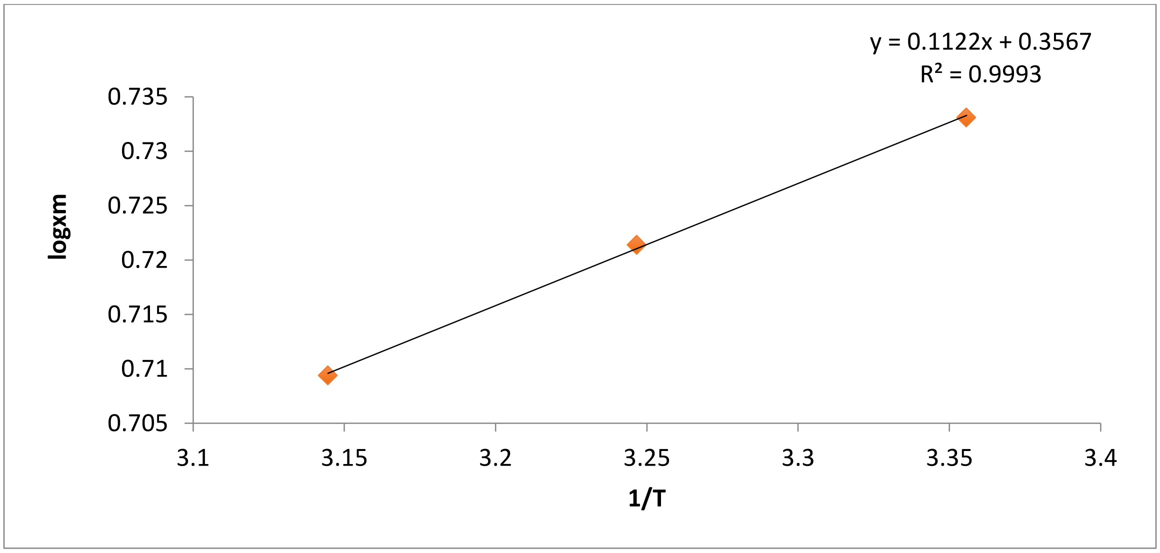


**Figure (3-24): shows a graph between the logarithm of the highest value in the reciprocal of the temperature of the Eosin yellow dye**

**Table (3-24): shows the values of 1 / T, Log Xm of Wrights Stain on the surface of the graft co-polymer within the experimental heat range (298,308,318 K)**

| T(K) | Xm(mg/g) | $1/T\times10^{-3}$ $K^{-1}$ | LogXm |
|---|---|---|---|
| **298** | 32935 | 3.3557 | 4.5176 |
| **308** | 30489.5 | 3.2467 | 4.4841 |
| **318** | 30217.5 | 3.1446 | 4.4802 |

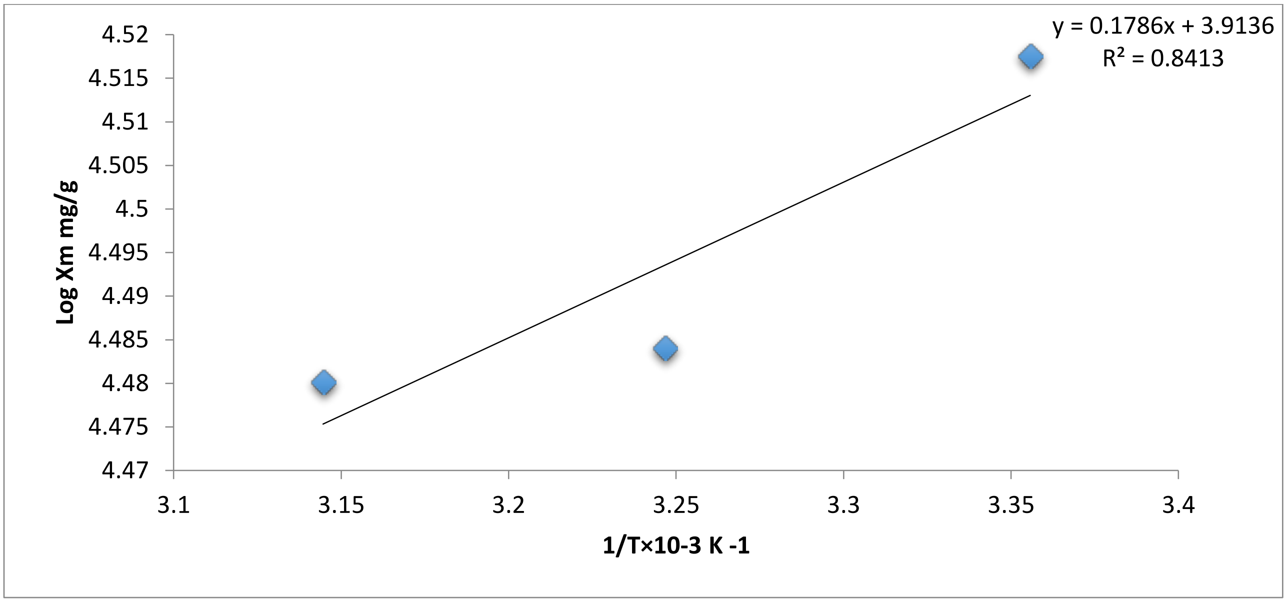


**Figure ( 3-25): shows a graph between the logarithm of the highest value in the reciprocal of the temperature of the Wrights Stain dye**

**Table (3-25): shows the values of 1 / Tand Log Xm of methyl orange on the surface of the graft co-polymer within the experimental heat range (298,308,318K)**

| Temp(k) | Xm | 1/T | LogXm |
|---|---|---|---|
| **298** | 41819.375 | 3.3557 | 4.6213 |
| **308** | 39201.875 | 3.2467 | 4.5933 |
| **318** | 37565.625 | 3.1446 | 4.5747 |

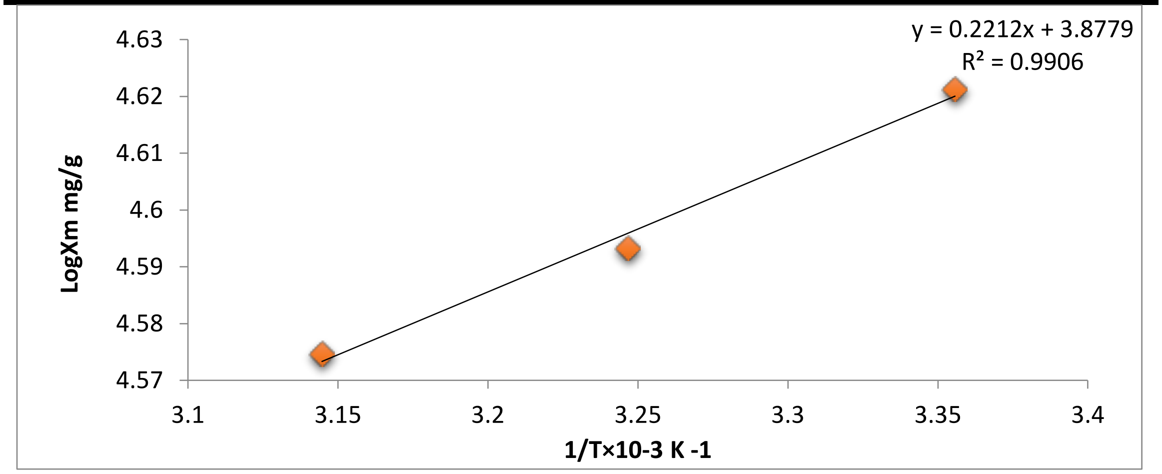


**Figure ( 3-26) shows a graph between the logarithm of the highest value in the reciprocal of the temperature of the methyl orange dye**

**Table (3-26): shows the values of the thermodynamic functions ΔH,ΔG, and ΔS to remove Eosin yellow, Wrights Stain and methyl orange dyes on the surface of the graft co-polymer at different temperature**

| Name s 'Dye | T(K). | ΔH KJ /mol.K | ΔG KJ/mol | ΔS J/mol |
|---|---|---|---|---|
| **Eosin yellow** | 298 | -2148.3 | -5857.4 | 12.446 |
| | 308 | | -5067.6 | 9.4785 |
| | 318 | | -4439.8 | 7.2059 |
| **Wrights Stain** | 298 | -3419.6 | -6148.5 | 9.1573 |
| | 308 | | -4021.5 | 1.9542 |
| | 318 | | -3852.6 | 1.3616 |
| **methyl orange** | 298 | -4063.0 | -7459.7 | 11.3983 |
| | 308 | | -5410.5 | 4.375 |
| | 318 | | -4301.7 | 0.7506 |

The results of adsorption of both the Eosin yellow, Wrights Stain and methyl orange and dispersion red dye showed that the (ΔH) values are negative, this indicates that the adsorption on the surface of the nano polymer is an exothermic reaction [118][117] The negative (ΔG) values indicate that the adsorption on the surface of the nano polymer is spontaneous, but if the values are positive, it indicates that the process is not spontaneous[119].

As for the negative (ΔS) values, it indicates that the adsorbed particles are irregular on the adsorbent surface, as a result of their binding to the surface. Whereas if the values are positive, then it is an indication that the adsorbed molecules are less regular when adsorption and absorption processes occur [121,120].

# Conclusion
# &
# Recommendation

# Conclusion

In light of the results and finding reached in the present work, it can be concluded that:

1- The grafted nano co-polymer resulting from the reaction of phthalic anhydride with glycerol was added, where the nano co-polymer was characterized by techniques (FT-IR, $^1$H-NMR, XRD, AFM and DSC,). The AFM results showed that the average particle size of the nano co-polymer is 22.04 nm, and this proves that the prepared co-polymer is in nanoscale.

2- The adsorption of dyes (Eosin yellow, Wrights Stain and methyl orange dyes) on the nano co-polymer was studied by changing the temperature and pH constant of the solution. The results showed that the adsorption of dyes (Eosin yellow, Wrights Stain and methyl orange dyes) decreases with increasing temperature.

# Recommendation

It is recommended that :

1. Determine the quantity of additional dyes that will adsorb using various polymers by other activities.

2. The use of polymers with nanoparticles as drug delivery methods.

3. Use of additional methods to clean up pollution in the air, water, and land.

4- Make use of different hydroxyl compounds to provide the carboxylic compounds more sites of linkage.

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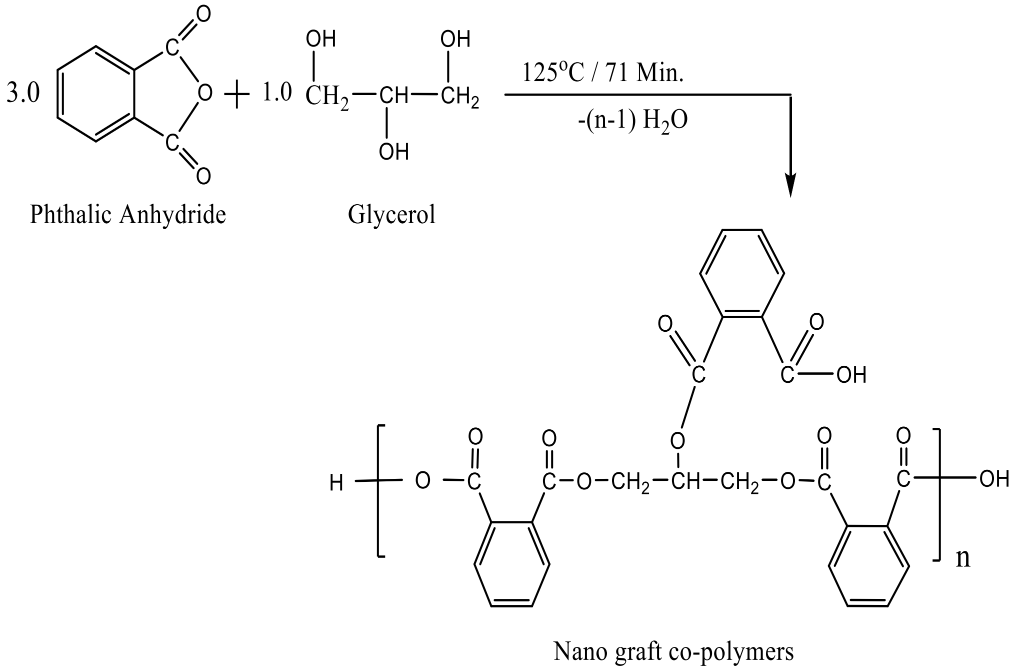
# الخلاصــة :

تم استخدام العمليات المطعمة لتحضير البوليمرات النانوية المشتركة وهي عملية الأسترة ؛ حيث يتم وصف طريقة التحضير كما هو موضح أدناه: تم تحضير البوليمر النانوي من تفاعل 3.0 مول من أنهيدريد الفثاليك مع 1.0 مول من الجلسرين



في هذه الرسالة ، التطعيم المطور من البوليمر النانوي عن طريق إسترة الجلسرين و أنهيدريد الفثاليك. تم استخدام تحليل حيود الأشعة السينية ، والمسعرات التفاضلية ، والفحص المجهري للقوة الذرية ، والتحليل الطيفي بالأشعة تحت الحمراء لتحليل بوليمر النانو (DSC). تم تحديد ما إذا كانت البوليمرات الاصطناعية ذات الميل النانوي يمكنها إزالة (المثيل اورنج , رايت ستين و ايوسين يلو) من المحاليل المائية. تمت دراسة تأثيرات ثلاثة تراكيز متميزة (1 ، 3 ، 5 ، 7 ppm) ودرجات الحرارة (298 ، 308 و 318 K) على

البوليمرات النانوية. كان متوسط ارتفاع البوليمر النانوي 22.04 نانومتر. أظهرت نتائج التجربة بوضوح أن البوليمرات النانوية الاصطناعية كانت جيدة جدًا في القضاء التام على صبغة (المثيل اورنج , رايت ستين و ايوسين يلو) من المحاليل المائية.

يتضح من الرسم أن الشكل العام حرارة الامتزاز هو من النوع (S1) وفقًا لتصنيف Giles). يشير هذا إلى أن سطح المادة الممتزة هو سطح غير متجانس أيضًا ، عندما يزداد الجزء المغطى من السطح الممتز ، تنخفض درجة حرارة الامتصاص. السطح في صفوف عمودية.

في هذا العمل تم استخدام معادلة فرندلش , لانكماير و تمكن وقد بينت النتائج تطابق العمل مع فرندلش

أظهرت النتائج نسبة الإزالة. تنخفض مع زيادة درجة الحرارة ، أي بزيادة درجة الحرارة ، تقل كمية المادة الممتزجة الموجودة على سطح البوليمر المشترك ، أي حدوث عملية امتزاز على سطح البوليمر عندما ترتفع درجة الحرارة ، أي سرعة انتشار الجسيمات على سطح البوليمر المشترك تنخفض ، وبالتالي فإن النسبة المئوية للإزالة ستنخفض عند زيادة درجة الحرارة.

جمهورية العراق
وزارة التعليم العالي و البحث العلمي
جامعة كربلاء
كلية التربية للعلوم الصرفة
قسم الكيمياء

# (إزالة بعض الأصباغ بطريقة الامتزاز باستخدام سطح نانو بوليمر جديد)

**هذه الرسالة مقدمة إلى**

مجلس كلية التربية للعلوم الصرفة - جامعة كربلاء ، كجزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

**من قبل**

**سمير كاظم بندر الزبيدي**

بكالوريوس كيمياء / جامعة القادسية ( 2014)

**إشراف**

**أ.د. محمد ناظم بهجت**

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