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Preparing Egg Shells in an Environmentally Friendly Way and Removing Methyl Orange Dye From the Aqueous Solution

Hani Kazem Hamza Hussein
Babylon University/ Collage of Science /Chemistry Department

Ghadeer Ali Hussein Ali Al-Shammari
University of Babylon/ College of Science/ Department of Chemistry

Ayat Rahim Kazar Harbi
University of Babylon/ College of Science / Women Department of Chemistry

Zainab Saleh Mahdi Mohammed
University of Basra/ College of Sciences/ Department of Chemistry

Fatima Saadi Fayyad Rawdan
Anbar University/ College of Science/Department of Chemistry

Abstract:

The auxiliary agent was prepared by taking eggshells and grinding them into a powder. It was used to remove the dye (Methyl orange) that contaminated the water (dissolves in water) as an assistant agent. The optimal conditions for the adsorption process were studied, starting from the equilibrium time, which was determined to be one hour. The optimal weight of the assistant agent was found to be 0.15 grams after measuring the maximum wavelength of the dye, which was 624 nm. A calibration curve was constructed using a range of concentrations (0.1500, 0.1, 0.05, 0.01), and the effect of temperature on the adsorption process was also investigated. Since adsorption is an exothermic process, an inverse relationship was observed with temperature. Different temperatures (10°C, 20°C, 30°C, 40°C, 50°C) were selected for the study.

General Introduction:

Methyl Orange:

Methyl Orange is an organic compound that belongs to the azo dye class. The dye consists of two different molecules: the first part is the colored molecule that bears the azo structure, and the second part is the methyl group (CH3) that is attached to the azo. The chemical formula of methyl orange is C14H14N3SO3Na.

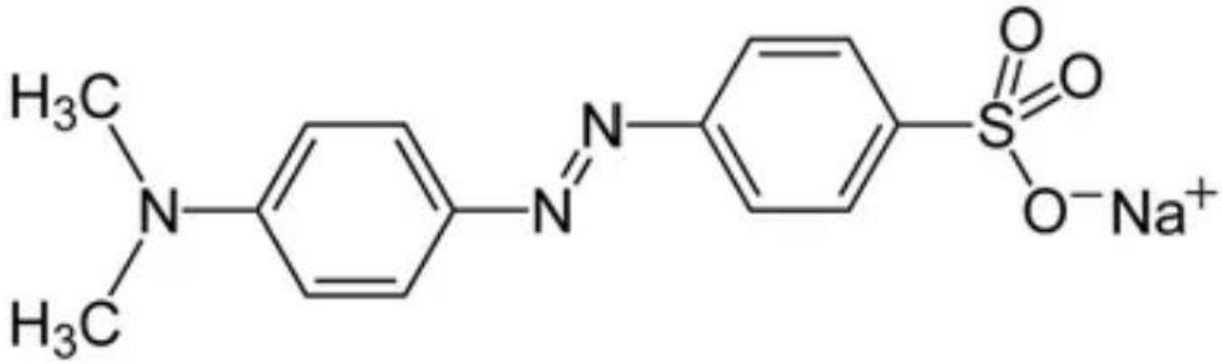


Figure 1: Structural formula of methyl orange dye

Methods for removing methyl orange dye

There are several methods for removing methyl orange dye from aqueous solutions:

- Adsorption: Activated carbon, clay minerals and other adsorbents can effectively remove methyl orange dye by adsorption. Simply mixing the adsorbent with the solution and then filtration or centrifugal sedimentation can separate the dye from the solution.
- Chemical precipitation: Chemicals such as calcium hydroxide or ferric chloride can be added to the solution, causing the methyl orange dye to precipitate. The precipitate can be analyzed and then separated by filtration.
- Photocatalytic degradation: Using photocatalysts such as titanium dioxide (TiO2) under ultraviolet light, methyl orange dye molecules can be decomposed into harmless by-products.
- Ion exchange: Ion exchange resins can remove methyl orange dye ions from the solution by exchanging them with other ions present in the resin.
- Biological treatment: Some microorganisms, such as some bacteria and fungi, are capable of degrading organic dyes such as methyl orange. Biological treatment methods can be effective for removing dyes on a large scale. The choice of method depends on factors such as the concentration of dye in the solution, available resources, and environmental considerations.

Benefits of Removing Methyl Orange Dye from Aqueous Solution:

Removing methyl orange dye from aqueous solutions has many benefits, including:

- Environmental protection: It contributes to reducing environmental pollution by removing harmful dye substances from water, which helps maintain the health of aquatic ecosystems.
- Improving water quality: It contributes to improving the quality of drinking water and water used in agriculture and industry, which protects public health and supports economic growth.
- Compliance with environmental legislation: It helps in complying with local and international environmental legislation and standards that set the permissible emission limits for organic pollutants in water.

- Saving natural resources: It reduces the need to use new water from natural sources, which contributes to providing water for life and industrial uses.
- Promoting sustainability: It contributes to improving the sustainability of water resources and maintaining the balance of ecosystems in the long term.

In short, removing methyl orange dye from polluted water is an important part of efforts to preserve the environment and public health, and contributes to building a more sustainable and healthy future for all.

Uses of Methyl Orange Dye:

Methyl orange dye is used in a variety of applications, including:

- Food industries: Methyl orange dye is used in the manufacture of food products such as beverages, sweets, and colored foods.
- Pharmaceutical industries: It is sometimes used as an indicator to measure pH in pharmaceutical industries.
- Chemical industries: It is used as an indicator to measure acidity in chemical laboratories and in chemical reaction processes.
- Textile industries: It is used in dyeing fabrics and textile fibers to give the desired color.
- Biological analysis: Methyl orange dye is used in acidity analysis in many biological and medical applications
- Scientific research: It is used as an indicator in scientific research and chemical and biological experiments.

Despite its many uses, methyl orange dye must be handled with caution due to its toxic and colorful properties, and it must be disposed of properly to avoid environmental pollution.

Adsorption:

Definition and classification:

Adsorption is defined as a phenomenon that collects extended molecules or their atoms or ions, called the extended substance (Adsorbate), on the surface of another substance, called the adsorbent (17), examples of which are porous clays and silica gel. The mechanism of adsorption goes through two stages. The first stage is the transfer of the adsorbed substance from the aqueous phase to active sites on the surface of the adsorbent. In the second stage, a chemical complex is formed. It is natural that the states of matter that have specific surfaces in space are the two states (liquid and solid), and therefore the areas of surface contact that lead to adsorption are liquid to liquid (solid to solid) (solid to liquid) (solid to gas). This method is the most widely used to remove pollutants that are present in low concentrations and that cannot be removed by traditional biological methods. The reason is that The phenomenon of adsorption is due to the presence of unsaturated force fields remaining due to the incomplete coordination or connection of a sufficient number of calculations on the particles on the surface particles, as is the case inside the liquid or solid phase, where adsorption leads to the saturation of the force fields on the surface, and therefore due to a decrease in the free energy values (AG) of the surface, the adsorption process occurs. The adsorption process is also accompanied by a decrease in the entropy value (SA) because the molecules that suffer adsorption are restricted due to their association with the atoms of the adsorbent surface, and therefore lose part of the degrees of freedom. There is a difference between the adsorption and absorption processes, as the opposite process to the adsorption process is the desorption process, and what happens in this process is the separation of the adsorbed molecules, atoms or ions from the adsorbent surface, and this requires returning the released energy to the system, while absorption is the process of transferring atoms or molecules from the liquid state to the solid state.

Types of adsorptions:

Chemical adsorption:

Chemical adsorption can be distinguished by the sharing of chemical bonds between gas molecules and adsorbent surface molecules. In addition, it results in a non-molecular layer and also includes the formation of a chemical compound on the solid surface called the surface compound and the exchange or sharing of electrons between the adsorbent surface and the adsorbent or adsorbed atom.

Characteristics of chemical adsorption:

- The specific process means that it will only occur if there is a chemical bond formation between the adsorbent and the adsorbent.
- It is an exothermic process and the process is accompanied by an increase in temperature.
- It occurs slowly at low temperature and occurs at a higher rate with increasing pressure.
- Chemical adsorption is directly proportional to the surface area and thus increases with increasing surface area.
- Since the process involves the formation of a chemical bond, the enthalpy is high.
- It requires a certain energy of activation.

Physical adsorption:

This type of adsorption occurs on the surface of some carrier materials such as activated carbon due to the saturation of its atoms electronically, as a result of the bonds that bind those atoms to the atoms adjacent to the material itself. Adsorption on such surfaces occurs through natural attractive forces or what are called van der Waals forces (3). This type of adsorption can be in the form of multiple layers of the adsorbed material on the surface of the adsorbent material when suitable conditions of pressure and temperature are available. We can distinguish this type of adsorption through the change in enthalpy (AH) the heat content that occurs during the association between the adsorbent material and the adsorbent material, which is estimated at less than (40kg/mole). Therefore, this type of adsorption does not require high temperatures or activation energy and occurs at temperatures and enthalpies similar to the process of condensation of vapors on the surfaces of liquid materials.

Characteristics of physical adsorption:

- Any gas can be absorbed on the surface.
- It is observed that highly fluid gases have greater physical adsorption.
- It is reversible in nature and depends on pressure as well as temperature. Increasing pressure reduces the volume of the gas and hence increases the adsorption of gas molecules. Conversely, decreasing pressure will remove gas molecules from the solid surface.
- Since the adsorption process is exothermic, physical adsorption occurs easily at low temperature and decreases with increasing temperature (Le-Chatelier).
- It does not require any specific energy for activation.

Adsorption Mechanism:

It is an exothermic process which means that energy is released during this process. The amount of heat that develops when one mole of adsorbent is adsorbed is known as enthalpy. The change in enthalpy indicates that it is negative, the reason is that when the adsorbed molecules are adsorbed on the surface, the freedom of movement of the molecules becomes restricted and this results in a decrease in entropy. At a constant temperature and pressure, adsorption occurs spontaneously.

Factors affecting adsorption:

- Temperature is an important factor affecting adsorption. Adsorption occurs better at low temperatures.
- Adsorption increases with increasing pressure to a certain extent until saturation is reached, after saturation no further adsorption is achieved regardless of the applied pressure.
- The relationship between the extent of adsorption and temperature at any constant pressure is called Isobar adsorption.
- Since adsorption is a surface phenomenon, the surface area will increase the rate of adsorption.
- Liquefied gases are easily adsorbed.

Applications of Adsorption:

- Gas masks used in coal mines are based on the principle of adsorption. These gas masks are used to absorb toxic gases. This makes the air clean for breathing.
- Noble gases can be separated by using coal as an adsorbent.
- Drug adsorption is used to kill germs.
- Chromatographic analysis is based on the phenomenon of adsorption.
- Adsorption also plays an important role in the paint industry. It should not contain dissolved gases, otherwise the paint will not adhere well to the surface to be painted and will therefore have poor covering power.
- The cleaning process of soaps and detergents is also caused by adsorption.

Freundlich equation:

In the Freundlich equation or adsorption isotherm, the adsorption isotherm, is the empirical relationship between the amount of gas adsorbed to a solid surface and the pressure of the gas. The same relationship is also applicable to the concentration of the solute adsorbed on a solid surface and the concentration of the solute in the liquid phase. In 1909, Herbert Freundlich gave an expression representing the isothermal variation of the adsorption of an amount of gas adsorbed by a unit mass of solid adsorbent at the pressure of the gas. [1] This equation is known as the Freundlich adsorption equation. Since this relationship is purely empirical, in the case where the adsorption behavior is properly fitted by an isotherm with a theoretical basis, it is usually convenient to use such isotherms instead (see for example the Langmuir and BET theories). The non-empirical Freundlich equation is also derived by attributing the change in the equilibrium constant of the binding process to the heterogeneity of the surface and the change in the heat of adsorption.

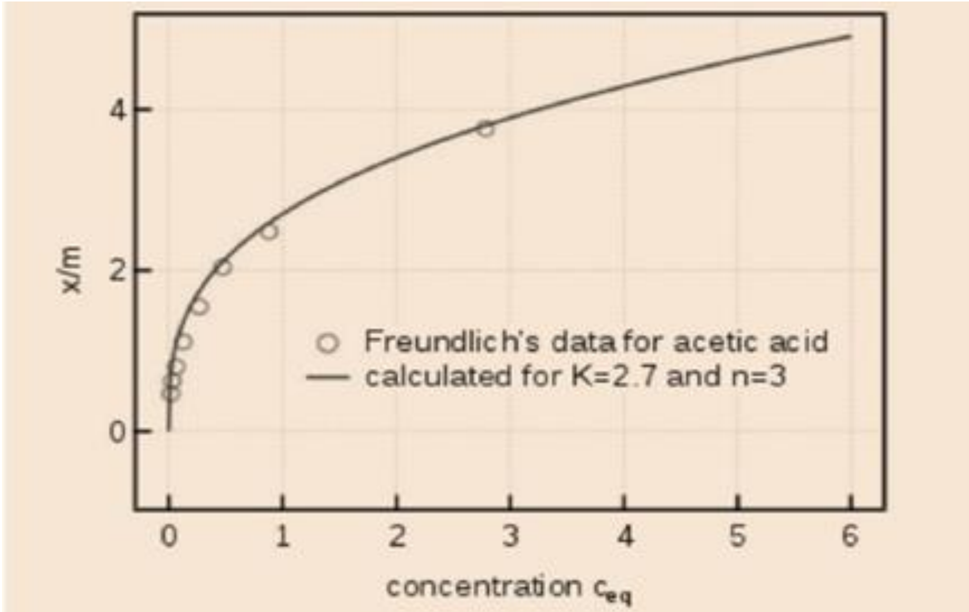


Figure 2: Freundlich adsorption isotherm.

The absorption isotherm is expressed mathematically as Freundlich:

$$\frac{x}{m} = Kp^{\frac{1}{n}}$$

It is also written as: $log\frac{x}{m} = log\, k + \frac{1}{n} log\, p$

or

$$\frac{x}{m} = kC^{\frac{1}{n}}$$

It is also written as:

$$log\frac{x}{m} = log\, k + \frac{1}{n} log\, p$$

Langmuir Equation

In the Langmuir adsorption model, adsorption is explained by assuming that the adsorbate behaves as an ideal gas under isostatic conditions. According to the model, adsorption and absorption are reversible processes. This model explains even the effect of pressure, i.e., in these conditions, the pressure of the adsorbate, , is related to its volume, V, at which it is adsorbed on a solid adsorbent. The adsorbent, as shown in the figure, is assumed to be an ideal solid surface consisting of a series of distinct sites capable of binding the adsorbate. Adsorbate binding is treated as a chemical interaction between a gaseous adsorbate molecule and the adsorbent site.

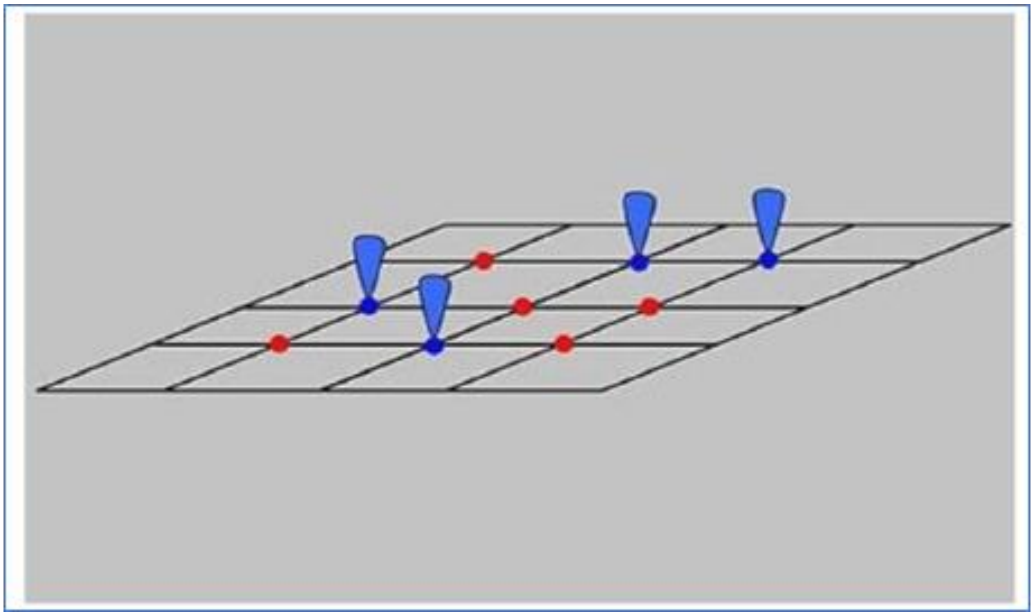


Figure 3: shows equivalent, occupied (blue) and unoccupied (red) sites to illustrate the basic assumptions used in the model. Adsorption sites (heavy points) are equivalent and can also occupy the unit, adsorbing does not move on the surface.

Langmuir equation: $\frac{c_e}{Qe} = \frac{c_e}{Q_{e\,max}} = \frac{1}{Q_{e\,max\,kl}}$

c_e: Amount of concentrations after adsorption mg/L.
Qe: Amount of adsorbed substance at equilibrium mg/g.
Q_(e max): Maximum adsorption amount at equilibrium.

Whereas

Nanotechnology

It is the science that is concerned with studying and processing very small matter in a molecular and material manner, and working to invent the latest advanced technologies and new means whose dimensions may be measured in what is called nanometers, which are very precise and very small dimensions compared to bacteria and living cells.

A nanometer is a unit of measurement that has been estimated as a part of a thousandth of a micrometer, which is a part of a thousandth of a millimeter, meaning that a nanometer is a part of a millionth of a millimeter, and this technology is concerned with the properties of materials on a wide scale despite the difference in its fields from semiconductors to inventing modern advanced methods that may depend on molecular assembly.

What is nanotechnology?

The tremendous technical development was the unique feature of the twentieth century that we bid farewell to a few years ago, and experts agreed that the most important technical development in the last half of the current century is the invention of silicon electronics or transistors and electronic laboratories, as their development led to the emergence of what is called microchips, which led to a technological revolution in all fields such as communications, computers, medicine, and others. Until 1950, there was only black and white television, and there were only ten computers in the entire world. There were no mobile phones, digital watches, or the Internet. All of these inventions are due to microchips, and the increasing demand for them led to a decrease in their prices, which facilitated their entry into the manufacture of all consumer electronics that surround us today. During the past few years, a new term has emerged that has weighed heavily on the world and has become the focus of great interest. This term is (nanotechnology). Many countries have tried, in their desire to conduct scientific research and special studies on this technology, and at the same time, many other countries have sought to establish many centers for scientific research and studies and universities that have been dedicated to nanotechnology. A group of distinguished experts and scientists with high competencies have been assigned to study this technology and attempt to develop it. This technology may face many difficulties due to the fragmentation of atoms and the difficulty of controlling all the materials they are composed of, as this requires more accurate devices in terms of size and methods of seeing molecules. This technology is used in many different fields such as agricultural, industrial, environmental and military fields.

Objective of the research:

- Preparation of an environmentally friendly catalyst for the purpose of breaking down the dye (methyl orange)
- Study the optimal conditions for the adsorption process from the best weight, equilibrium time and the effect of temperature.
- Study the kinetics of the adsorption reaction and identify its type, whether it follows the kinetics of the false first order or the false second order.

Devices and tools used:

- Mechanical shaker GEMMY Orbit Shaker
- Spectrophotometer UV-VISBLE Spectrophotometer
- Thermometer sensitive balance
- Shaking water bath

Glassware used:

- Beaker capacity 200 ml
- Volumetric bottles capacity 25 ml
- Watch bottle
- Glass funnel
- Graduated cylinder 25 ml
- Filter papers

Materials used:

- Eggshells
- Methyl orange dye
- Distilled water

How to work:

We take 1ml of Methyl orange dye at 10 ppm.

Dissolve 0.01gm of the dye in 100ml of distilled water.

Put the mixture in a glass beaker and place it in the vibrating device for an hour at a temperature of 25 °C.

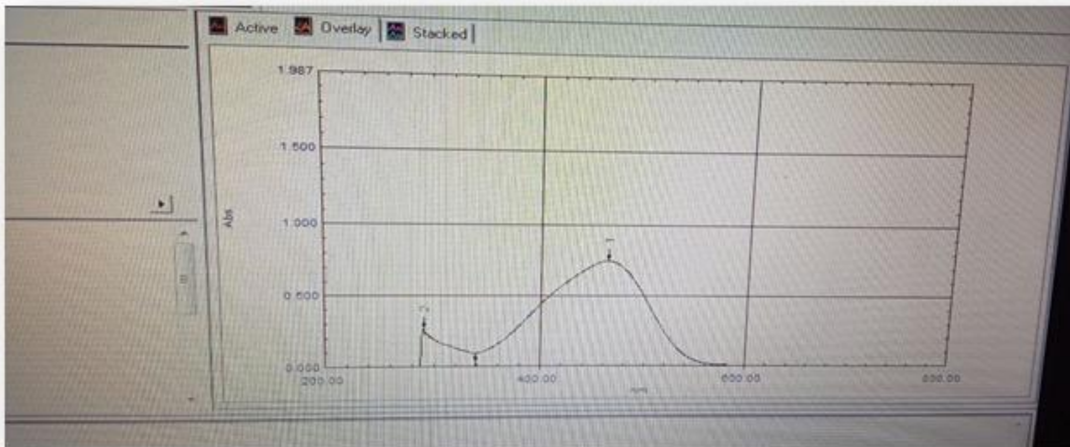
We take a reading every 10 minutes.

Filter the solution and take the filtrates while ignoring the precipitate and then read the absorbance.

Results and calculations:

To measure the highest wavelength A solution of ((methyl orange)) dye was prepared at a concentration of 10 ppm and mixed with a volumetric flask of distilled water and the maximum wavelength was calculated and the wavelength was between.(800 - 200)

It was found that the maximum wavelength λ_max=624nm.



To obtain the volumes of these concentrations, the dilution law was applied, where these concentrations were diluted to 25 ml of distilled water according to the dilution law:

$$M_1V_1 = M_2V_2$$

- ✓ $1 \times 25 = 10 \times V_2 \rightarrow V_2 = \frac{25}{10} = 2.5mL$
- ✓ $3 \times 25 = 10 \times V_2 \rightarrow V_2 = \frac{75}{10} = 7.5mL$
- ✓ $5 \times 25 = 10 \times V_2 \rightarrow V_2 = \frac{125}{10} = 12.5mL$
- ✓ $8 \times 25 = 10 \times V_2 \rightarrow V_2 = \frac{200}{10} = 20mL$

C	Abs.

1	0.032
3	0.066
5	0.079
8	0.151

Then we measure its absorbance as follows:

Measurement of the best weight

10ppm was taken and diluted with 100 ppm and four flasks were taken from it and 10 ml of the solution was added to each flask and diluted with 10 ml of distilled water and different weights of the auxiliary agent eggshells were added to it to obtain the best weight(0.15 ,0.05 ,0.001 ,0.1)

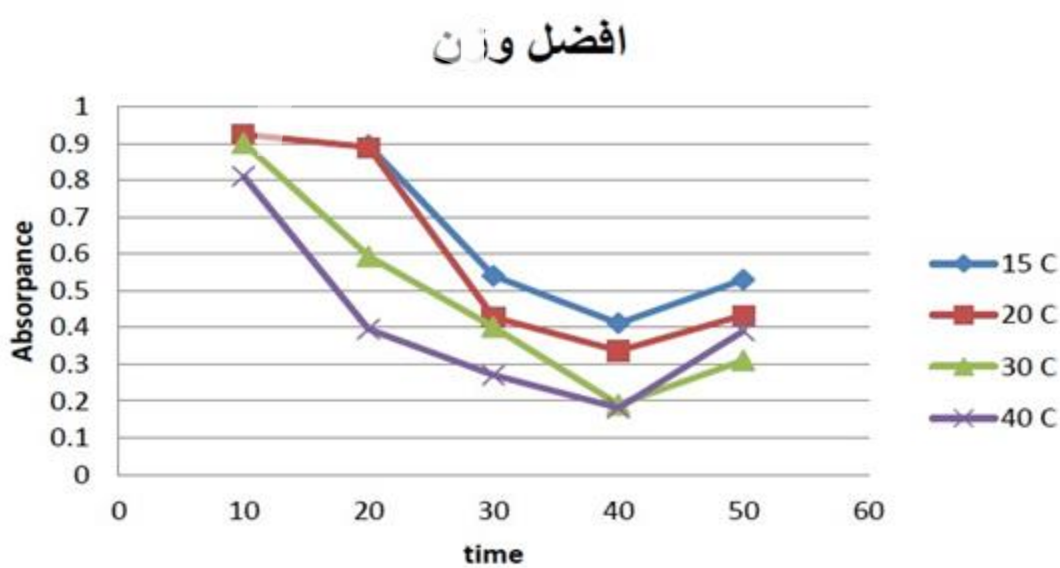
Then it was placed in a water bath with continuous withdrawal from it for every 10 of each weight

	Contact time
10	0.304
20	0.270
30	0.262
40	0.230
50	0.235
60	0.141

and then filtered to obtain the filtrate and neglected the sediment to measure the absorbance.

Min/wt	**0.01**	**0.05**	**0.1**	**0.15**
10	0.931	0.925	0.901	0.811
20	0.895	0.890	0.593	0.395
30	0.540	0.428	0.401	0.270
40	0.411	0.336	0.190	0.181
50	0.530	0.433	0.310	0.390

He found that the best weight is 0.15 at 40 degrees.



Measuring the best temperature:

1ppm of the dye was prepared in 100 ml of distilled water and added to four 200 ml volumetric flasks and the best weight of the catalyst, eggshells, was added to it, which is 0.15 gm.

$$M_1V_1 = M_2V_2$$

$$1ppm \times 100ml = 10ppm \times V2$$

$$V2 = 10ml$$

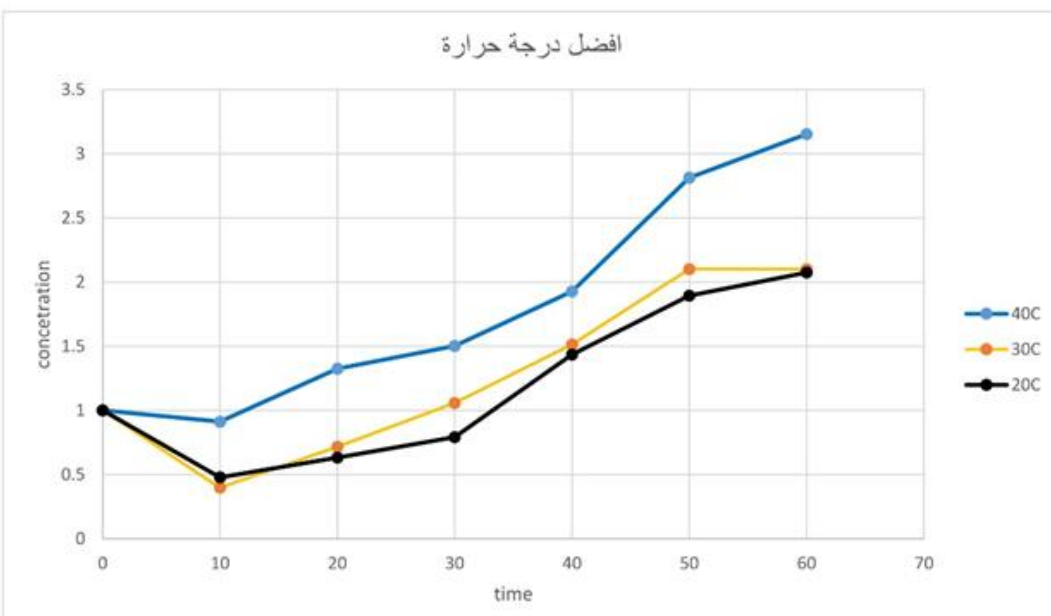
That is, 10 mL of the solution was taken and 100 mL of distilled water was added to each flask. Then, the best weight of eggshells, 50.1 g, was added to these solutions. The absorbance of these solutions was calculated at different temperatures at (10, 20, 30, 40, 50, 60 C) for each temperature. The absorbance was calculated between one period of time and another, amounting to 10 min. The absorbance was as follows:

Min	**10**	**20**	**30**	**40**
0	1	1	1	1
10	0.1884	0.3978	0.4782	*0.9130*
20	0.3405	0.7173	*0.6319*	*1.3254*
30	0.6811	1.0579	*0.7925*	*1.5019*
40	0.9855	1.5144	*1.4351*	*1.9270*
50	1.1449	2.1014	*1.8936*	*2.8142*
60	1.1956	2.1003	*2.0745*	*3.1537*

Discussion:

Discussion of weight:

The increase in the amount of adsorption due to the increase in the weight of the catalyst is due to the possibility of increasing the surface area that provides more effective sites for dye adsorption. At first, the adsorption rate increases rapidly and then decreases with the increase in the amount of the catalyst. This phenomenon is explained on the basis of the fact that the amount of the catalyst is small for dye adsorption at first and then it will decrease due to the decrease in the number of effective sites prepared for dye adsorption.



Discussion of temperature:

The amount of dye adsorption decreases with increasing temperature, and this is clear from the results. The reason is that the adsorption process is essentially an exothermic process, so the inverse relationship between temperature and adsorption enthalpy.

Discussion of the calibration curve:

A series of diluted solutions of the dye were taken from 1ppm to 10ppm, and we found that the best concentration for the dye adsorption process on eggshell surfaces is a concentration of 10ppm.

Discussion of the wavelength:

The λ_max of the dye was taken, and we found it to be around 640 nm, and we relied on it in our study of the research .

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