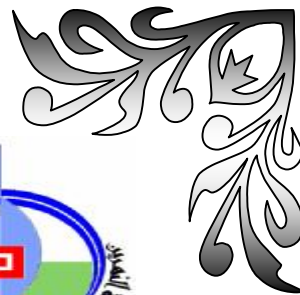




Ministry of Higher Education
and Scientific Research
Al-Nahrain University
College of Science
Department of Chemistry



Sorption study of Some Organic Pollutants on Titanium Dioxide

A thesis

*Submitted to the College of Science Al-Nahrain University
as a Partial Fulfillment of the Requirements for the Degree of Master
of Science in Chemistry*

By

Qabas Mohammad Abd-Al-Hussani
(B.Sc. 2006)

Supervised by

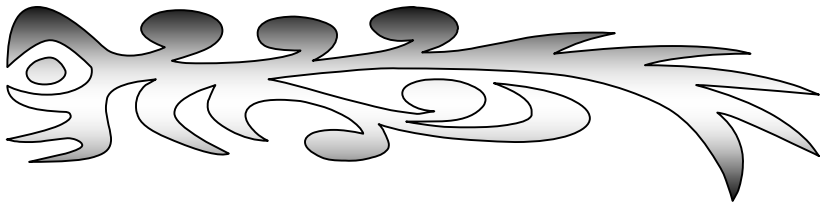
Dr. Khulood A. Al-Sa'adi



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Dedication

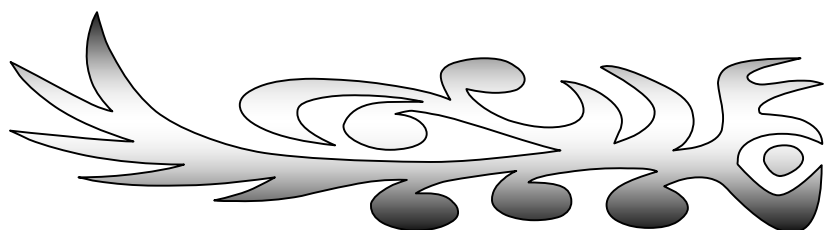
I dedicate this work

To my beloved Father

and Mother

My dearest Brother

and Sister



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Finally, I must not forget to express my deep gratitude of my family for this patient and never ending assistance.

Qabas

Supervisor Certification

We certify that this thesis was prepared under our supervision at the Department of Chemistry, College of Science, Al-Nahrain University, as a partial requirement for the **Degree of Master of Science in Chemistry.**

Signature:

Name: Dr. Khulood A. Al-Sa'adi

Date: / / 2009

In view of the available recommendation, I forward this thesis for debate by the examining committee.

Signature:

Name: Dr. Salman A. Ali

Head of the Department of

Chemistry College of

Science Al-Nahrain University

Date: / / 2009

Examination Committee

We, examining committee, certify we have read this thesis and examined the student in its content, and that in our opinion it is adequate with standing as a thesis for the Degree of **Master in Chemistry**.

Chairman

Signature:

Name: Dr. Alhum M. Al-Rufaie

Title: Assist. Professor

Date: / / 2009

Member

Signature:

Name: Dr. Sameer H. Kareem

Title: Assist. Professor

Date: / / 2009

Member

Signature:

Name: Dr. Tagrad Ali Salman

Title: lecture

Date: / / 2009

Supervisor/Member

Signature:

Name: Dr. Khulood A. Sa'adi

Title: Assist. Professor

Date: / / 2009

Approved by the College of Science

Signature:

Name: Prof. Dr. Laith Abdul Aziz Al-Ani

Dean of the College of Science

Date: / / 2009

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Notations and Abbreviations

Abbreviation	Meaning
UV-Vis	Ultra Violet-Visible Radiation
PVA	Poly Vinyl Alcohol
LAS	Linear Alkylbenzene Sulfonate
ppm	Part per million
ΔH	Enthalpy change
ΔG	Gibbs free energy change
ΔS	Entropy change
IUPAC	International Union of Pure and Applied Chemistry
NAWQA	National Water Quality Assessment
Q_e	Quantity of adsorbate (mg.g^{-1})
C_e	Concentration of adsorbate (mg.L^{-1})
R^2	Correlation Coefficient
Z_1	Zerolite 225 SRC22
Z_2	Zerolite 226 SRC45
Z_3	Zerolite 225 SRC18

Abstract

The subject of this thesis involves studying the possibility removed of four organic compound by TiO_2 . These organic compounds (considered as pollutants) which are; Birlliant blue (dye), polyvinyl alcohol (PVA), Linear alkyl benzene sulfonate (LAS) and Lambdacy holothrin as (pesticides).

The thermal and photo-stability were studied and the results showed that all pollutants are stable in temperature range about (288-318) K, and stable against UV-linght in the wave length range (290-320) nm.

Titanium dioxide succeeded in removing; 95-54% of dye, 6.2% of PVA, 13.19% of LAS and failed in removeing pesticides.

UV-Vis absorption spectrophotometric technique was used to follow the pollutants concentration before and after adsorption process and after different periods of time, since the sorption isotherms were obtained by obeying Langmiur and Freundlich adsorption isotherms, with R^2 (1-0.9993) for dye, R^2 (0.9992-0.9574) for PVA, R^2 (0.9503-0.9813) for LAS.

The dye adsorption isotherms take S-shapes which related to a strong interaction between dye and TiO_2 with thermodynamic values $\Delta H = +(5.962-26.57)\text{J}$, $\Delta G = -(966-999)\text{J}$, $\Delta S = +(3.45-9.1906)\text{J}$.

The thermodynamic parameters were studied by using the sorption process of the three pollutants on TiO_2 of different temperatures ranging (293-318)K, and from the sorption isotherms the values of ΔH , ΔG , and ΔS for PVA $\Delta H = -(133.4-212.83)\text{J}$, $\Delta G = +(78-157.4)\text{J}$, $\Delta S = -(500)\text{J}$, LAS $\Delta H = +(53.14-66.14)\text{J}$, $\Delta G = -(1.21-1.38)\text{kJ}$, $\Delta S = +(4-14)\text{J}$.

The sorption process of dye and LAS a positive ΔH values, negative ΔG values and positive ΔS values, which indicates the

spontaneous absorption process, which for the negative ΔH values, positive ΔG values and negative ΔS values are due to the non spontaneous adsorption process for PVA.

The kinetic study of pollutants sorption on TiO_2 was studied depending on three kinetic equations:

- 1- Lagergren equation: it was used to obtain the order of the sorption process, and the results showed a good obey with $R^2 = (0.9477-0.9995)$ for dye, $R^2 = (0.956-0.9942)$ for PVA, $R^2=(0.9948)$ for LAS, to this equation, which indicates that the sorption process followed a pseudo- 1st order kinetics, and from the linear Lagergren equation for the pollutants sorption the rate constants of sorption were calculated at different temperatures, and the activation energy for the sorption process was also calculated which reached $39.011 \text{ kJ.mol}^{-1}$ for sorption of dye.
- 2- Morris-Weber model: was employed and it gave a good match with the straight linear equation with $R^2 = (0.98-0.994)$ for dye, $R^2=(0.9892)$ for PVA, $R^2 = (0.9989)$ for LAS. This relation indicates that the diffusion process was so obvious, and it involves the transport of pollutant from the bulk solution into the TiO_2 surface, which is considered the rate-limiting step.
- 3- Reichenberg model: was employed and it gave a good linear relationship between B_t and time with acceptable correlation coefficient $R^2 = (0.9891)$ for dye, $R^2 = (0.9306)$ for PVA, $R^2 = (0.9776)$ for LAS.

This relation indicates that the rate limiting mechanism is the absorption and the sorption process involving three steps: absorption, adsorption and desorption).

CHAPTER ONE



Introduction

1-1- Adsorption

Adsorption is the tendency for accumulation of a substance to take place at a surface or at an interface the commencement of adsorption is due to the atoms in any surface being subject to unbalanced forces of attraction perpendicular to the surface plane and these are possessing a certain unsaturation⁽¹⁾.

The contact of immiscible phases may in addition to adsorption, result in penetration of the bulk of one phase by the other. This is called "absorption"⁽²⁾.

1-2- Kinds of Adsorption

Adsorption has traditionally been divided into two kinds: weak physisorption, and strong chemisorption.

Physisorption occurs when vapors near their saturation pressures adsorb to a dry surface in a process that resembles condensation. The Van der Waals forces and weak dipole interactions present here have heats of adsorption typically a few hundred cal/mol⁽³⁾, as shown in Fig.(1-1).

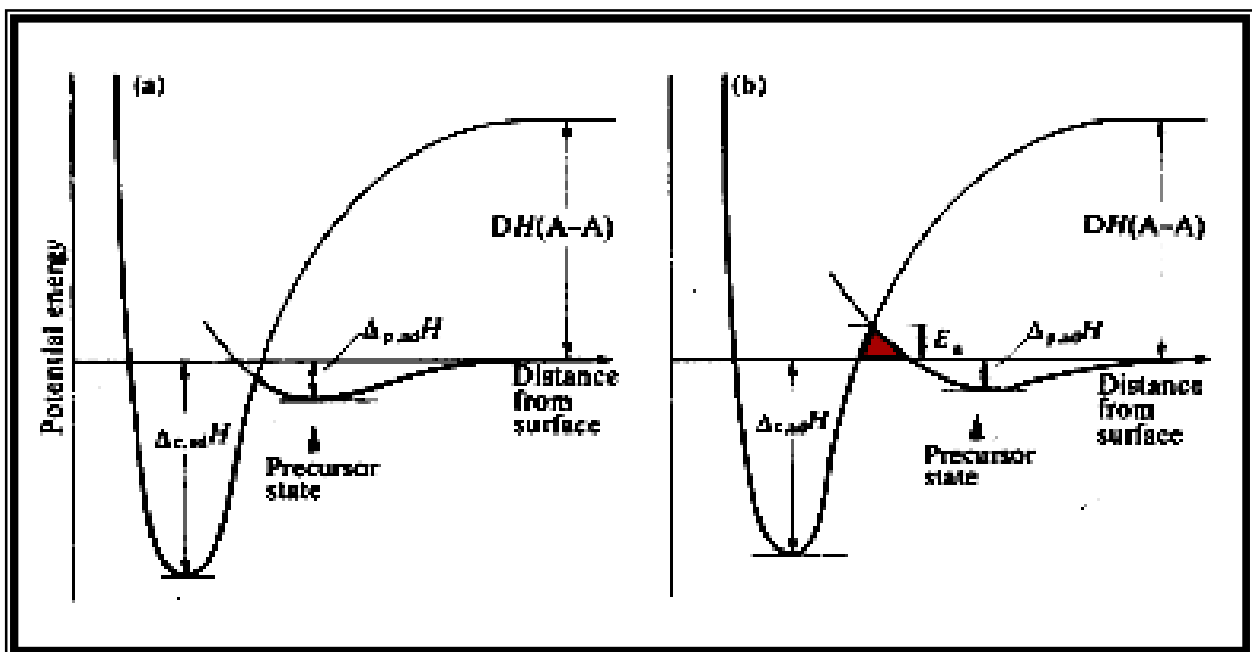


Fig.(1-1): The potential energy diagram of physisorption (a), and chemisorption (b) processes

Physi-sorption is very rapid, and reversible, with equilibrium established quickly as the gas pressure is varied. It is non specific, because the molecule or atom that undergoes a physi-sorption process is not chemically bind to the surface of adsorbate, but it occupies a specific area on the entire surface of adsorption, and the adsorbed species are not limited on the monolayer formation, since multilayer is highly expected⁽⁴⁾ as shown in Fig.(1-2).

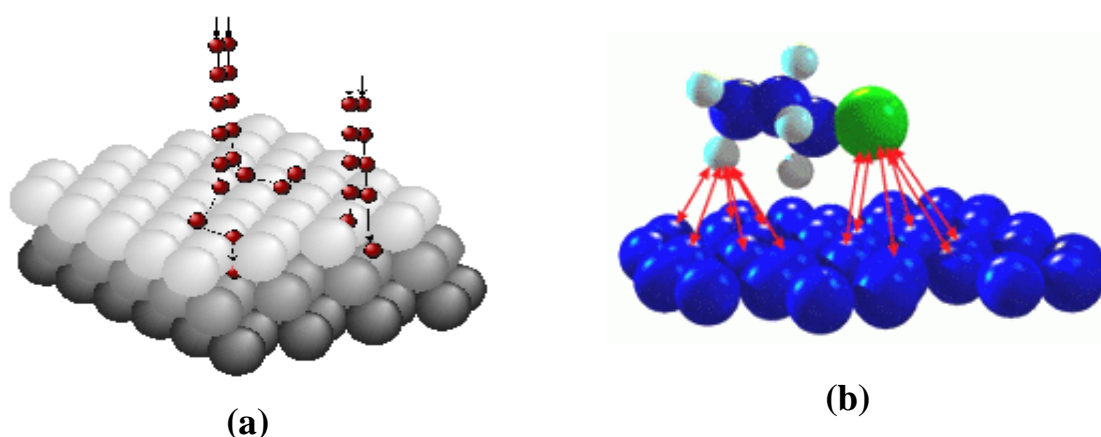


Fig.(1-2): The schematic representation of chemi-sorption (a), and physi-sorption (b) processes

Chemi-sorption is totally different from physi-sorption, since there is a strong chemical binding between the adsorbate and the adsorbent⁽⁵⁾, as shown in Fig.(1-2).

Chemi-sorption is characterized by the high adsorption energies (>30 kcal/mol), the process is likely to be slow, and less readily reversible, in the sense of that equilibrium may take a longer time to be achieved, adsorbed species are limited to the formation of a monolayer⁽⁶⁾.

1-3- Adsorption Isotherms

When a gas comes into contact with a solid surface, molecules of the gas will adsorb (stick) to the surface in quantities that are a function of their partial pressure in the bulk. The measurement of the amount of

gas adsorbed over a range of partial pressures at a single temperature results in a graph known as "adsorption isotherm" ⁽⁷⁾.

These isotherms can be very different shapes depending on the types of adsorbent, the type of adsorbate and inter molecular interactions between the gas and the surface⁽⁸⁾.

The first systematic attempt to interpret adsorption isotherms for gas solid equilibria was introduced by Brunauer, Deming, Deming, and Teller⁽⁹⁾ (BDDT) in 1940. These authors classified isotherms into five types. The BDDT classification has become the core of the modern IUPAC classification of the adsorption isotherms⁽⁹⁾ these BDDT isotherms and an additional one introduced much later by Sing, which completes the IUPAC classification are illustrated in Fig.(1-3-A), and Fig.(1-3-B).

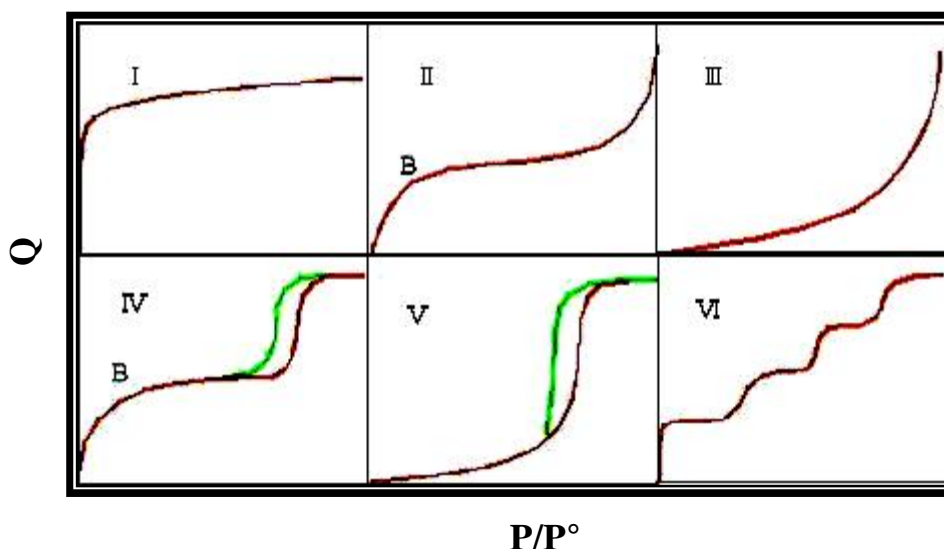


Fig.(1-3-A): IUPAC classification of adsorption isotherms, where Q is the adsorption quantity, and P is the partial pressure of adsorbed gas

Type I isotherms characterize microporous adsorbents. Types II and III describe adsorption on macroporous adsorbents with strong and weak adsorbate-adsorbent interactions, respectively. Types IV and V represent adsorption isotherms with hysteresis. Finally type VI has steps.

The BDDT and IUPAC have two deficiencies: they are incomplete and they give the incorrect impression that adsorption isotherms are always monotonic functions of pressure. This is because the IUPAC classification takes into account the adsorption at subcritical temperatures⁽¹⁰⁾.

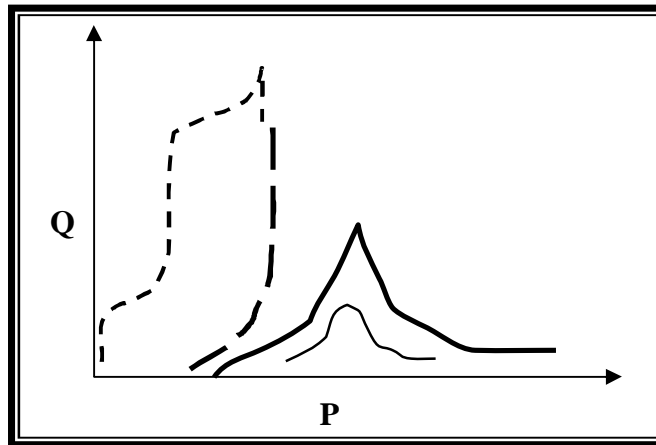


Fig.(1-3-B): The other hysterical isotherms according to IUPAC classification

The second systematic attempt to interpret adsorption isotherms for solutions was introduced by Giles. This authours classified isotherms types shown in Fig.(1-4).

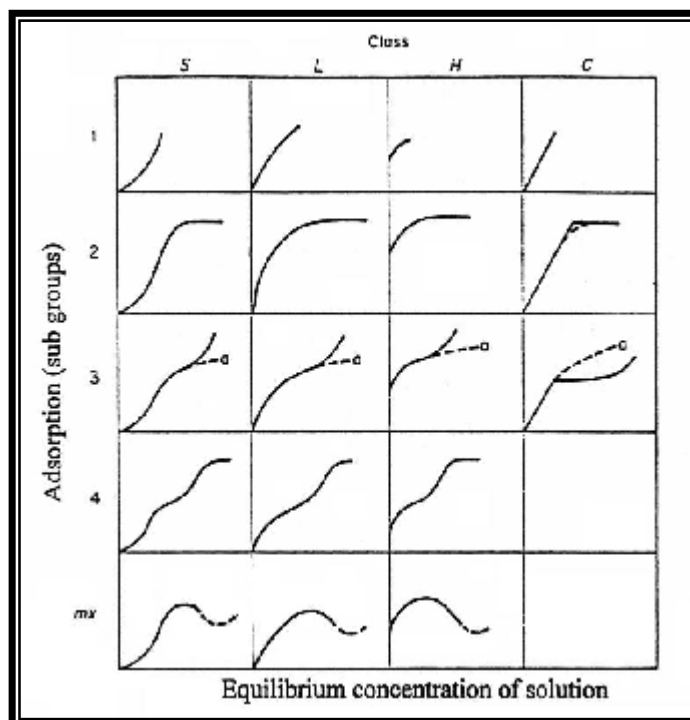


Fig.(1-4): Giles classification of adsorption isotherms

1-3-1- Langmiur Isotherm

It is a good representation of chemisorption, and usually represents the low P portion of other isotherms⁽¹¹⁾. Adsorption sequentially fills surface sites until mono-layer coverage is achieved. No multilayer coverage is included. Each site is equivalent in energy as shown in Fig.(1-5).

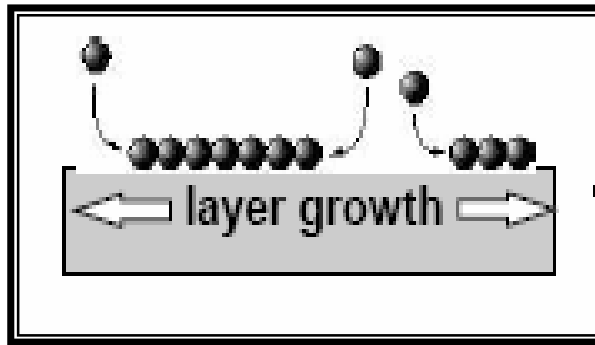


Fig.(1-5):The mono-layer formation

Langmiur behavior assumes a rapid reversible sorption, and interaction only between sorbate molecules and a surface site^(12,13).

The Langmiur equation could be expressed as:

$$\left[\frac{C_e}{Q} = \frac{1}{k} + \frac{a}{k} C_e \right] \dots \dots \dots (1-1)$$

Where Q is the amount of adsorbate (mg/g), C_e is the equilibrium concentration (mg/L), and a, k are constants related to adsorption capacity and energy of adsorption respectively or sometimes called Langmiur constants^(12,13).

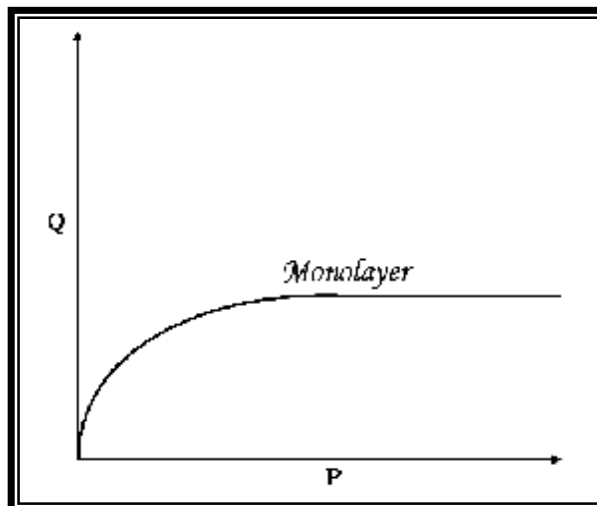


Fig.(1-6): Langmiur adsorption isotherm

1-3-2- Freundlich Isotherm

It is one of the most important isotherms that deals with sorption at solid-liquid interface, which has been introduced by (Herbert Max Finaly Freundlich) a German scientist in 1926⁽¹⁴⁾.

Most of surfaces are heterogeneous, so the change in potential energy is regular, and the adsorption sites are not equivalent in energy⁽¹⁵⁾, hence the multi-layer formation is highly expected, and as shown in the following figure.

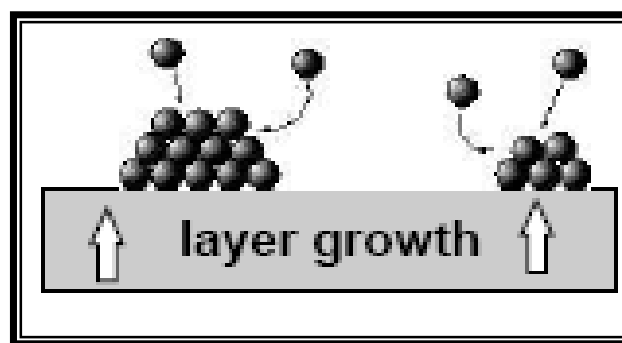


Fig.(1-7):The multi-layer formation

This leads to a significant change in the adsorption isotherm, since Freundlich equation has been employed to represent the change in the amount of adsorbate per unit area, or mass of adsorbent with equilibrium concentration of the adsorbate. The adsorption isotherm of Freundlich could be shown as in Fig.(1-8).

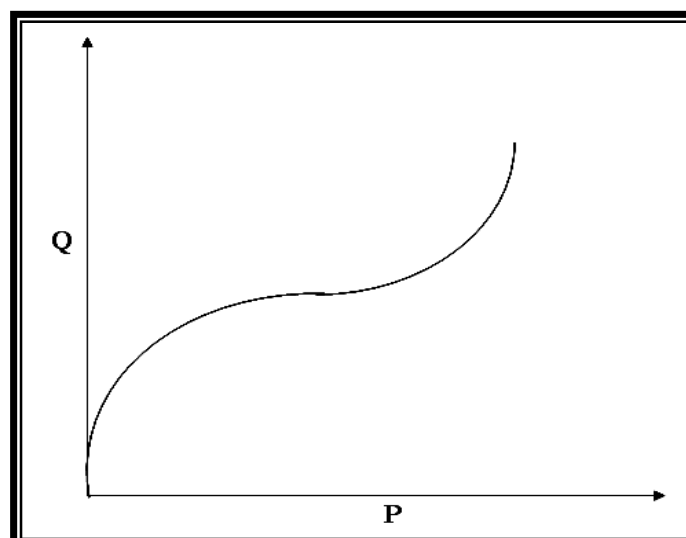


Fig.(1-8): Freundlich adsorption isotherm

Freundlich equation could be written as follows^(16, 17):

$$Q = k_F C_e^{1/n} \dots\dots\dots(1-2)$$

$$\log Q = \log k_F + 1/n \log C_e \dots\dots\dots(1-3)$$

where Q is the adsorbate quantity (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L), k_F, and n are Freundlich constants.

Plotting of log Q versus log C_e gives a linear relationship as shown in Fig.(1-9).

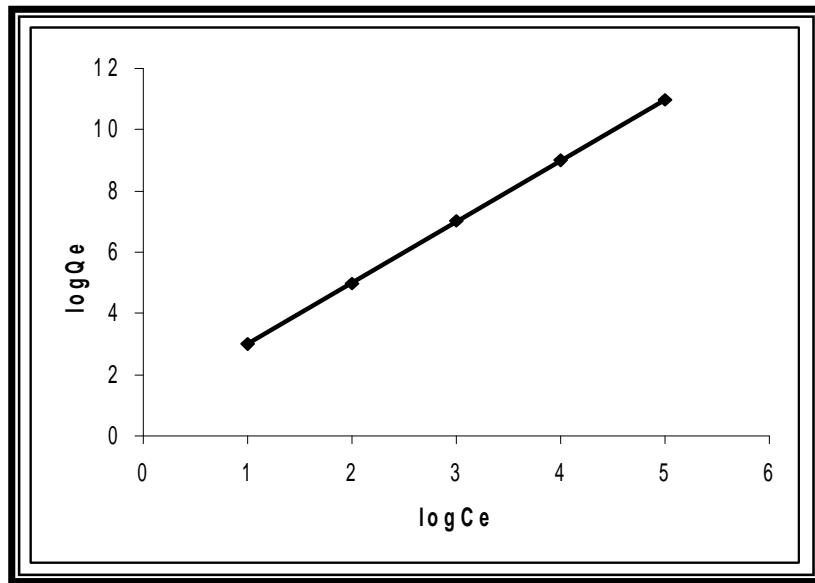


Fig.(1-9): Linear relationship of Freundlich isotherm

1-4- Pollution

Pollution of surface water and ground water is a major concern throughout the world. There are two basic types of pollution:

Point and Non point⁽¹⁸⁾

Point pollution is contamination that can be traced to a particular source such as an industrial site, septic tank, or waste water treatments plant.

Non point pollution results from large areas and not from any single source and includes both natural and human activities⁽¹⁹⁾. Sources of non point pollution include agricultural, human, forestry, urban, and mining activities and atmospheric deposition. There are also naturally occurring non point source pollutants that are important. These include geologic erosion, saline seeps, and breakdown of minerals and soils that may contain large quantities of nutrients⁽²⁰⁾.

To assess contamination of ground and surface waters with plant nutrients such as pesticides, and other pollutants a myriad of inter connections including geology, topography, soils, climate and atmospheric inputs⁽²⁰⁾.

These plants can clog water pipes and filters and impact recreational endeavors such as fishing, swimming, and boating. When algae decays, foul odors, obnoxious tastes, and low levels of dissolved oxygen in water (hypoxia) can result⁽²¹⁾.

Phosphorus, as phosphate, is usually not a concern in groundwater, since it is tenaciously held by soils through both electrostatic and non electrostatic mechanisms and usually does not leach in most soils. However, in sandy soils that contain little clay, Al or Fe oxides, or organic matter, phosphate can leach through the soil and impact groundwater quality⁽²¹⁾. Perhaps the greatest concern with phosphorus is contamination of streams and lakes via surface runoff and erosion. Nitrate-N is weakly held by soils and readily leaches in soils⁽¹⁹⁾.

An extensive case study that illustrates pollution of department of energy sites and military bases in the united states has recently been conducted⁽²²⁾. These are located around the united states and were sites for weapons production. Substantial radioactive wastes were produced. At some military bases toxic chemicals were disposed of in water supplies and other areas that are now leaking⁽²²⁾.

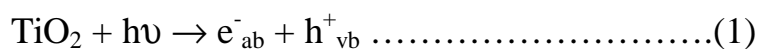
A report (Riley et al., 1992)⁽²²⁾ documented contamination of soils/sediments and groundwater at waste sites on 18 department of energy facilities. These facilities occupy 7280 km² in the 48 contiguous states. Most of the wastes were disposed of on the ground or in ponds, pits, injection wells, and land fills, and are contamination the subsurface environment.

1-5- Titanium Dioxide

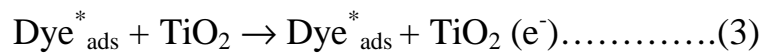
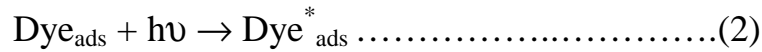
Titanium dioxide is considerably the most extensively studied photocatalytic material because of the high resistance to dark and photoinduced corrosion, easy availability and low cost. The titanium dioxide surface was explored many studies as a means of improving its photocatalytic activity⁽²³⁾.

Titanium dioxide supported or coated photocatalyst is becoming more popular in waster and air purification in the recent days⁽²⁴⁾.

Titanium dioxide absorbs a photon energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band (E_{ab}) leaving behind an electron vacancy or (hole) in the valence band (h^+_{vb}). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reaction, with sorbed species, as indicated in eqs.(1).



The electron in the conduction band can be picked up by the adsorbed dye molecules, leading to the formation of dye radical anion and subsequent reaction of the radical anion can lead to degradation of the dye or direct absorption of light by the dye can lead to charge injection from the excited state of the dye to the conduction band⁽²⁵⁾. In the following eqs.



However the titanium dioxide (TiO₂) has been vigorously used as the photocatalyst for environmental cleanup, and it has been utilized for technological applications because of distinguished characteristics⁽²⁶⁾.

- (a) It is inexpensive, nontoxic, and very stable with high photocatalytic efficiency.
- (b) It promotes ambient temperature oxidation of the major classes of indoor air pollutants.
- (c) Complete degradation of a broad range of pollutants can be achieved under certain operation conditions.
- (d) No chemical additives are required.

It is expected that the TiO₂ particle surface are the main reaction fields for the direct oxidation of adsorbed substrate. However, only a few quantitative studies have been reported on the oxidation processes of organic compounds on the TiO₂ particle surfaces and the interaction between the substrate and TiO₂ surface⁽²⁶⁾.

1-6- Effect of Light on The Adsorption by TiO₂

Many reactions can be initiated by the absorption of electromagnetic radiation via different mechanisms. The most important of all are the photochemical processes that capture the radiant energy of these reactions lead to the heating of the atmosphere during the daytime^(27,28).

Other includes the absorption of visible radiation during photosynthesis processes in plants⁽²⁸⁾.

Photochemistry is a natural phenomenon, which began at the origin of the universe world. Modern science describes the interactions between

light and matter in several main sciences such as chemistry, physics and biology⁽²⁹⁾.

Photochemistry plays a fundamental role in life (photosynthesis, vision, photoaxis, photo degradation, etc..)⁽³⁰⁾.

The photochemical and photo physical processes of thousands of organic and organometallic, the major parts of photo chemical investigations were focused on molecular species with simple process (i.e. molecular photo chemistry)⁽³¹⁾.

The past two decades have witnessed intensive studies related to the light induced mineralization of hazardous organic pollutants with the use of TiO₂ photocatalysts, other process can break down a large variety of organic compounds⁽³²⁾.

However, the photocatalytic degradation of reactive dyes in an aqueous solution and destruction of several classes of organic dyes using TiO₂ respectively⁽³²⁾, photocatalytic process involving TiO₂ semiconductor particles under UV-light illumination has been shown to be potentially advantageous and useful in the treatment of waste water pollutants⁽³³⁾.

The photocatalytic oxidation of organic compound in water has received the most attention, but there is a rapidly increasing amount of work on the oxidation of a volatile organic compound⁽³³⁾. Photocatalytic reduction of organic compound and metal containing ions is also well established^(32,33).

As the photocatalytic mechanism suggest, both TiO₂ and a light source are necessary for the photo-oxidation reaction to occur⁽³⁴⁾.

A control experiment was conducted on three different conditions:

- 1- Under UV illumination in absence of TiO₂.
- 2- In the dark with TiO₂.
- 3- Under UV illumination in presence of TiO₂.

1-7- Organic Pollutants

1-7-1- Dyes

The use of natural dyes for painting and dyeing has been known since ancient time. The recent discovery in the Chauvet-Pont-d'Audoubert caves in France of 30000 year old Paleolithic rock paintings provide the ancientest testimony of the millenary use of inorganic compounds such as also along history, especially as textile dyes⁽³⁵⁾.

Due to the fact that these plants and materials were usually native from the regions where they were used in the dyeing processes the diffusion of these methods has not been possible for along time.

In 1856 Young English chemist W.H. Perkin, in the attempt to synthesize quinine, discovered and patented a substance with excellent dyeing properties that later would come to be known as aniline purple. In the following years other dyes have been developed⁽³⁵⁾.

All molecules absorb electromagnetic radiation, but different in the specific wave length absorbed. Some molecules have the ability to absorb light in the visible spectrum (400-800 nm) and, as a result, they are themselves colored. The dyes are molecules with delocalized electron systems with conjugated double bonds that contain two groups: the chromophore and auxochrome⁽³⁷⁾.

The chromophore is a group of atoms, which controls the color of the dye, and it is usually an electron withdrawing group. The most important chromophores are -C=C- , -C=N- , -C=O , -N=N- , -NO_2 and -NO groups^(37,38).

The auxochrome is an electron-donating substituent that intensifies the color of the chromophore by altering the overall energy of the electron system and provides solubility and adherence of the dye to the fiber⁽³⁷⁾.

In 1950, powdered detergents were more or less white⁽³⁹⁾, consistent with color of their components. Thereafter, products were commonly encountered in which colored granules were present along with the basically white powder: certain components had been deliberately dyed to make the products more distinctive. In the meantime, uniformly colored detergents have also appeared on the market and the idea of introducing coloring agents has become quite common. The preferred colors for both powder and liquid are blue, green, and pink⁽³⁹⁾.

There are two important factors for selecting a coloring agent:

- 1- Good storage stability with respect to other detergent components and to light.
- 2- No significant tendency to affect textile fiber.

1-7-1-A- Classification of dyes⁽⁴⁰⁾

1- Acid Dyes

Highly water-soluble to the presence of sulphonic acid groups. From ionic interaction between the protonated functionalities of the fibers ($-\text{NH}_3^+$) and the negative charge of the dyes. Also Van der Waals, dipolar and hydrogen bonds are formed. The most common structures are azo, anthraquinone and triarylmethane.

2- Basic Dyes

Basic dyes work very well on acrylics due to the strong ionic interaction between dye functional groups such as $-\text{NR}_3^+$ or $=\text{NR}^+$ and the negative charges in the copolymer. The most common structures are azo, diarylmethane, triarylmethane.

3- Natural Dyes

Natural dyes are in textile processing operations is very limited fluorescent brighteners mask the yellowish tint of natural fibers by absorbing ultraviolet light and weakly, emitting blue light. No listed inaseperate class in the color index, many metal complex dyes can be found (generally chromium, copper, cobalt or nickel). The metal complex dyes are generally azo compounds.

1-7-2- Polymers

Polymers are macro molecules built up the linking together of large numbers of much smaller molecules. The small molecules that combine with each other to form polymer molecules are termed monomers, and the reactions by which they combine are termed polymerizations⁽⁴¹⁾. There may be hundreds, thousands, tens of thousands, or more monomer molecules linked together in a polymer molecule.

Polymers are used in a wide range of applications, as coatings, as adhesive, as engineering and structural materials, for packaging, and for clothing to name a few⁽⁴²⁾.

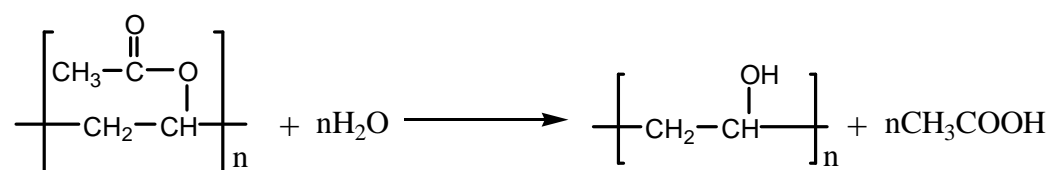
A key feature of the success and versatility of these materials is that it is possible to built in properties by careful design of the (largely) organic molecules from which the chains are built up.

It is important that the molecular weight characteristics of polymers can be accurately determined of course, the precise molecular weight determined will depend on the technique used, thus techniques that rely on the measurement of colligative properties, such as osmotic pressure, count the number of molecules in solution polymer nomenclature in general leaves much to be desired.

A standard nomenclature system based on chemical structure as is used for small inorganic and organic compounds is most desirable.

The most simple and commonly used nomenclature system is probably that based on the source of the polymer⁽⁴²⁾. This system is applicable primarily to polymers synthesized from a single monomer as in addition and ring-opening polymerizations.

Some polymers are named as being derived from hypothetical monomers. Thus poly(vinyl alcohol) is actually produced by the hydrolysis of poly(vinyl acetate).



It is, however, named as a product of the hypothetical monomer vinyl alcohol (which in reality exists exclusively as the tautomer-acetaldehyde)⁽⁴¹⁾.

1-7-2-A- Classification of Polymer

Materials classified as polymer are long chain molecules with a repetition of structural unit. The structural units are called monomer, which are connected to each other by covalent bond macromolecule. Big molecule also are used to define polymer term. However, large molecule of complex structure can be covered better by this name "polymer" since the latter carries with it the connection of simple repeating unit⁽⁴³⁾.

There are three main structural shapes in which polymer molecules are produced, which can be classified into⁽⁴²⁻⁴³⁾.

- 1- Linear polymers: like polyethylene and polyvinyl alcohol.
- 2- Branched polymers: like low density polyethylene.
- 3- Cross-linked polymers: like thermosetting resins, phenoplast, and uroplast.

1-7-3- Linear Alkylbenzene Sulfonate (LAS)

1-7-3-A- Definition

Linear alkylbenzene sulfonate (LAS) is the major anionic surfactant used world wide in detergents and house hold cleaning product formulation⁽⁴⁴⁾.

LAS is manufactured from alkylbenzene, the alkyl chain length C₈-C₁₅, its properties are mainly influenced by the average molecular weight and the spread of carbon number of the alkyl side chain.

Commercial LAS is composed of linear alkyl chain consisting of 10-14 carbon atoms. And usually prepared by the addition of fuming sulfuric acid into alkylbenzene in a reaction called "sulfonation"⁽²³⁾.

1-7-3-B- Environmental Impacts of LAS

Linear alkylbenzene sulfonate (LAS) are major ingredients of commonly used surfactants and detergents⁽⁴⁵⁾. High concentrations of these anionic surfactants may occur in sewage sludge processed in waste water treatment plants, LAS are deposited in agricultural soils by the application of sludge as fertilizer and the use of untreated waste water for irrigation.

The toxicity of LAS in soil on the form in which LAS was applied, as well as on the characteristics of each particular soil⁽⁴⁶⁻⁴⁸⁾.

Presently, most of the LAS used in the formation of industrial and house cleaning products are disposed of in domestic sewage and then conducted to municipal waste water treatment plants (wwtp)⁽⁴⁹⁾.

Other LAS derivatives, originating from industrial detergents used in the textile finishing industry and for the cleaning of production vessels, may arrive to these plants and are consequently treated⁽⁵⁰⁾.

LAS are introduced into agricultural soils by several

- Application of sewage sludge as an agricultural fertilizer.

- Application of waste water as irrigation water.
- Soil infiltration of waste water or polluted river water.
- Application of pesticide formulation containing LAS as emulsifiers or dispersion agents⁽⁵¹⁻⁵³⁾.

The application of sewage sludge as an agricultural fertilizer is the major route for LAS presence in soils.

Several physical and chemical factors such as temperature, oxygen, supply, water content, the amount of LAS applied and its molecular characteristic (length of chain and position of benzene ring) may condition the biodegradation in soil ecosystems⁽⁵⁴⁾.

Several studies⁽⁵⁵⁻⁵⁸⁾ have repeatedly reported LAS to have a short half-life (1-4) weeks in agricultural soils due to its degradation by soil microbiota⁽⁵⁹⁾, and as shown below in Table (1-1).

Table (1-1): Half-life of LAS reported in agricultural soils⁽⁵⁵⁾

Soil type	Half-life (days)
Grapevine form (Spain)	26
Vegetable form	33
Agricultural soils (USA)	2-4
Vegetable farm (UK)	22

Although, the adsorption of LAS to soil depends on the type of soil and the particular chemical characteristic of the LAS homologues added, however, it has been demonstrated that LAS homologues with long chains can strongly be adsorbed to soil particles⁽⁵²⁾, thereby becoming unavailable for microbial degradation and consequently can accumulate in soils.

Recent studies have shown that current domestic and industrial uses of LAS do not have a potential risk for soil organisms and plants⁽⁴⁹⁾.

In this way, LAS doses between (10-50) mg/kg have been reported to be ineffective against soil microbiota⁽⁵³⁾.

The main biological effect of LAS is the disruption of biomembrances and the denaturation of protein⁽⁴⁶⁾.

In microorganisms LAS adsorption produces a depolarization of cell membranes and consequently decreases the absorption of nutrients and modifies the release of substances from cell metabolism⁽⁶⁰⁾.

In general, surfactants, and specifically LAS in the less industrially developed countries of the third world have a major role in environmental pollution⁽⁶¹⁾. Since surfactants cause foams at sewage treatment plants and pollute underground waters, which are hazardous for health. They exert a solubility effect on many organic compounds and create carcinogenic impacts. Penetrated into water and change its quality by causing it to have unpleasant smell and taste⁽⁶²⁾. So the quality would be changed and the water becomes not potable and unhealthy.

1-7-4- Pesticides

Pesticides can be classified as herbicides, those used to control weeds, insecticides, to control insects, fungi cides to control fungi, and others such as nematicides and rodenticides.

Pesticides were first used in agricultural production in the second half of the 19th century. Examples included lead, copper, and zinc salts, and naturally produced plant compounds such as nicotine⁽⁶³⁾.

As the use of pesticides increased concerns were expressed about their appearance in water and soils, and their effects on humans and animals. Total pesticide use in the united states has stayed constant at about 409 million kg per year after increasing significantly.

The NAWQA studies showed that pesticides were prevalent in streams and groundwater in urban and agricultural areas. However, the average concentration in streams and wells seldom exceeded established standards and guidelines to protect human health. The highest detection frequency of pesticides occurred in shallow groundwater below agricultural and urban areas while the lowest frequency occurred in deep aquifers⁽⁶⁴⁾.

1-8- Literature Survey

Dane Shvar, N., et al⁽⁶⁵⁾ have studied the Decolourization of various dye by photocatalysis using ZnO as an alternative catalyst to TiO₂. They found that the degree of degradation of dyes was obviously affected by the mixture of dyes. The photocatalytic decolorization of synthetic effluents was most efficient than natural effluents the complete removed of color could be achieved in a relatively short time of about 30min. we can conclude that the ZnO can be used in the degradation of dyes as an alternative to TiO₂.

Guillard C., et al⁽⁶⁶⁾ have studied the comparison of different characteristics of TiO₂ films and their photocatalytic properties. They addition layers of TiO₂ also result in higher thickness of the films and consequently in higher photocatalytic activities of the prepared films but the photo degradation rates don not increase linearly with the number of coatings because photoenerated holes and electrons from the bottom of the thicker films recombine before they reach the surface of the films.

Hakimch V., et al⁽²⁶⁾ have studied the photo oxidation of some organic sulfides under UV light irradiation using titanium dioxide photo catalyst they discussed they photo oxidation products and their chemical yields, mechanism of products formation over TiO₂. they found the photo generated hole localized at the surface of the irradiated semiconductor is

trapped by an adsorbed organo sulfur compound, which generated an adsorbed cation radical. The chemical bonding important role in the oxidation mechanism as well as adsorption on the surface of TiO₂ particles.

Liyun Q. et al⁽⁶⁷⁾ have studied the adsorption of cationic surfactants on swelling (bentonite) and non-swelling (kaolinite) clays. Adsorption studies showed that Gemini cationic surfactants are more efficient than of the conventional surfactants on both bentonite and kaolinite they studied the adsorption isotherms of freundlich type and concluded that the cation exchange was the dominant, besides the hydrophobic interaction in both Gemmini and conventional surfactants.

Zahir R. and Najwa N.⁽⁶⁸⁾ have studied the characteristics of phenol and chlorinated phenols sorption or to surfactant modified bentonite. They found that phenols and derivatives can exert a negative effect on drinking water and on different biological processes, so they proposed a sorption mechanism which has a great influence in removing these phenol compounds from water.

Biswas and Chattoraj⁽⁶⁹⁾ have studied the adsorption of cationic surfactants (C₁₆TAB, C₁₄TAB, C₁₂TAB) on silica-water interface at different bulk concentrations, pH, ionic strength, temperature and electrolyte. It is shown that adsorption follows a two-step first order rate process with different rate constants.

They noticed a remarkable increase in adsorption amount when the temp increases and the rate constant of process increases as well.

Huang et al⁽⁷⁰⁾ have studied the adsorption of cationic and anionic surfactants on silica from the mixture of anionic and cationic surfactants. They have found that the individual cationic surfactants can be strongly adsorbed onto the silica gel, but no significant adsorption of anionic

surfactant can be detected. However, in the mixed systems, the adsorption amount of both cationic-anionic mixture was enhanced.

Qamar M. et al⁽⁷¹⁾, have studied the titanium dioxide mediated photo catalytic degradation of two selected azo dye derivatives chrysoidine R and acid red 29 (chromotrop 2R). in aqueous suspensions. They discussed the result on the photodegradation of the model compounds using different kinds of TiO₂ photocatalyst with different bulk and surface properties, i.e., BET-surface impurities, lattice mismatches or density of hydroxyl groups on the catalysts surface are apparently responsible for the photocatalytic activity, since they will effect the adsorption behaviour of a pollutant or intermediate molecule and the life time and re-combination rate of electron-hole pairs.

Lara I. Halaoui, et al⁽⁷²⁾, have studied the increasing the conversion efficiency of dye-sensitized TiO₂ photo electrochemical cells by coupling to photonic crystals. They found the increase the light conversion efficiency of dye-sensitized nonocrystalline TiO₂ solar cells, and at bilayer electrodes of photonic crystals and disordered layers coupled to noncrysalline TiO₂ films. The possibility of achieving a stronger localization of light in thicker titania photonic crystals with different degrees of disorder.

Gueltai N., et al⁽⁷³⁾, have studied the photocatalytic oxidation of methyl orang (Meo) in presence of titanium dioxide in aqueous suspension. They found that the disappearance of Meo followed satisfactory the pseudo-1st order kinetic according to Langmuir-Hinshel wood (L-H) model using linear from this model, the rate and adsorption constants were calculated for comparison, k_{ads} from kinetic degradation was quietly higher then k_{ads} deducted from isotherm adsorption.

Otoniel, et al⁽⁷⁴⁾, have studied the sorption process and the removal of surfactants from aqueous media. They studied the thermodynamic

parameters, ΔH , ΔG , ΔS for the sorption process, and they observed negative values for ΔH , and ΔG and positive ΔS . They also studied the dynamics of sorption process and calculated the rate constant and the energy of activation of sorption process.

Wang X. et al⁽⁷⁵⁾, have studied the coating of magnetite surface with sodium dodecyl benzene sulfonate and sodium oleic. The study has revealed that sodium oleic has been chemically adsorbed on the surface of magnetite. And the sodium dodecyl benzene sulfonate has been physically adsorbed on the magnetite and the binding with sodium oleic was via a Van der Waals forces.

They also studied the adsorption isotherms of both adsorption processes. Since the sodium oleic adsorption isotherm was Langmuir type, but the adsorption isotherm of sodium dodecyl benzene sulfonate was of freundlich type. however, experimental results have revealed that adsorption in both cases was monolayer.

Ghassan S.⁽⁷⁶⁾, has studied the adsorption of lead ions on the surfaces of ion exchange resin and some Iraqi clays. He found the results how that the adsorption capacity and efficiency of Iraqi clays were very high and reach to the adsorption capacity and efficiency of ionic exchangers Z_1 and Z_3 . The ionic exchanger Z_2 show lowest adsorption efficiency which reached to 35%. as maximum value, while Z_1 and Z_3 gave higher adsorption efficiency reached to 99.7%.

Lekaa H.⁽⁸⁷⁾, has studied Adsorption of some dyes on surface of white Iraqi kaolin clay, She found the adsorption isotherm in the rang of concentrations of studied dyes was revealed by using ultra-violet spectroscopy technique, the results showed that the dyes isothermes of Neutral Red, Safranin O, the Brilliant blue G250, Congo Red, Rhodamine 6G, Brilliant Green, crystal violet were similar to Freundlich and Langmuir isotherms.

Ali A.⁽⁷⁷⁾, has studied The adsorption of linear alkylbenzene sulfonate (LAS) on Iraqi Bentanite clays. He found UV-Vis absorption spectrophotometric technique was used to follow the LAS concentration before and after sorption process and after different periods of time. Since the sorption isotherms were obtained by obeying freundlich and Langmuir adsorption isotherms. Sometimes the isotherms take a hysteric form due to the low interaction forces between LAS and clay. And sometimes the isotherms take an S or H-shaped figure according to IUPAC classification.

Brinkely and Engel⁽⁸⁸⁾ has studied the photocatalytic reaction of 2-propanol to acetone and water on TiO₂. only the most tightly bound propanol molecules were reactive for the photocatalytic dehydrogenation reaction, and no reaction was found in the absence of co-adsorbed O₂. and it was found that about 0.08% of surface sites are active. The presence of oxygen vacancies increases the number to 0.15.

1-9- Aim of The Work

The pollution by organic compounds is the major problem of industrial progress. Since a large amount of those compounds are disposed into the environment and specifically into the rivers and lakes, consequently, the major objection of this research is to minimize the environmental impacts of these compound via an adsorption study using titanium dioxide.

The main organic compounds used in the present research included; Birlliant blue dye, polyvinyl alcohol, linear alkylbenzen sulfonate and Lambdacyholothrin (pesticides).

The present study also included study the effect of time contact, temperature and irradiation by UV-light (290-320)nm to find out the optimum conditions for the adsorption process.

The detailed kinetic and thermodynamics studies has been employed to investigate the mechanism, rate and order of the sorption process for all pollutants.

CHAPTER TWO



*Experimental
Part*

2-1- Instruments

The following instruments were used in this study:

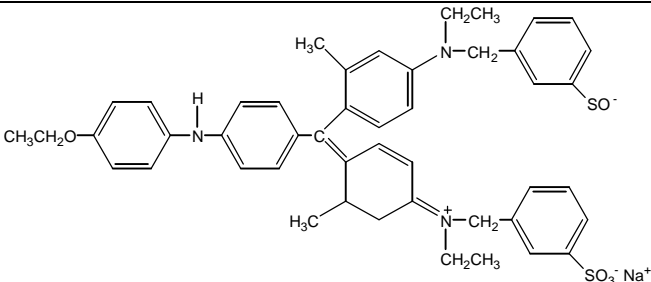
No.	Instruments	Manufacturer
1	Griffin Flask Shaker	Griffin and George LTD, London, Gt. Britain
2	Electronic Balance	Sartorius AG Gottingen, BL 2105, W. Germany
3	Magnetic Stirrer with hot plate	JTASSO-India
4	Oven	Gallenkamp hot box, England.
5	Water bath	Gallenkamp, Technico, compenstat – England.
6	UV-Vis Spectrophotometer	Shimadzu – 160, Japan
7	Centrifuge, Magafuge	1.0.Herouse Sepatech.

2-2- Chemicals

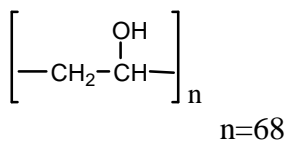
The following chemicals were used in this study:

No.	Material	%Purity	Supplied from
1	Linear Alkyl benzene sulfonate (LAS)	48	State company for vegetable oils- Iraq.
2	Titanium dioxide	95	BDH
3	Birlliant blue	99	BDH
4	Lambdacy holothrin	99	VAPCO, Syngenta
5	Poly Vinyl alcohol	75	BDH
6	Cerric amoninum nitrate (Indicater)	99	BDH

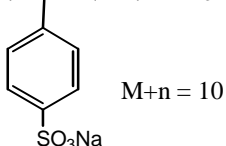
2-2-1- Brilliant blue G250 (Natural Dyes)

Specification sheet		Structure of Brilliant blue ⁽¹⁴⁾
Empirical formula	$C_{47}H_{49}N_3O_7S_2Na$	
Molecular weight	710.01 g/mol	
Melting point	206°C	
Solubility	Water	N-141[4-(4-Ethoxy phenyl) amine] phenyl]-[4-[ethyl[(3-sulfophenyl)methyl] amino]-2-methyl phenyl] methylene]-3-methyl-2,5-cyclohexadien-1-ylidene]-N-ethyl-3-sulfobenzene methanaminium mono-sodium salt

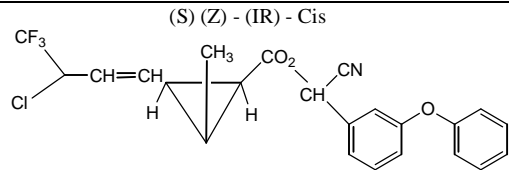
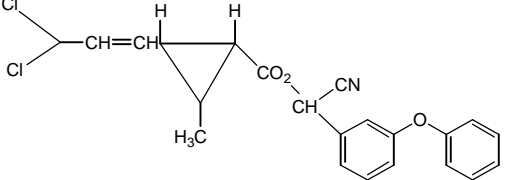
2-2-2- Poly Vinyl Alcohol

Specification sheet		Structure of PVA
Empirical formula	$[CH_2CH(OH)]_n$	
Molecular weight	3000 g/mol	
Melting point	210°C	
Solubility	Water	

2-2-3- Linear Alkyl Benzene Sulfonate

Specification sheet		Structure of LAS
Empirical formula	$C_{11}H_{21}SO_3Na$	$H_3C-(CH_2)_n-CH-(CH_2)_m-CH_3$ 
Molecular weight	342.49 g/mol	
Melting point	277°C	
Solubility	Water	

2-2-4- Lambdacy holothrin (Pesticide)

Specification sheet		Structure of Lambdacy holothrin
Empirical formula	$C_{23}H_{19}ClF_3NO_3$	<p>(S) (Z) - (1R) - Cis</p> 
Molecular weight	449.9 g/mol	
Melting point	49.2°C	
Solubility	Water	<p>(R) (Z) - (1S) - Cis</p>  <p>[1α(s), 3α(z)]-(\pm)Cyano-(3-phenoxy phenyl)methyl-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl cyclopropane-carboxylate</p>

2-3- Preparation of Solutions

A solutions of 1000 ppm of pollutant (dye, polymer, pesticide or detergent) were prepared by dissolving 1g of pollutants in distilled water in 1L volumetric flask, thereafter solutions of different concentration were prepared by a subsequent dilution.

2-4- Determiration of λ_{max}

A sample of 1000 ppm pollutants solution were taken and a spectrum scan were measured using UV-Vis spectrophotometer. The pollutants showed different λ_{max} , which shown in Figs. (2-1), (2-2), (2-3), (2-4).

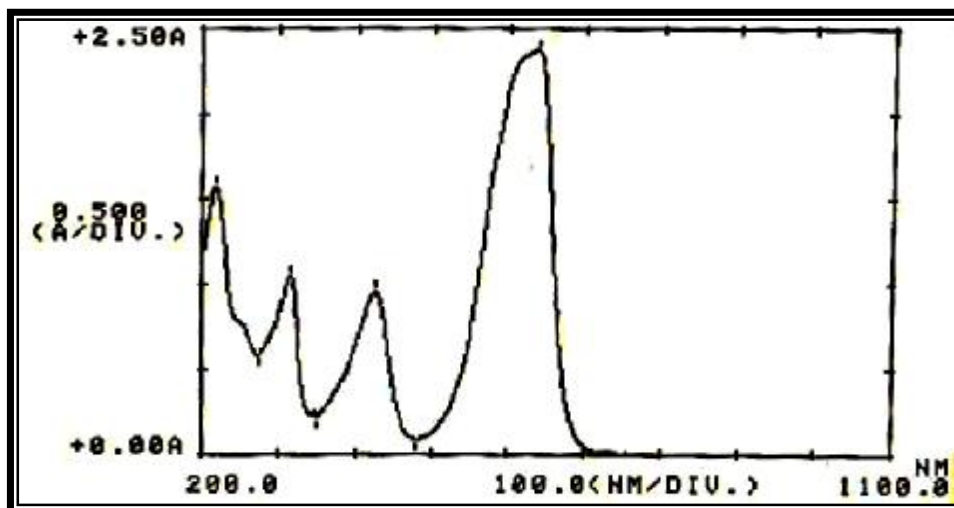


Fig.(2-1): The λ_{max} for 1000 ppm Brilliant blue solution at 636nm

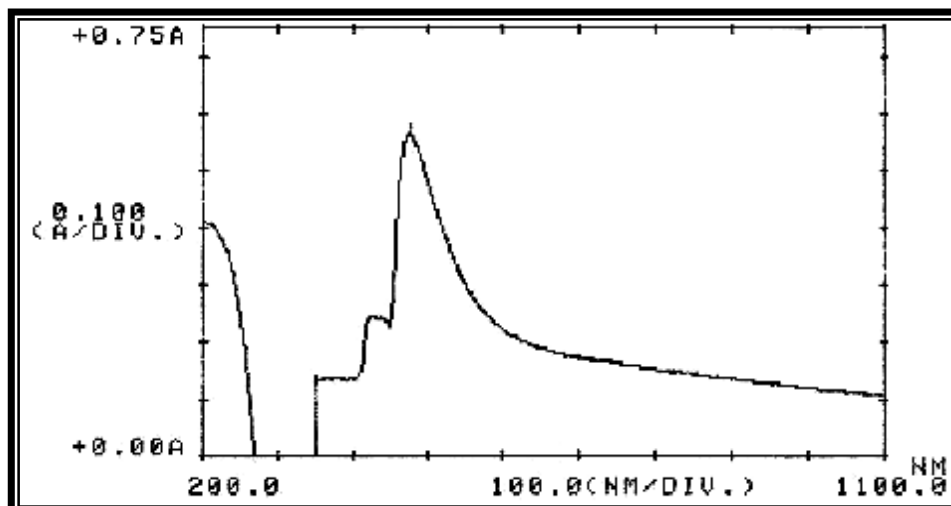


Fig.(2-2): The λ_{max} for 1000 ppm PVA solution at 472nm

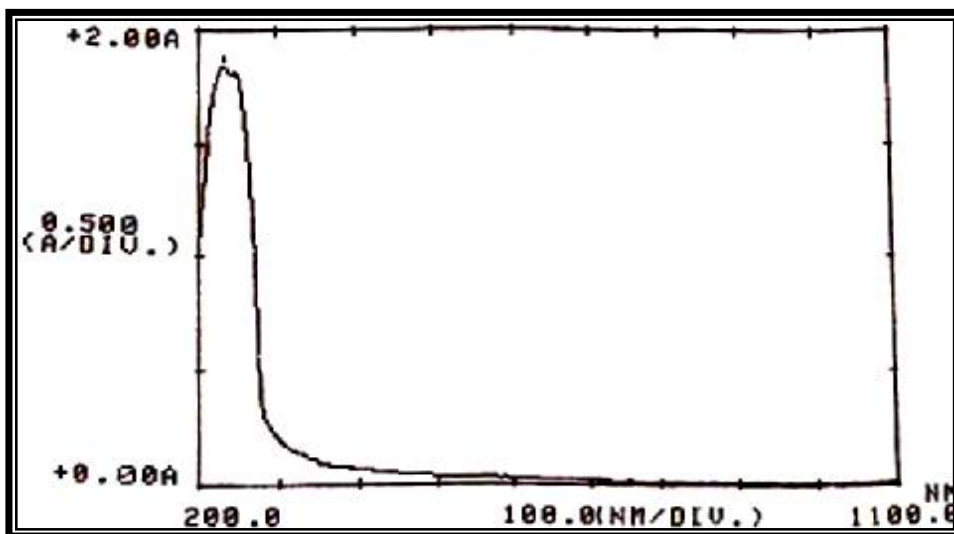


Fig.(2-3): The I_{\max} for 1000 ppm LAS solution at 234nm

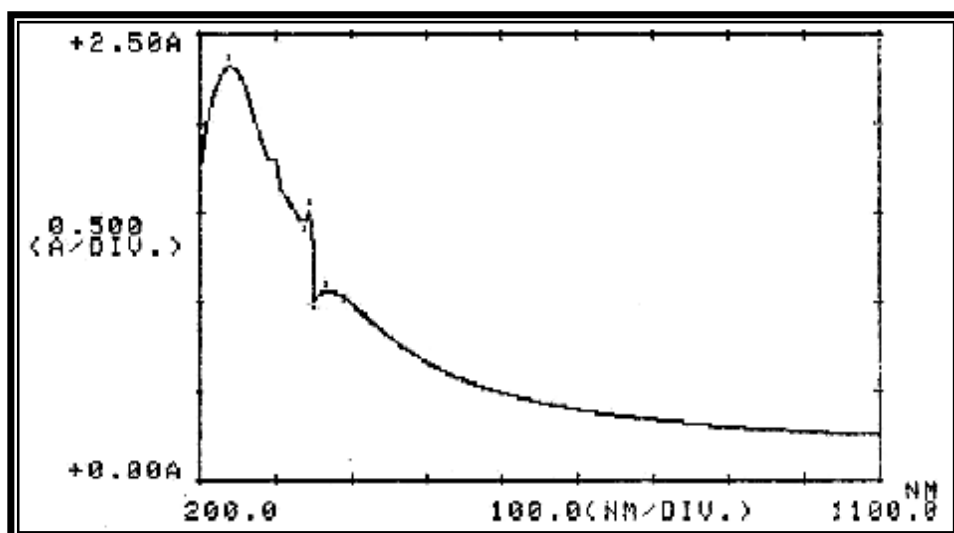


Fig.(2-4): The I_{\max} for 1000 ppm Lambdacy holothrin solution at 344nm

2-5- Calibration Curve

2-5-1- Birlliant Blue Solutions

The calibration curve was accomplished by measuring the absorbance of solution (10, 20, 30, 40, and 50 ppm) at 636 nm. Table (2-1) shows the absorbance of each solution, thereafter plotting of absorbance vs. concentration and as show in Fig.(2-5).

Table (2-1): Value of the absorbance for a series of Birlliant blue solutions

Concentration (ppm)	Absorbance
10	0.558
20	0.986
30	1.1417
40	1.731
50	1.927

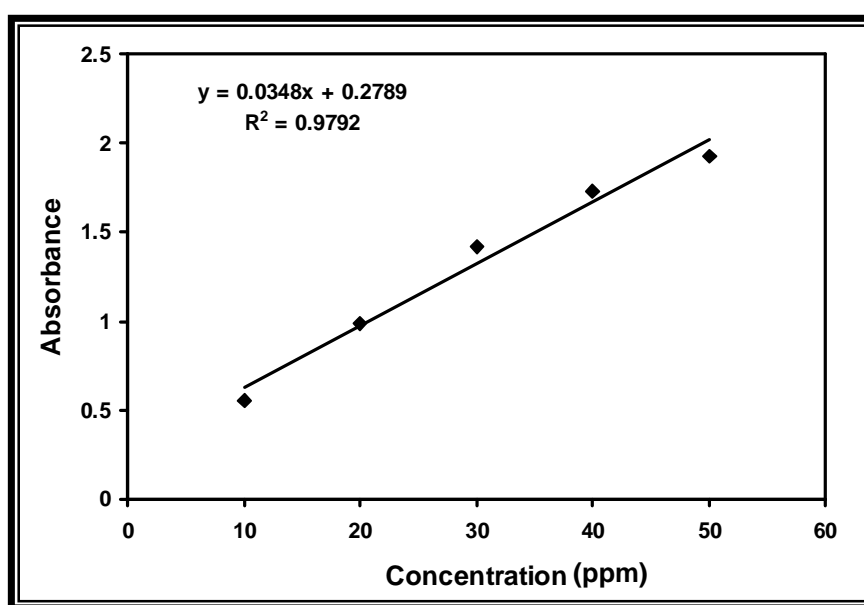


Fig.(2-5): The calibration curve of a series of Birlliant blue solutions

2-5-2- Polyvinyl Alcohol Solutions

The calibration curve was accomplished by measuring the absorbance of solutions (10, 20, 30, 40, 50, 75, and 100 ppm) at 472nm. Table (2-2) shows the absorbance of each solution, thereafter plotting of absorbance vs. concentration, gives the calibration curve as shown in Fig.(2-6).

Table (2-2): Value of the absorbance for a series of PVA solutions

Concentration (ppm)	Absorbance
10	0.167
20	0.239
30	0.401
40	0.556
50	0.628
75	1.021
100	1.041

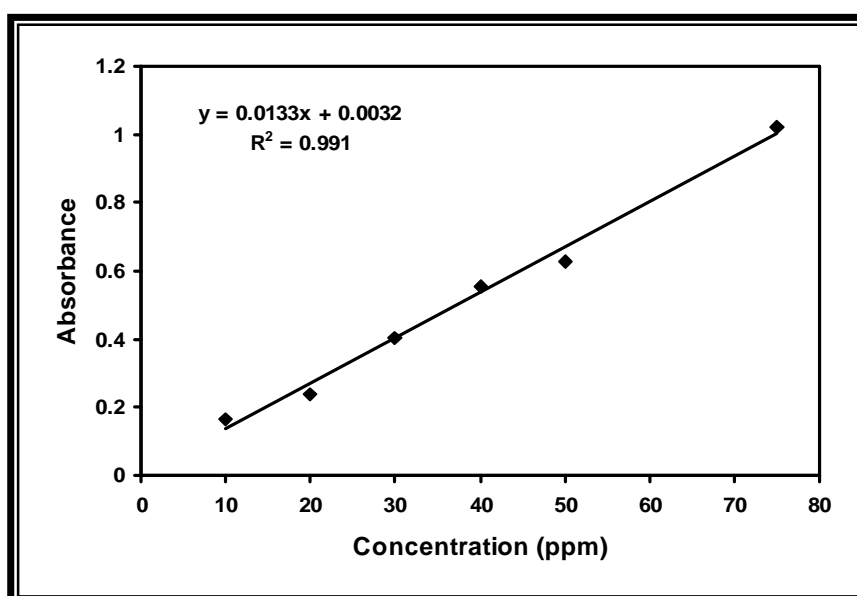


Fig.(2-6): The calibration curve of a series of PVA solutions

2-5-3- Linear Alkyl Benzene Sulfonate (LAS) Solutions

The calibration curve was accomplished by measuring the absorbance of solutions (10, 20, 30, 40, 50, 75, and 100 ppm) at 234nm. Table (2-3) shows the absorbance of each solution, thereafter plotting of absorbance vs. concentrations gives the calibration curve as shown in Fig.(2-7).

Table (2-3): Values of the absorbance for a series of LAS solutions

Concentration (ppm)	Absorbance
10	0.133
20	0.266
30	0.331
40	0.526
50	0.613
75	0.864
100	1.134

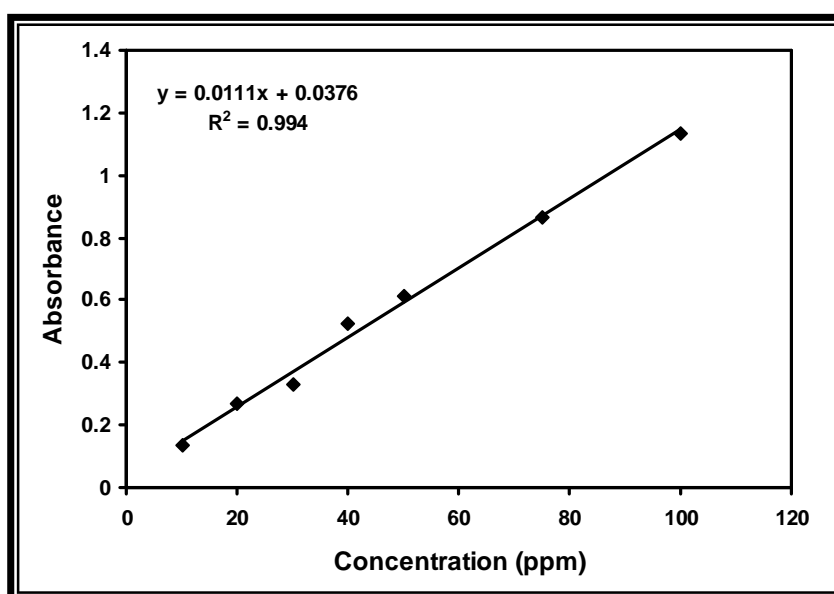


Fig.(2-7): The calibration curve of a series of LAS solutions

2-5-4- Lambdacy holothrin Solutions

The calibration curve was accomplished by measuring the absorbance of solutions (20, 50, 60, 80, and 100 ppm) at 344nm. Table (2-4) shows the absorbance of each solution, thereafter plotting of absorbance vs. concentrations gives the calibration curve as shown in Fig.(2-8).

Table (2-4): Values of the absorbance for a series of Lambdacy holothrin solutions

Concentration (ppm)	Absorbance
20	0.005
50	0.009
75	0.01
80	0.013
100	0.016

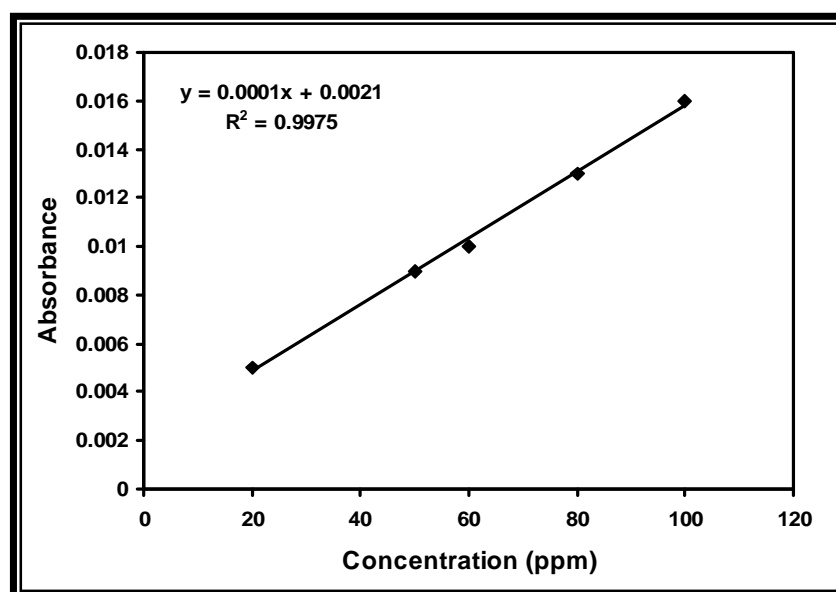


Fig.(2-8): The calibration curve of a series of Lambdacy holothrin solutions

2-6- Calculation of Adsorbat Quantity

The quantity of adsorbate was calculated by using the following formula:

$$Q_e = V_{\text{sol}} (C_o - C_e) / M \dots\dots\dots(2-1)$$

Where

Q_e = Quantity of adsorbate (mg/g).

V_{sol} = Total volume of adsorbate solution (L).

C_o = Initial concentration of adsorbate solutions (mg/L).

C_e = Concentration of adsorbate solution at equilibrium (mg/L).

M = Weight of adsorbate (g).

2-7- Calculation of Sorption Percentage

The percentage of sorption was calculation by using the following formula:

$$\%Q = \frac{(C_o - C_e)}{C_o} \times 100 \dots\dots\dots(2-2)$$

where

$\%Q$ = Sorption percentage.

C_o = Initial concentration of adsorbate solution (mg/L).

C_e = Final concentration of adsorbate solution (mg/L).

2-8- Effect of UV-Light Exposure on Solutions

Two flasks containing 10 mL of organic pollutants of different concentrations, and 1000 ppm were taken and irradiated by UV-light [$\lambda=(290-320 \text{ nm})$], for 1,2, and 3 hours, after 24 hours and at 20°C; thereafter, the absorbance of each solution was measured after the irradiation by U.V-Vis spectrophotometer.

2-9- Effect of Temperature on Sorption Process

A 0.1 g of adsorbent TiO_2 was added into a flask containing 10 mL of different concentrations of pollutants and shaken for 30 minutes and at different temperatures; thereafter, the solutions were filtered and the absorbance of each solution was measured by UV-Vis. Spectrophotometer.

2-10- Determination of Equilibrium Time

To determine the equilibrium time for the sorption process, a 0.1 g of adsorbent TiO_2 was added into a flask containing 10 mL of different concentrations at room temperature and for specific periods of time (5, 10, 20, 25 and 30 minutes). The time needed to reach the equilibrium was 30 minutes.

2-11- Effect of Contact Time

To determine the contact time, a 0.1g of adsorbent TiO_2 was added into a flask containing 10 mL of different concentrations at (288-318)K, and for 30 minutes, show the variation of Q_e with the contact time.

CHAPTER THREE



*Result and
Discussion*

3-1- Stability of Birlliant Blue Solutions

3-1-A- Thermal Stability

The study of the thermal stability of five concentration of dye was achieved after a constant time (30 min.), which revealed that dye is stable at temperature range (288-293)K.

Table (3-1-1), (3-1-2), (3-1-3), (3-1-4), and (3-1-5) show the absorbance of dye at different temperature after 30 min., the data obtained revealed that dye is entirely stable over range of temperatures and nondecompostable.

Table (3-1-1): The absorbance of 10 ppm Birlliant blue at different temperatures after 30 min at 636nm

10 ppm Birlliant blue solution	
T (°K)	Absorbance
288	0.511
289	0.470
291	0.54
293	0.498

Table (3-1-2): The absorbance of 20 ppm Birlliant blue at different temperatures after 30 min at 636nm

20 ppm Birlliant blue solution	
T (°K)	Absorbance
288	0.508
289	0.442
291	0.586
293	0.690

Table (3-1-3): The absorbance of 30 ppm Birlliant blue at different temperatures after 30 min at 636nm

30 ppm Birlliant blue solution	
T (°K)	Absorbance
288	0.341
289	0.347
291	0.449
293	0.375

Table (3-1-4): The absorbance of 40 ppm Birlliant blue at different temperatures after 30 min at 636nm

40 ppm Birlliant blue solution	
T (°K)	Absorbance
288	0.515
289	0.347
291	0.674
293	0.341

Table (3-1-5): The absorbance of 50 ppm Birlliant blue at different temperatures after 30 min at 636nm

50 ppm Birlliant blue solution	
T (°K)	Absorbance
288	0.515
289	0.391
291	0.581
293	0.432

3-1-B- Photo Stability of Birlliant Blue Dye

The photo stability of two concentration of dye revealed that dye is stable afterspecific periods of irradiation by UV-light (290-320)nm, the data obtained proved that the dye is non decomposable even at a prolonged period of exposure to UV-light, and as shown in Table (3-1-6).

Table (3-1-6): The absorbance of Birlliant blue after different irradiation time by UV-light (290-230)nm

C (ppm)	1 hrs.	2 hrs.	3 hrs.	24 hrs.
Absorbance				
40	0.220	0.222	0.224	0.224
1000	1.140	1.142	1.145	1.145

3-1-2- Contact Time

Tables (3-1-7), (3-1-8), (3-1-9), (3-1-10), and Fig.(3-1-1) show the variation of Q_e with the contact time for a solution of 40 ppm dye to be in an attachment with 0.1g of TiO_2 . The data obtained revealed that there was considerable increase in the value of Q_e at the temperature range (288-293)K with increase time upto constant Q_e value which indicate the equilibrium time⁽⁷⁸⁾.

Tables (3-1-7), (3-1-8), (3-1-9), (3-1-10): The values of Q_e and C_e at specific periods time for 40 ppm Brilliant blue at different temperatures

Table (3-1-7) at 288K

t (min.)	C_e (mg.L⁻¹)	Q_e (mg.g⁻¹)
0	0	0
5	3.25	3.67
10	4.05	3.59
20	4.16	3.58
25	6.66	3.33
30	6.78	3.32

Table (3-1-8) at 289K

t (min.)	C_e (mg.L⁻¹)	Q_e (mg.g⁻¹)
0	0	0
5	0.185	3.78
10	1.231	3.79
20	3.645	3.93
25	2.951	3.9
30	1.955	3.8

Table (3-1-9) at 291K

t (min.)	C_e (mg.L⁻¹)	Q_e (mg.g⁻¹)
0	0	0
5	4.169	3.58
10	4.134	3.67
20	4.112	3.58
25	7.731	3.22
30	11.353	2.86

Table (3-1-10) at 293K

t (min.)	C_e (mg.L⁻¹)	Q_e (mg.g⁻¹)
0	0	0
5	3.2	2.33
10	4.89	2.36
20	6.98	2.41
25	8.39	3.87
30	9.01	3.91

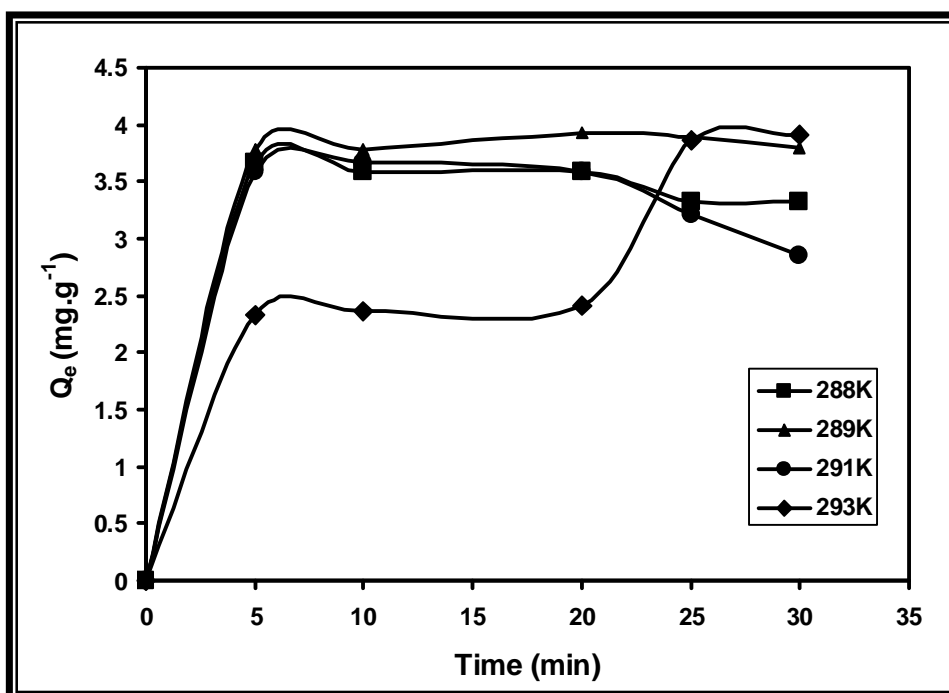


Fig.(3-1-1): The variation of Q_e with contact time for 40 ppm Brilliant blue solution at different temperatures

3-1-3- Adsorption Isotherms

Fig.(3-1-2) shows the adsorption isotherm (freundlich type) for different concentrations of dye at different temperatures after equilibrium (30 min.). In the heterogenous photocatalytic degradation process, adsorption of dye on the catalytic surface was assumed to be a primary step of the reaction⁽⁷⁸⁾. The adsorption experiments were carried out to evaluate the equilibrium quantity of adsorbate⁽⁷⁹⁾. According to the modern classification of isotherms, it is S-shapes isotherm, this may be due to a strong interaction between adsorbate and adsorbent⁽¹⁰⁾.

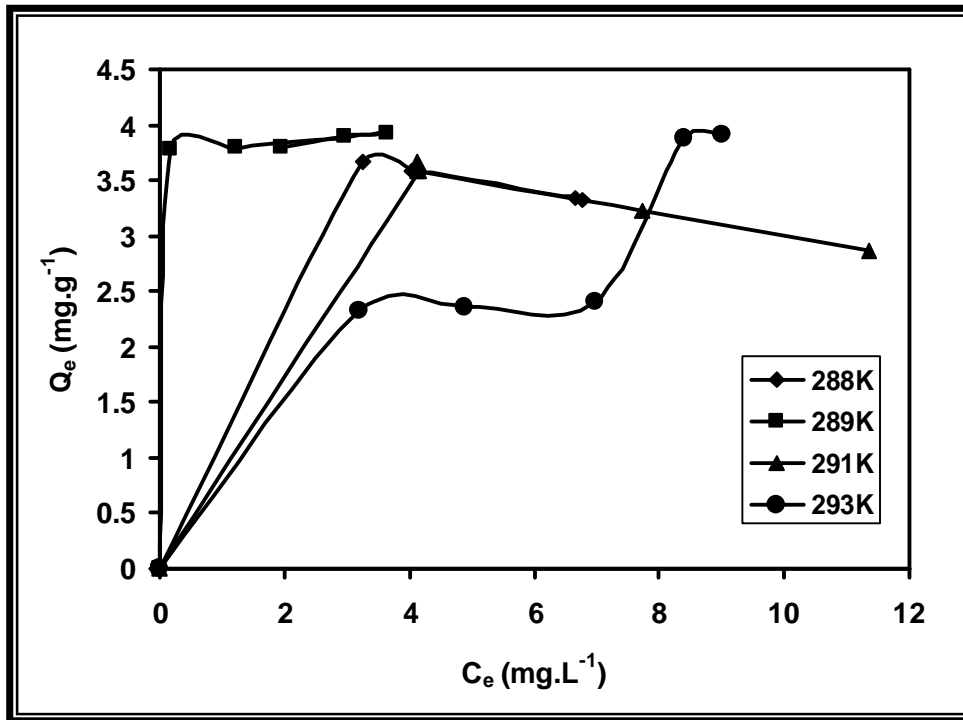
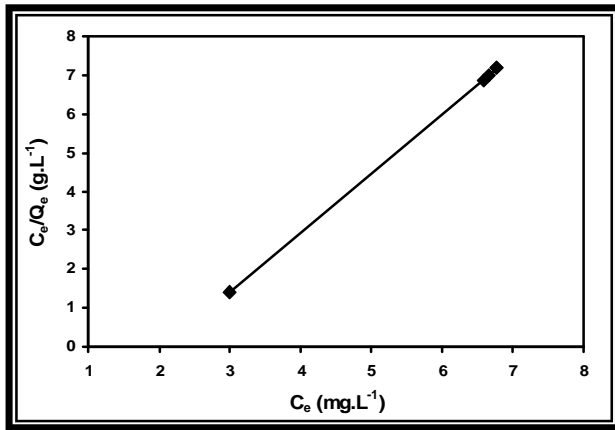


Fig. (3-1-2): The adsorption isotherms of different concentration of Birlliant blue on TiO₂ at different temperatures

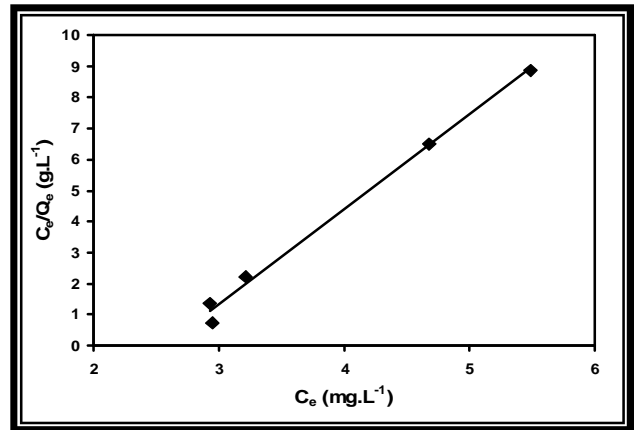
The plot of C_e/Q_e against C_e which represented in Table (3-1-11) indicate that Langmiur linear plot could be applied as show in Fig.(3-1-3).

Table (3-1-11): The values of C_e and C_e/Q_e for the sorption of different concentrations Birlliant blue dye at different temperatures

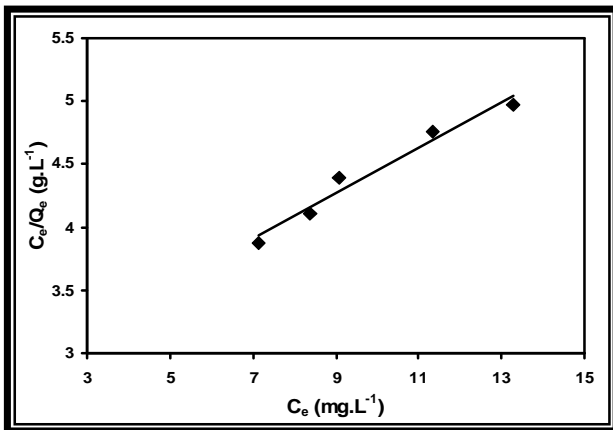
C_0	288K		289K		291K		293K	
	C_e (mg.L ⁻¹)	C_e/Q_e (g.L ⁻¹)	C_e (mg.L ⁻¹)	C_e/Q_e (g.L ⁻¹)	C_e (mg.L ⁻¹)	C_e/Q_e (g.L ⁻¹)	C_e (mg.L ⁻¹)	C_e/Q_e (g.L ⁻¹)
10	6.67	7.01	5.49	8.89	7.15	3.87	5.01	4.32
20	6.58	6.87	4.68	6.51	8.39	4.11	6.36	4.55
30	2.995	1.405	2.92	1.35	9.08	4.39	6.68	5.35
40	6.78	7.18	1.955	0.75	11.35	4.76	9.01	8.62
50	6.78	7.18	3.22	2.22	13.27	4.97	7.73	6.36



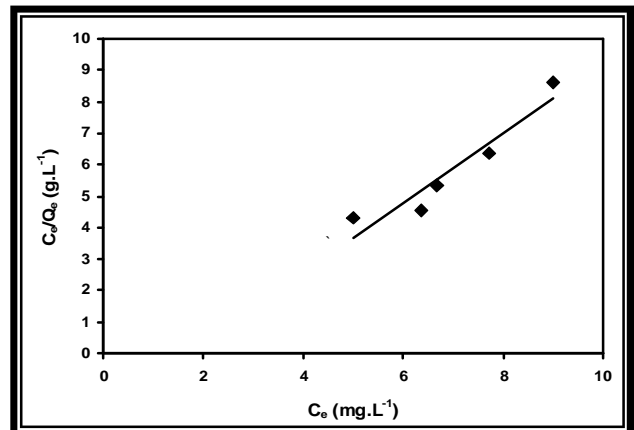
at 288K



at 289K



at 291K



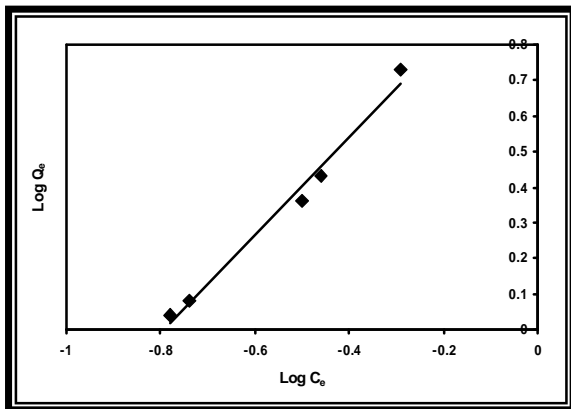
at 293K

Fig.(3-1-3): The plot of C_e/Q_e against C_e for the sorption of different concentrations of Birlliant blue on TiO_2 at different temperature

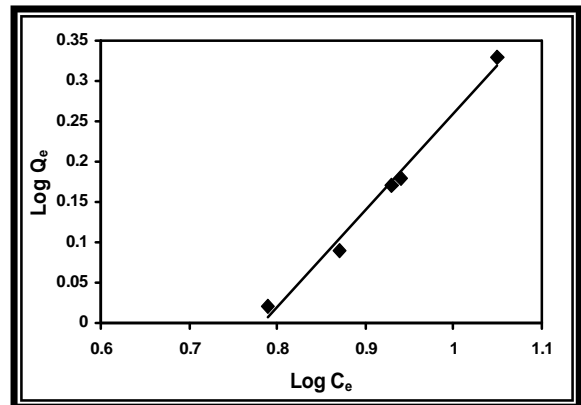
Table (3-1-12), and Fig.(3.1.4) shows the values of $\log Q_e$ against $\log C_e$

Table (3-1-12): The values of $\log Q_e$ and $\log C_e$ for the sorption of different concentrations Birlliant blue on TiO_2 at different temperatures

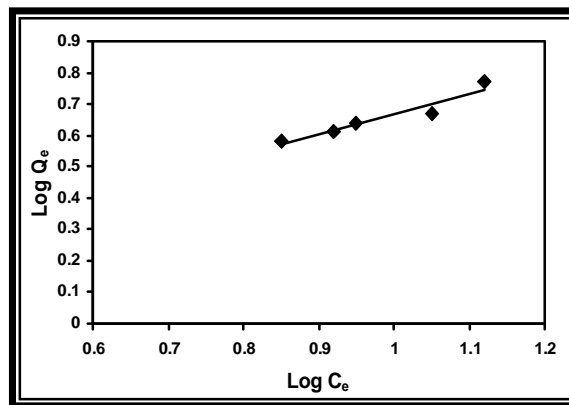
C_0	288K		289K		291K		293K	
	$\log C_e$	$\log Q_e$	$-\log C_e$	$\log Q_e$	$\log C_e$	$\log Q_e$	$\log C_e$	$\log Q_e$
10	0.82	0.2	0.74	0.08	0.85	0.58	0.69	0.63
20	0.81	0.21	0.64	0.04	0.92	0.61	0.80	0.65
30	0.47	0.39	0.46	0.43	0.95	0.64	0.82	0.72
40	0.83	0.2	0.29	0.73	1.05	0.67	0.95	0.93
50	0.83	0.2	0.5	0.36	1.12	0.77	0.88	0.80



at 289K



at 291K



at 293K

Fig.(3-1-4): The freundlich linear relation ship between log Q_e and log C_e for the sorption of different concentrations of Birlliant blue on TiO_2 at different temperatures

From this plot a very useful information were obtained by applying freundlich equation that has been formerly mentioned in chapter one.eq.1-3

Table (3-1-13): The freundlich and Langmiur constant for adsorption of dye on TiO₂ at different temperatures sorption isotherms

T	Langmiur			Freundlich		
	R ²	a	K _L	R ²	n	K _f
288	1	-0.48	-0.31	0.9993	1.8807	1.38
289	0.9942	-0.39	-0.12	0.9999	0.5405	1.56
291	0.9935	-0.064	0.047	0.9998	0.7448	0.083
293	0.9938	-0.066	0.044	0.9994	1.5119	1.44

For all that, many studies^(80,81) shows that freundlich constant have no obvious physical or chemical, meaning regarding the sorption processes at liquid-solid interfaces.

3-1-4- Effect of Sorbent Quantity

Fig.(3-1-5) shows the effect of the TiO₂ dose on the sorption process.

The plot of (C_o-C_e) against sorbent quantity m(g), indicated that the sorption increased as the quantity of sorbent increased. Then exhibited a maximum uptake at 0.1g of sorbent.

Table (3-1-14): The value of (C_o-C_e) and m (quantity of sorbent) for 40 ppm at 293K

m (g)	(C _o -C _e) (mg.L ⁻¹)
0.05	38.72
0.1	40.45
0.2	39.99
0.3	38.88
0.4	39.03

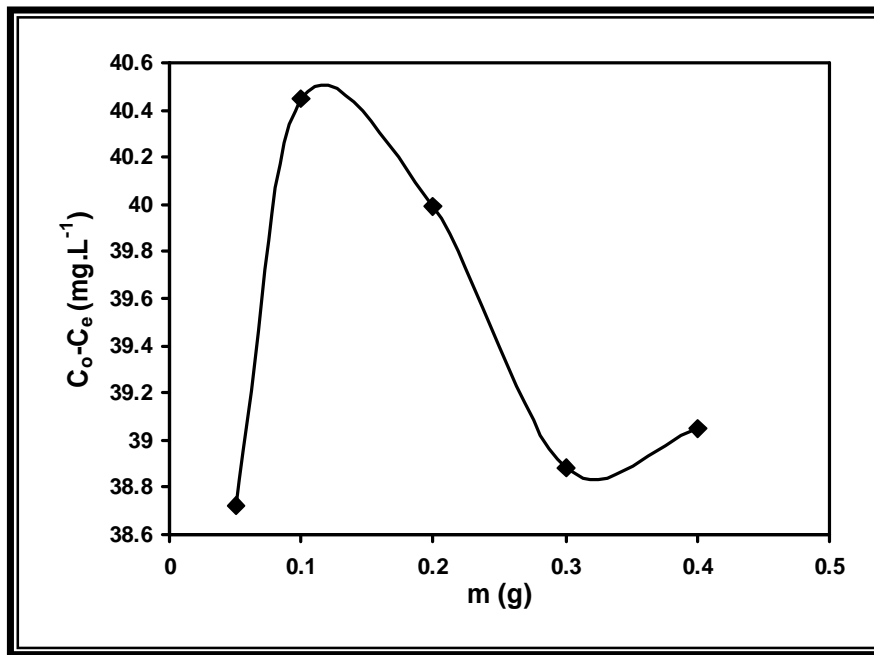


Fig.(3-1-5): The effect of TiO₂ on the sorption process for 40 ppm Brilliant blue at 293K

3-1-5- Effect of Temperature on Sorption Process

Table (3-1-15), and Fig.(3-1-6) show that the sorption percentage decrease as the temperature increase.

Knowing that the adsorption process is an exothermic process⁽²⁾, while the absorption process is an endothermic process. However, the sorption process could be exothermic or endothermic depending on the dominant process, in other words the adsorption or absorption or both of them.

Following the sorption percentage in Fig.(3-1-6), reveals at 288-293 K, the sorption percentage decreased, and then the proposed mechanism is adsorption, since it is an exothermic process.

Table (3-1-15): The sorption percentage and C_e values for 40 ppm at different temperature

T (K)	C_e (mg.L ⁻¹)	%Q
288	6.78	95.54
289	1.955	95.11
291	11.353	71.61
293	9.01	66.82

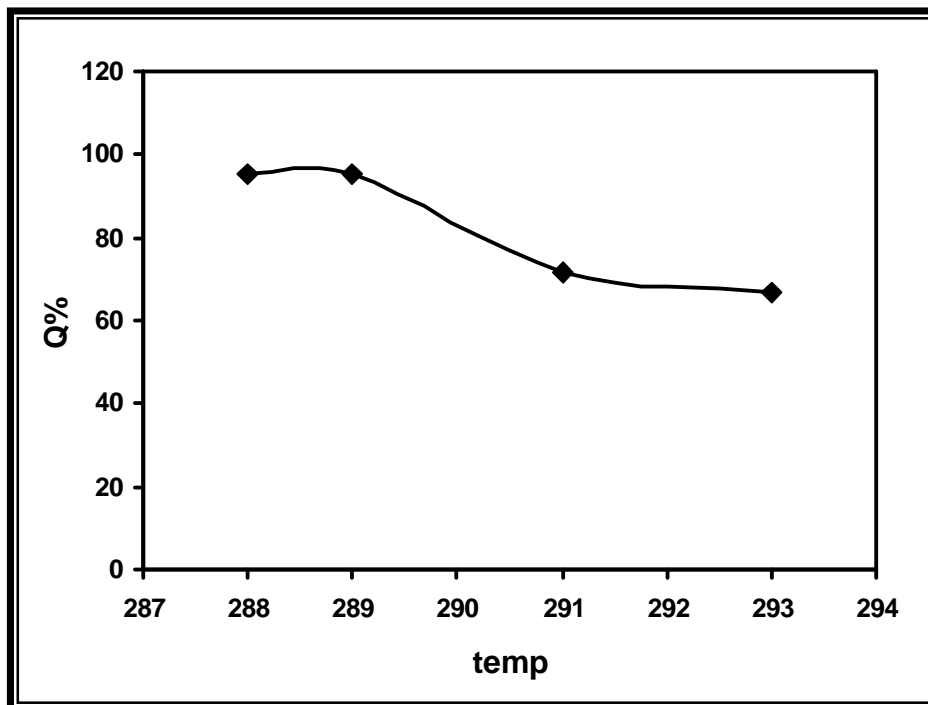


Fig.(3-1-6): The effect of temperature on the sorption percentage for 40 ppm

3-1-6- Effect of Time on Sorption Process

Table (3-1-16), and Fig.(3-1-7) show that the sorption percentage almost increases as the time increase to 20 min. at different temperature.

Table (3-1-16): The sorption percentage at different time

288K		289K		291K		293K	
t (min)	%Q _e	t (min)	%Q _e	t (min)	%Q _e	t (min)	%Q _e
0	0	0	0	0	0	0	0
5	70.7	5	89.07	5	89.57	5	58.35
10	78.44	10	94.93	10	91.87	10	57.77
20	88.71	20	98.41	20	89.72	20	53.52
25	94.67	25	97.5	25	80.67	25	96.97
30	95.54	30	95.11	30	71.61	30	66.82

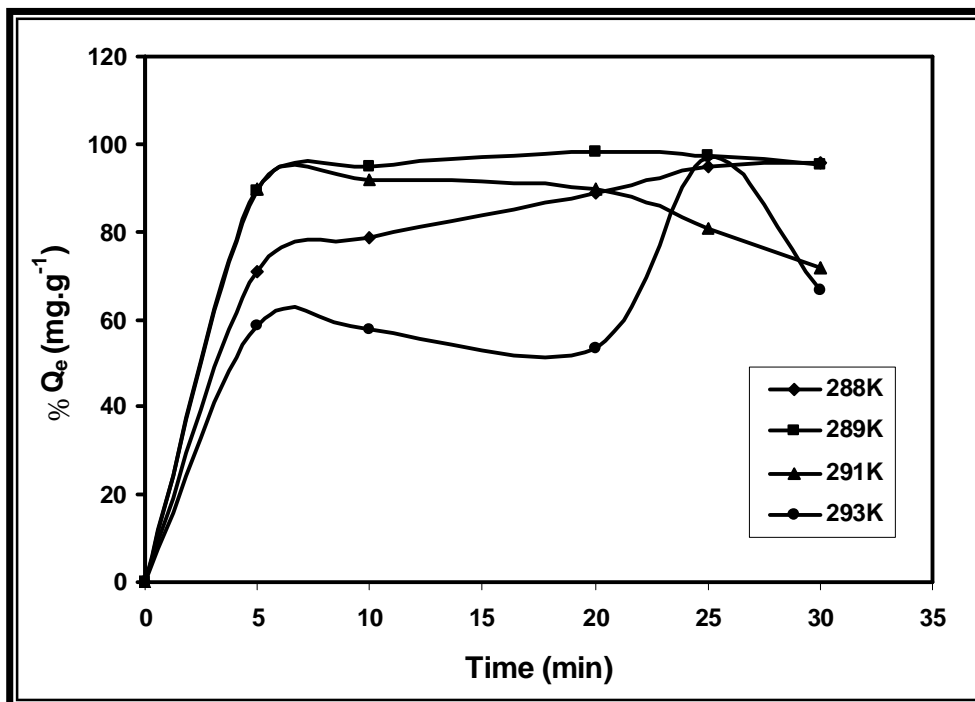


Fig.(3-1-7): Effect of time on sorption percentage

3-1-7- Effect of Initial Brilliant Blue Dye Concentration on Sorption Process⁽⁸¹⁾

Table (3-1-17), and Fig.(3-1-8) show the variation of sorption percentage with different initial concentrations of the dye.

The data shows the high efficiency of TiO₂ to adsorbed dye at the temperature range (288-293 K). When the initial concentration of dye increase, dye molecules are adsorbed on to the surface of TiO₂ upto maximum value then the efficiency decreased^(82,83).

Table (3-1-17): The sorption percentage at different initial of dye concentration after 30 minute at different temperatures

288K		289K		291K		293K	
C _o	%Q _e	C _o	%Q _e	C _o	%Q _e	C _o	%Q _e
10	73.83	10	45.09	10	25	10	37.1
20	90.21	20	76.57	20	58.8	20	46.8
30	89.36	30	93.58	30	79.2	30	90.2
40	95.54	40	95.11	40	71.61	40	89.62
50	93.61	50	93.55	50	32.63	50	73.46

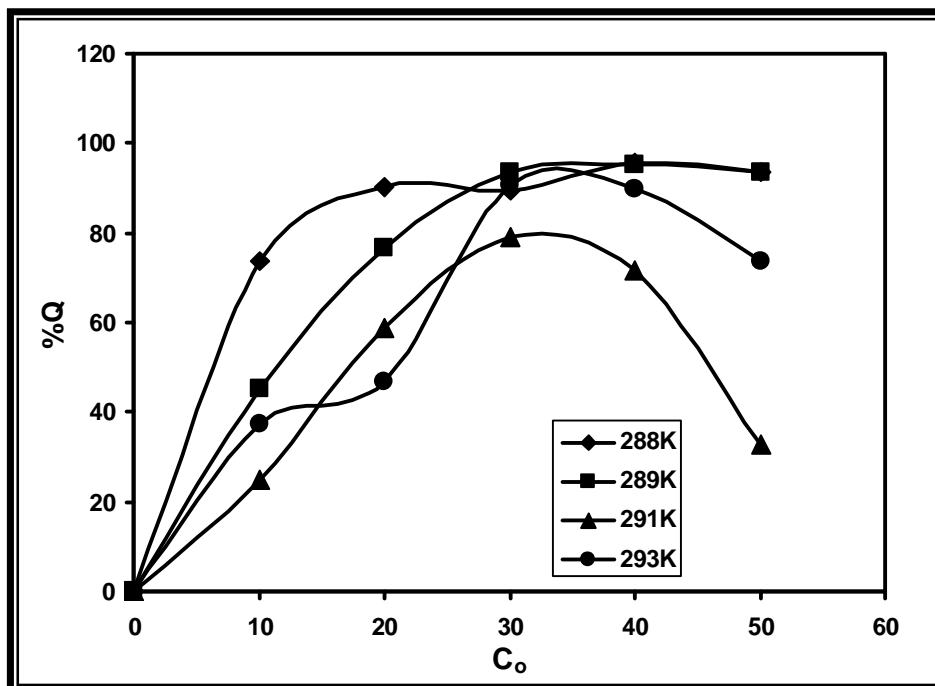


Fig.(3-1-8): Effect of initial of dye concentration on sorption percentage

3-1-8- Calculation of Thermodynamic Function of Sorption

The thermodynamic function ΔH , ΔG , and ΔS were calculated using the following formulas:

$$b = a \cdot \exp (-\Delta H/RT) \dots\dots\dots(3-1)$$

$$\ln b = \ln a - (\Delta H/R) \cdot 1/T \dots\dots\dots(3-2)$$

$$\ln a = \Delta S/R \dots\dots\dots(3-3)$$

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots(3-4)$$

Where b is the maximum sorption quantity for 50 ppm dye solutions on TiO_2 and could be obtained from the plot of C_e/Q_e versus C_e Fig.(3-1-3).

The equation(3-2) was used to calculated the ΔH , by plotting of $\ln b$ versus $1/T$.

Table(3-1-15), Fig.(3-1-6), showed a linear relationship and the slope represents $-\Delta H/R$, R is the gas constant ($8.314 \text{ JK}^{-1} \cdot \text{mol}^{-1}$). And the values of ΔH of sorption were calculated.

Table (3-1-18): The values of the reciprocal of temperature and $\ln b$

T (K)	$\frac{1}{T \cdot 10^{-3}}$	b	$\ln b$
288	3.47	3.32	1.19
289	3.46	3.40	1.22
291	3.43	3.86	1.35
293	3.41	3.91	1.36

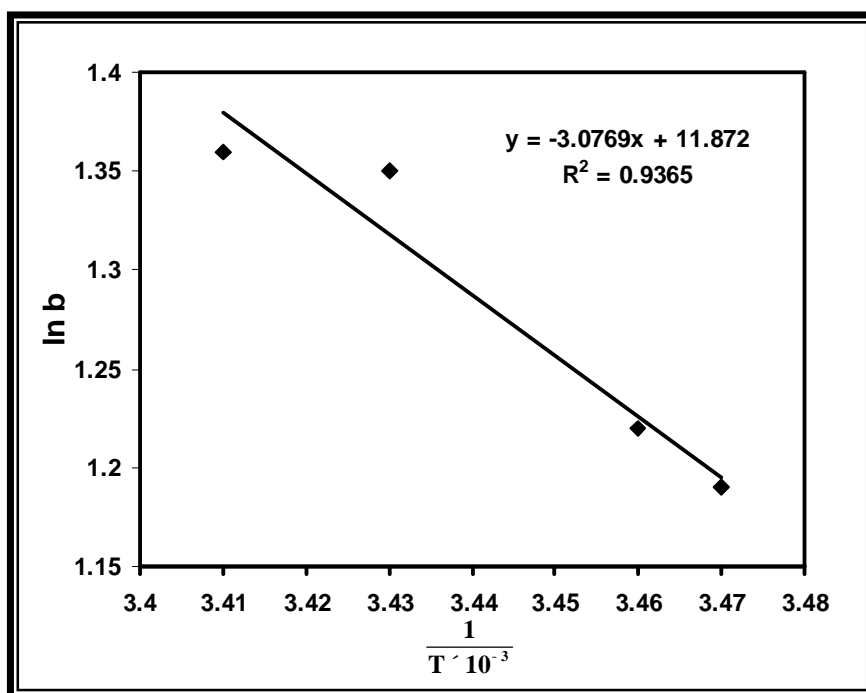


Fig.(3-1-9): The plot of $\ln b$ vs. the reciprocal of temperature

Table (3-1-19): The thermodynamic function values for the dye sorption process at different temperatures

T (K)	DH (J.mol ⁻¹)	DG (J.mol ⁻¹)	DS (J.mol ⁻¹ .K ⁻¹)
288	+25.58	-966.86	+3.446
289	+5.962	-975.12	+9.1906
291	+17.73	-985.05	+3.446
293	+26.57	-999.8	+3.503

Table (3-1-19) shows the positive values (endothermic process of the ΔH at 288, 289, 291, and 293K, which indicate the process is almost absorption process.

Table (3-1-19) shows that all values of ΔG were negative, so the sorption of dyes on the surface of TiO_2 was considered a spontaneous process⁽⁸⁴⁾.

The equation (3-3) has been used to calculate the entropy (ΔS), which is an important factor in the sorption process, and table (3-1-19) shows positive values of ΔS . which indicate to the disorder of the system.

3-1-9- Kinetic of Sorption Process

The kinetic of sorption process was studied via introducing three models, there after calculate the rate constant and the energy of activation of sorption process.

3-1-9-A- Lagergren Model

The rate constant k_{sorp} was determined from the following pseudo-1st order rate expression, which could be expressed as follows:

$$\ln (q_e - q_t) = \ln q_e - k_{\text{sorp}} t \dots\dots\dots(3-5)$$

Where q_t and q_e are the amount sorbed at time $t/\text{min.}$ and at equilibrium time successively, and $k_{\text{sorp}} / \text{min}^{-1}$ is the rate constant, all values are given in Tables (3-1-20),(3-1-22),(3-1-24), and (3-1-26).

The liner relationship was obtained via $\ln (q_e - q_t)$ versus $t / \text{min.}$, and as shown in Fig.(3-1-10).

Table (3-1-20): The parameters of Lagergren equation at 288 K

10 mg/L				20 mg/L			
T (min)	q _t	(q _e -q _t)	ln(q _e -q _t)	t (min)	q _t	(q _e -q _t)	ln(q _e -q _t)
5	0.902	0.569	-0.31	5	1.82	0.48	-0.73
10	0.792	0.459	-0.7	10	1.709	0.36	-0.99
20	0.63	0.297	-1.51	20	1.57	0.23	-1.46
25	0.422	0.089	-2.4	25	1.47	0.12	-2.04
30 mg/L				40 mg/L			
T (min)	q _t	(q _e -q _t)	ln(q _e -q _t)	t (min)	q _t	(q _e -q _t)	ln(q _e -q _t)
5	2.74	0.09	-2.44	5	3.67	0.35	-0.63
10	2.72	0.07	-2.53	10	3.59	0.27	-1.3
20	2.65	0	∞	20	3.58	0.26	-2.94
25	2.71	0.06	-2.8	25	3.33	0.01	-4.6
50 mg/L							
t (min)		q _t	(q _e -q _t)	ln(q _e -q _t)			
5		4.64	0.32	-0.66			
10		4.61	0.29	-1.23			
20		4.59	0.27	-2.7			
25		4.33	0.01	-4.6			

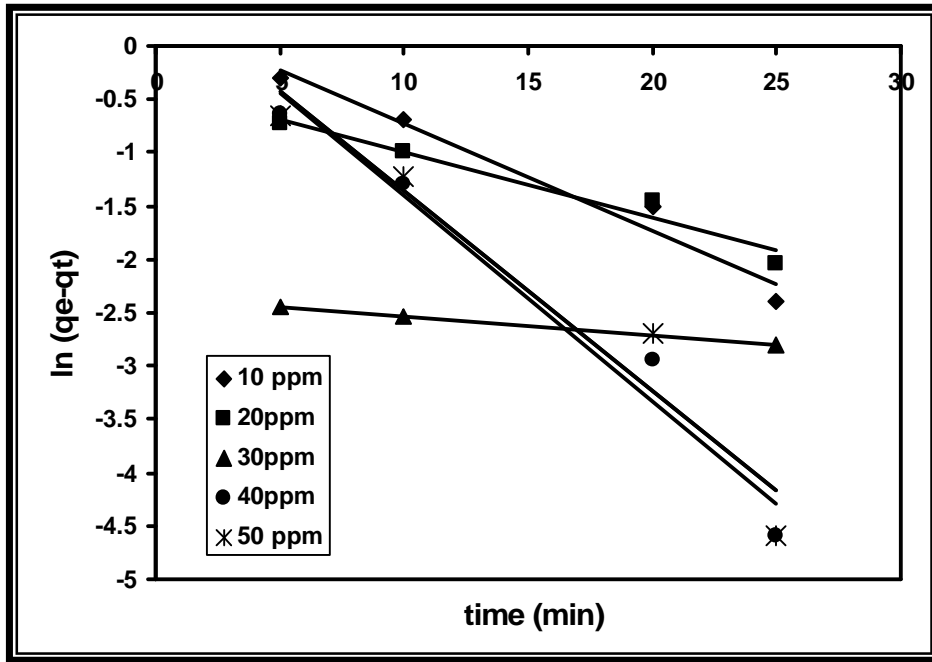


Fig.(3-1-10): The Lagergren kinetic model at 288 K

Table (3-1-21): The rate constants of adsorption process at 288 K

C_o	$k_{ad} (min.^{-1})$
10	0.0414
20	0.265
30	0.689
40	0.386
50	0.438

Table (3-1-22): The parameters of Lagergren equation at 289 K

10 mg/L				20 mg/L			
t (min)	q _t	(q _e -q _t)	ln(q _e -q _t)	t (min)	q _t	(q _e -q _t)	ln(q _e -q _t)
5	0.89	0.47	-0.83	5	1.83	0.3	-0.88
10	0.85	0.43	-0.903	10	1.91	0.38	-1.35
20	0.63	0.21	-1.047	20	1.64	0.11	-2.27
25	0.43	0.47	-1.119	25	1.48	0.05	-2.74
30 mg/L				40 mg/L			
t (min)	q _t	(q _e -q _t)	ln(q _e -q _t)	t (min)	q _t	(q _e -q _t)	ln(q _e -q _t)
5	2.94	0.11	-2.2	5	3.78	0	∞
10	2.94	0.1	-2.3	10	3.79	0	∞
20	2.9	0.06	-3.7	20	3.93	0.13	-2.04
25	2.85	0.01	-4.6	25	3.9	0.1	-2.3
50 mg/L							
t (min)	q _t	(q _e -q _t)	ln(q _e -q _t)				
5	4.81	0.14	-1.96				
10	4.81	0.13	-1.87				
20	4.97	0.3	-1.707				
25	4.81	0.14	-1.62				

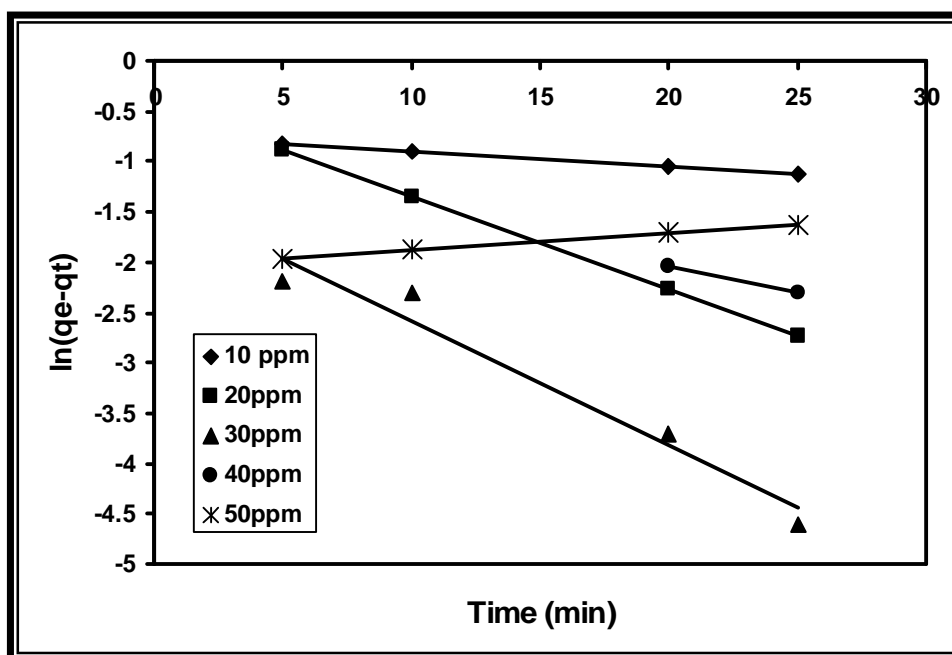


Fig.(3-1-11): The Lagergren kinetic model at 289 K

Table (3-1-23): The rate constants of adsorption process at 289 K

C_o	$k_{ad} (min.^{-1})$
10	0.1428
20	0.296
30	0.655
40	0.681
50	0.706

Table (3-1-24): The parameters of Lagergren equation at 291 K

10 mg/L				20 mg/L			
t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$	t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$
5	0.88	0.63	-0.46	5	1.91	0.79	-0.37
10	0.85	0.6	-0.51	10	1.67	0.55	-0.46
20	0.64	0.39	-0.51	20	1.56	0.44	-0.64
25	0.61	0.36	-1.062	25	1.68	0.56	-0.73

30 mg/L				40 mg/L			
t (min)	q _t	(q _e -q _t)	ln(q _e -q _t)	t (min)	q _t	(q _e -q _t)	ln(q _e -q _t)
5	2.63	0.26	-0.81	5	3.58	0.72	-0.16
10	2.81	0.44	-0.76	10	3.67	0.81	-0.31
20	2.91	0.54	-0.66	20	3.58	0.72	-0.61
25	2.67	0.3	-0.61	25	3.22	0.36	-1.02

50 mg/L			
t (min)	q _t	(q _e -q _t)	ln(q _e -q _t)
5	4.61	0.48	-0.52
10	4.6	0.47	-2.24
20	4.58	0.45	-1.17
25	4.24	0.11	-1.17

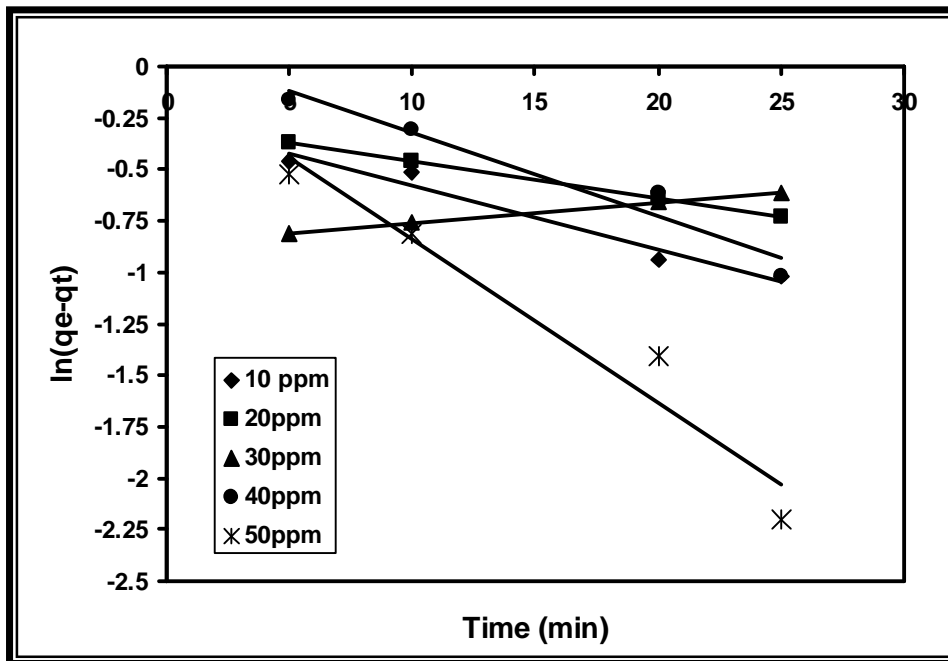


Fig.(3-1-12): The Lagergren kinetic model at 291 K

Table (3-1-25): The rate constants of adsorption process at 291 K

C_o	$k_{ad} \text{ (min.}^{-1}\text{)}$
10	0.0666
20	0.203
30	0.355
40	0.287
50	0.409

Table (3-1-26): The parameters of Lagergren equation at 293 K

10 mg/L				20 mg/L			
t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$	t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$
5	0.61	0.24	-2.56	5	1.71	0.9	-0.25
10	0.39	0.02	-2.24	10	1.39	0.58	-0.75
20	0.06	0.31	-1.17	20	0.76	0.05	-1.75
25	0.06	0.31	-1.17	25	0.56	0.25	-2.25
30 mg/L				40 mg/L			
t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$	t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$
5	1.8	0.92	-0.57	5	2.33	1.58	0.98
10	1.15	1.57	-0.06	10	2.36	1.55	0.43
20	1.95	0.74	-1.34	20	2.44	1.47	-1.22
25	2.67	0.05	-1.95	25	3.87	0.04	-1.96
50 mg/L							
t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$				
5	4.92	0.36	-1.17				
10	4.77	0.21	-1.21				
20	4.16	0.4	-1.3				
25	4.35	0.21	-1.34				

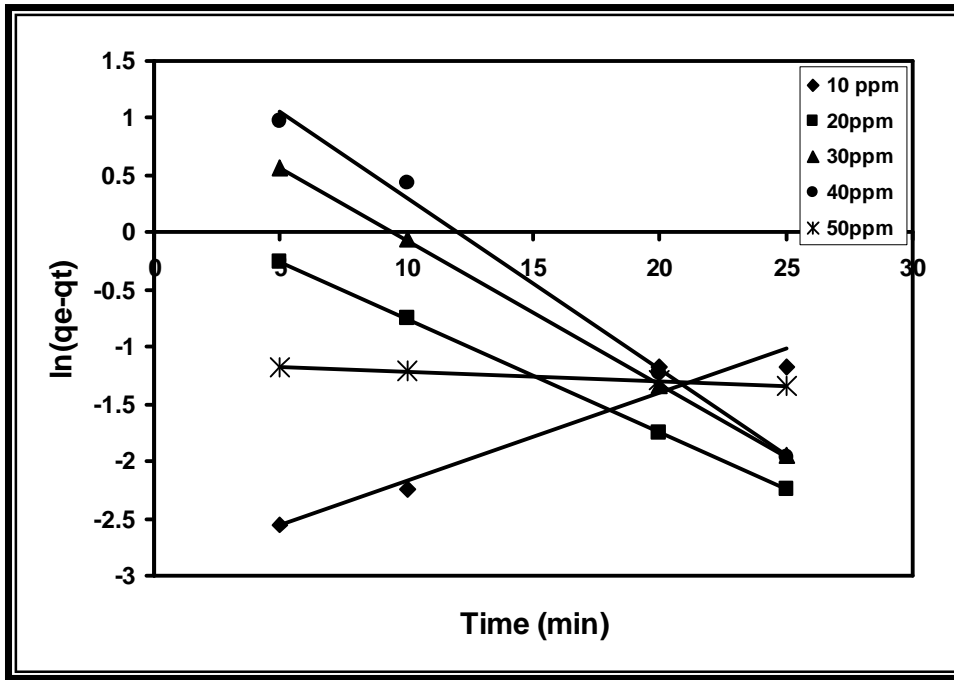


Fig.(3-1-13): The Lagergren kinetic model at 293 K

Table (3-1-27): The rate constants of adsorption process at 293 K

C_o	$k_{ad} (min.^{-1})$
10	0.4132
20	0.157
30	0.0035
40	0.026
50	0.552

3-1-9-B- Morris-Weber Model⁽⁷⁴⁾

This kinetic model was introduced by Morris and Weber (Swedish Scientists)) in 1963, and by using this kinetic model, the rate limiting step of any physi-sorption process could be easily estimated, and they have presented an equation which could be expressed as follows:

$$q_t = k_d \sqrt{t} \dots \dots \dots (3-6)$$

Where q_t is the quantity of the sorbed material at any time (mg/g). k_d is the diffusion constant, and t is the time of diffusion (min). The

plotting of q_t versus \sqrt{t} was accomplished at 289, and 293K and as shown below in Fig.(3-1-14), and (3-1-15).

Table (3-1-28): The Morris-Weber parameters at 289K

t (min)	\sqrt{t}	q_t (mg.g ⁻¹)
5	2.23	3.78
10	3.16	3.79
20	4.47	3.93
25	5.0	3.94
30	5.4	3.96

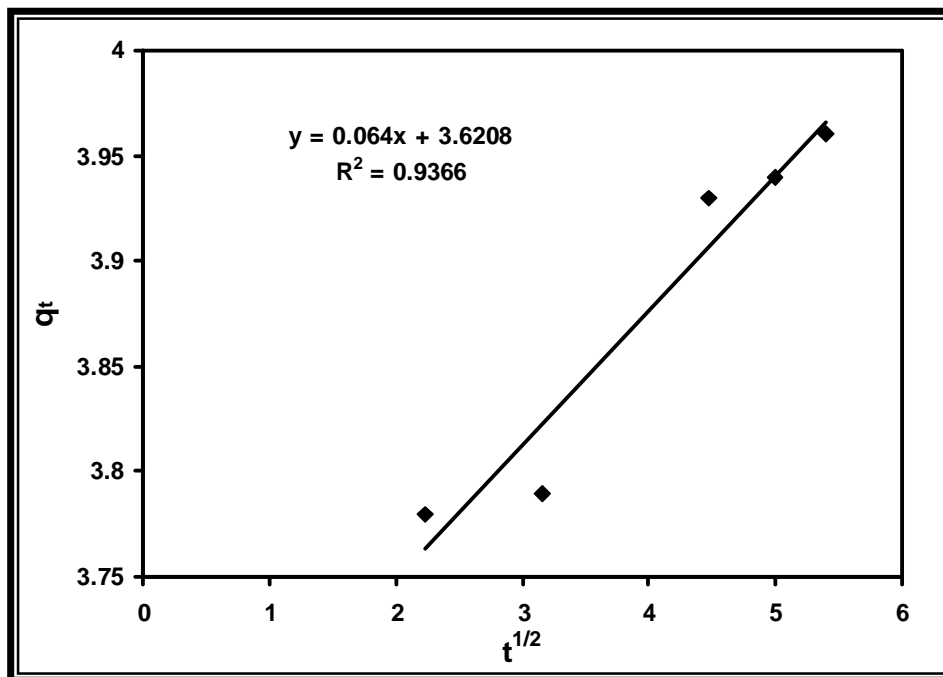


Fig.(3-1-14): The plot of q_t vs. $t^{1/2}$ at 289 K

Table (3-1-29): The Morris-Weber parameters at 293K

t (min)	\sqrt{t}	q_t (mg.g ⁻¹)
5	2.23	2.33
10	3.16	2.36
20	4.47	3.44
25	5.0	3.87
30	5.4	3.91

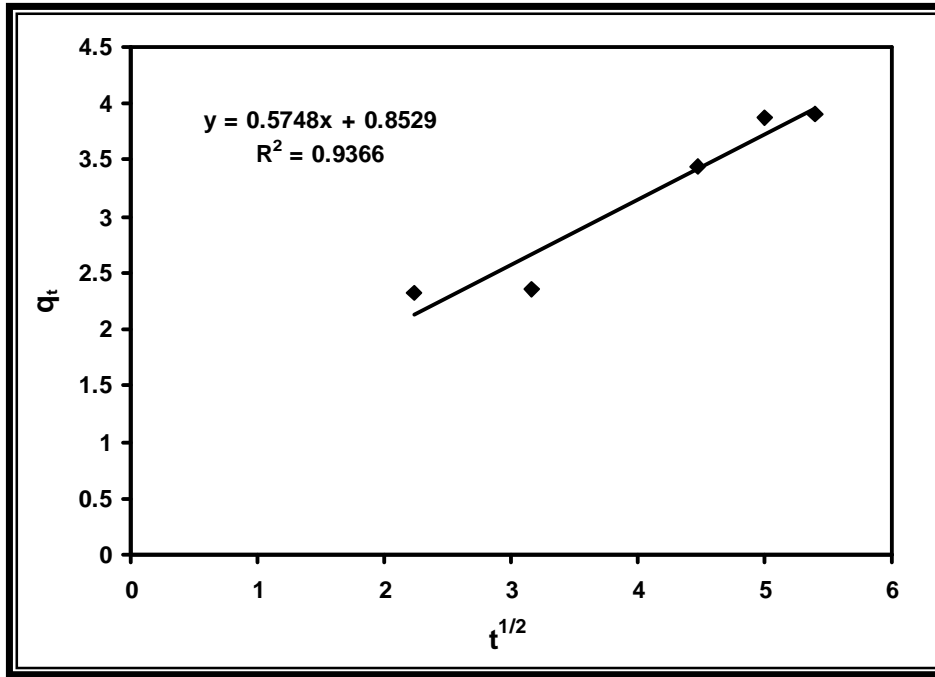


Fig.(3-1-15): The plot of q_t vs. $t^{1/2}$ at 293K

The slope represents the k_d value, which was considerably greater at 289 K than at 293 K, and this was attributed to the following reasons:

- 1- Brilliant blue dye adsorbed on TiO_2 from the solution.
- 2- A strong binding between the adsorbate and adsorbent.
- 3- The value of k_d at 289 K was 1.269, and at 293K was 1.291.

3-1-9-C- Reichenbery Model⁽⁷⁴⁾

This kinetic model was proposed to discuss the behaviors of many sorption processes in solution and Reichenbery has introduced the following formula:

$$F = [1 - 6/\pi^2] e^{-Bt} \dots\dots\dots(3-7)$$

$$B_t = -0.4977 - \ln(1-F) \dots\dots\dots(3-8)$$

$$F = q_t / q_e \dots\dots\dots(3-9)$$

Plotting of time (min.) versus B_t revealed a linear relationship with relatively acceptable R^2 value and as shown in Fig.(3-1-16).

According to this model, it characterized the rate determining mechanism which was a diffusion process for the dye molecules in the bulk solution and absorption occurred.

Table (3-1-30): The change of Reichenberg parameters with time

B_t	t (min)
2.1745	5
2.2683	10
2.4323	20
5.5723	25

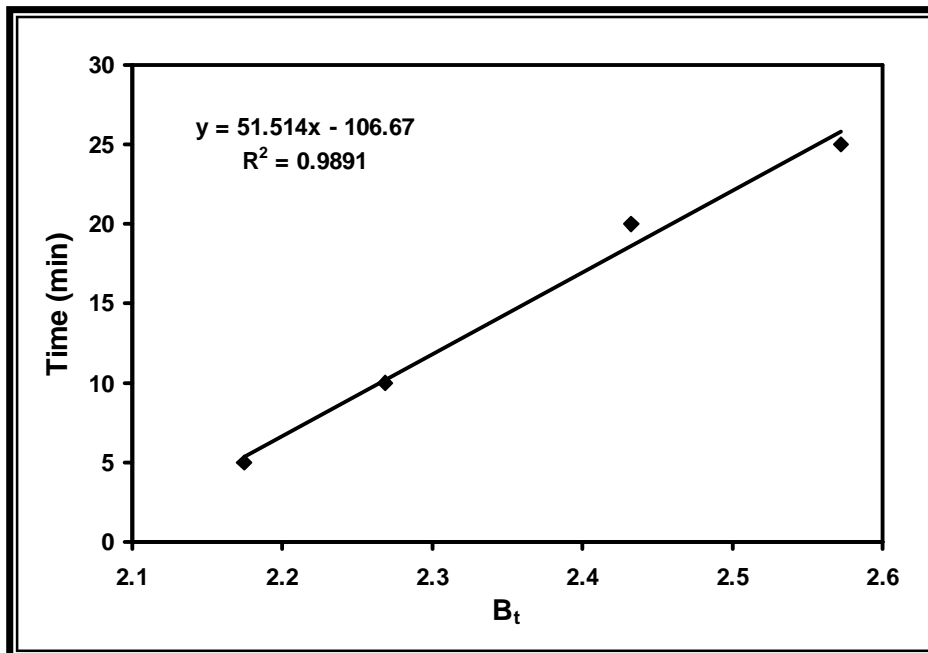


Fig.(3-1-16): The variation of B_t with time

3-1-9-E- Activation Energy Calculation

The activation energy of the sorption process was calculated via introducing Arrhenius equation as shown:

$$\ln k_{\text{sorp}} = \ln A - E_a / RT \dots\dots\dots(3-10)$$

where k_{sorp} are calculated from Lagergreen equations and A is Arrhenius parameter, which is a temperature independent factor in the temperature study range (288-293) K.

E_a is the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$) and R is the gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), and T is the temperature in Kelvin.

Plotting of $\ln k_{\text{sorp}}$ against the reciprocal of temperature in K^{-1} yield Fig.(3-1-17), and as shown below.

Table (3-1-31): The values of rate constant at different temperature (reciprocal of temperature)

$\frac{1}{T} \cdot 10^{-3}$	k_{sorp}	$\ln k$
3.47	0.265	-1.32
3.46	0.269	-1.21
3.43	0.203	-1.59
3.41	0.157	-1.85

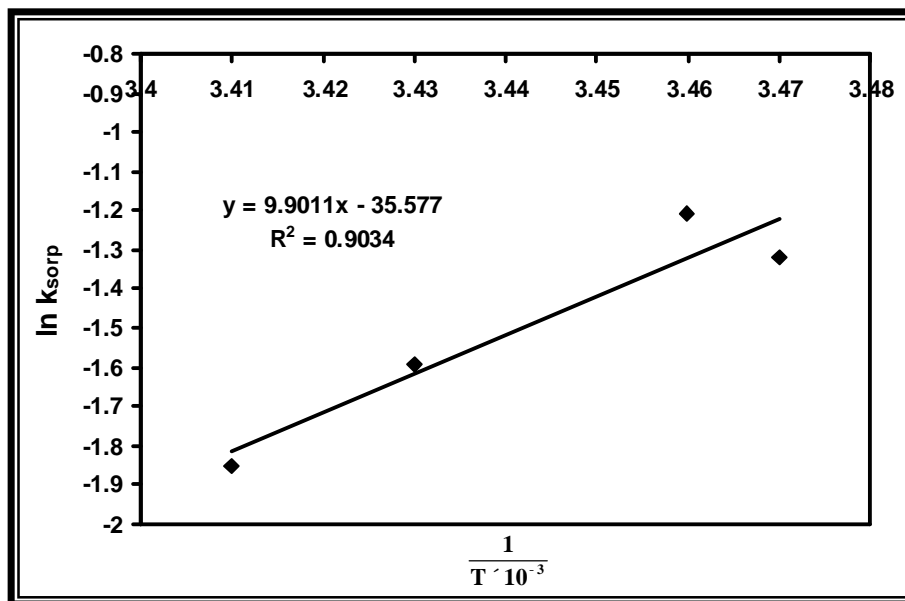


Fig.(3-1-17): The plot of $\ln k_{\text{sorp}}$ vs. reciprocal of temperature

This Fig.(3-1-17), reveals a linear relationship between the $\ln k_{\text{sorp}}$ and the reciprocal of temperature and thereafter from the slope, the value of E_a was obtained.

The value of E_a has a very important role in estimating the dynamic of the sorption process, and it represents the energy barrier for a process to occur, the activation energy of the sorption process was equal to 39.011 kJ.mol⁻¹.

3-2- Stability of Poly Vinyl Alcohol

3-2-1- Thermal Stability

The study of the thermal stability of four concentrations of PVA was achieved after a constant time (30 min.), which revealed that PVA is stable at a temperature (298-318) K.

Tables (3-2-1), (3-2-2), (3-2-3), and (3-2-4) show the absorbance of PVA at different temperatures after 30 min., the data obtained revealed that PVA is entirely stable over abroad range of temperature and non decomposable.

Table (3-2-1): The absorbance of 40 ppm PVA at different temperatures after 30 min at 472 nm

40 ppm PVA solution	
T (K)	Absorbance
298	0.476
308	0.480
318	0.481

Table (3-2-2): The absorbance of 50 ppm PVA at different temperatures after 30 min at 472 nm

50 ppm PVA solution	
T (K)	Absorbance
298	0.545
308	0.566
318	0.570

Table (3-2-3): The absorbance of 75 ppm PVA at different temperatures after 30 min at 472 nm

75 ppm PVA solution	
T (K)	Absorbance
298	0.662
308	0.678
318	0.688

Table (3-2-4): The absorbance of 100 ppm PVA at different temperatures after 30 min at 472 nm

100 ppm PVA solution	
T (K)	Absorbance
298	0.901
308	0.978
318	0.992

3-2-2- Contact Time

Tables (3-2-5), (3-2-6), (3-2-7), (3-2-8), and Fig.(3-2-1) show the variation of Q_e with the contact time for a solution of 40 ppm PVA to be in attachment with 0.1g of TiO_2 , the data obtained revealed that there was a considerable decrease in the value of Q_e during the periods 5-30 minutes which means that adsorption process has occurred.

Tables (3-2-5), (3-2-6), (3-2-7), (3-2-8): The values of Q_e and C_e at specific periods for different concentrations PVA of time at 298 K

Table (3-2-5) for 40 ppm

t (min.)	C_e (mg.L⁻¹)	Q_e (mg.g⁻¹)
0	0	0
5	34.37	0.56
10	34.81	0.518
20	37.45	0.25
25	38.54	0.014
30	39.31	0.06

Table (3-2-6) for 50 ppm

t (min.)	C_e (mg.L⁻¹)	Q_e (mg.g⁻¹)
0	0	0
5	36.02	1.39
10	39.42	1.06
20	42.44	0.71
25	44.26	0.56
30	46.9	0.31

Table (3-2-7) for 75 ppm

t (min.)	C_e (mg.L⁻¹)	Q_e (mg.g⁻¹)
0	0	0
5	35.47	3.95
10	38	3.76
20	37.45	3.75
25	48.87	2.61
30	59.75	1.52

Table (3-2-8) for 100 ppm

t (min.)	C_e (mg.L⁻¹)	Q_e (mg.g⁻¹)
0	0	0
5	76.57	2.34
10	77.56	2.24
20	80.30	1.97
25	83.82	1.61
30	86.02	1.39

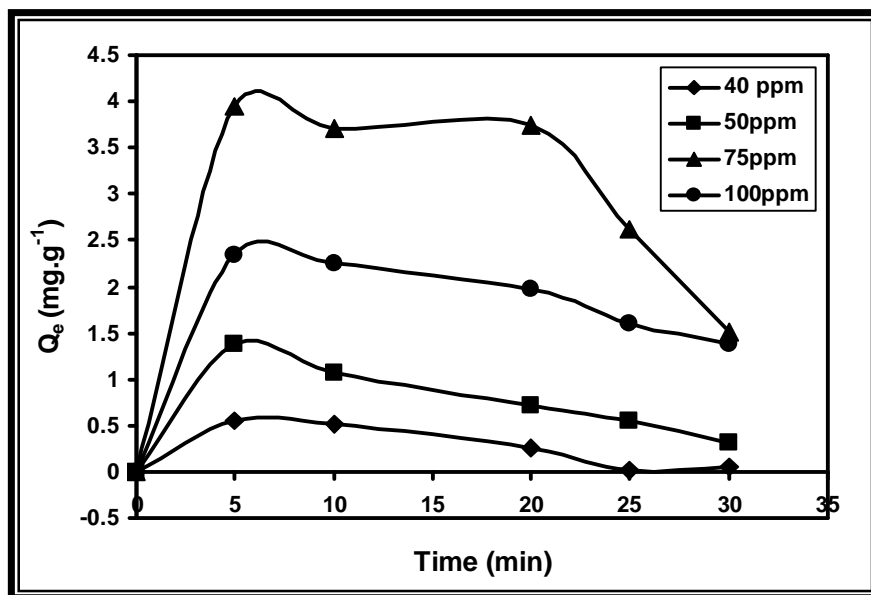


Fig.(3-2-1): The variation of Q_e with contact time for different concentrations PVA solution at 298 K

3-2-3- Adsorption Isotherms

Fig.(3-2-2) shows the sorption isotherms of freundlich type for different PVA concentration at different temperatures at constant time (30 min.). According to the modern classification of isotherms, curve is a typical S-shaped isotherm, which may be due to a weak interaction between sorbate and sorbent⁽⁸⁵⁾.

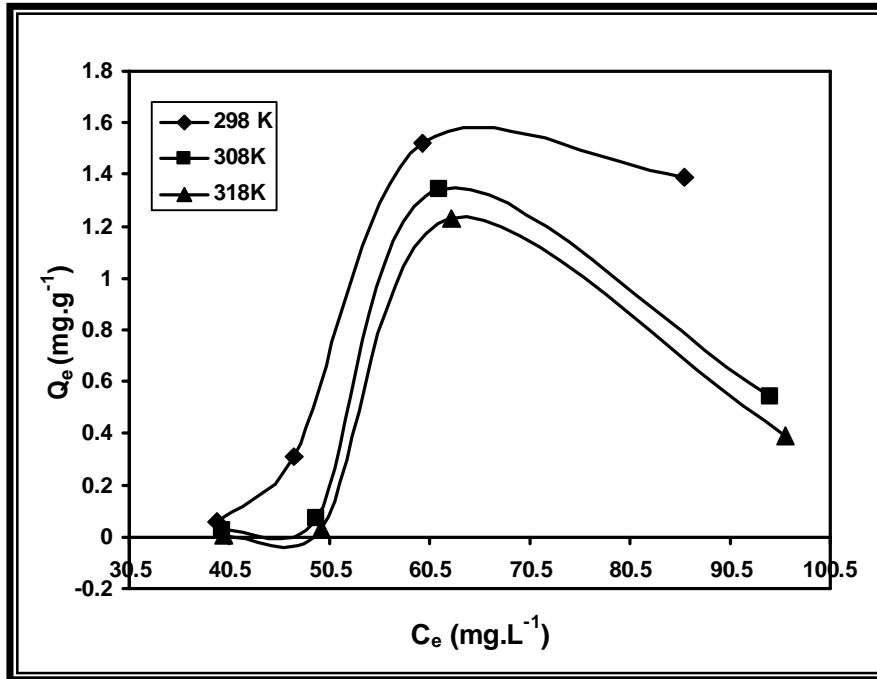


Fig.(3-2-2): The sorption isotherms of different PVA concentrations at different temperatures

The plot of C_e/Q_e against C_e and Table (3-2-9) indicate that Langmiur linear relationship could be applied as show in Fig.(3-2-3).

Table (3-2-9): The values of C_e and C_e/Q_e for the sorption of different PVA concentrations at different temperatures

C_o	298 K		308 K		318 K	
	C_e (mg.L ⁻¹)	C_e/Q_e (g.L ⁻¹)	C_e (mg.L ⁻¹)	C_e/Q_e (g.L ⁻¹)	C_e (mg.L ⁻¹)	C_e/Q_e (g.L ⁻¹)
40	39.31	411.7	39.75	1124.3	39.97	646.36
50	46.9	337.63	49.20	913.4	49.64	572.9
75	59.75	212.25	61.51	638.87	62.61	474.37
100	86.02	61.88	94.50	175	96.02	246.2

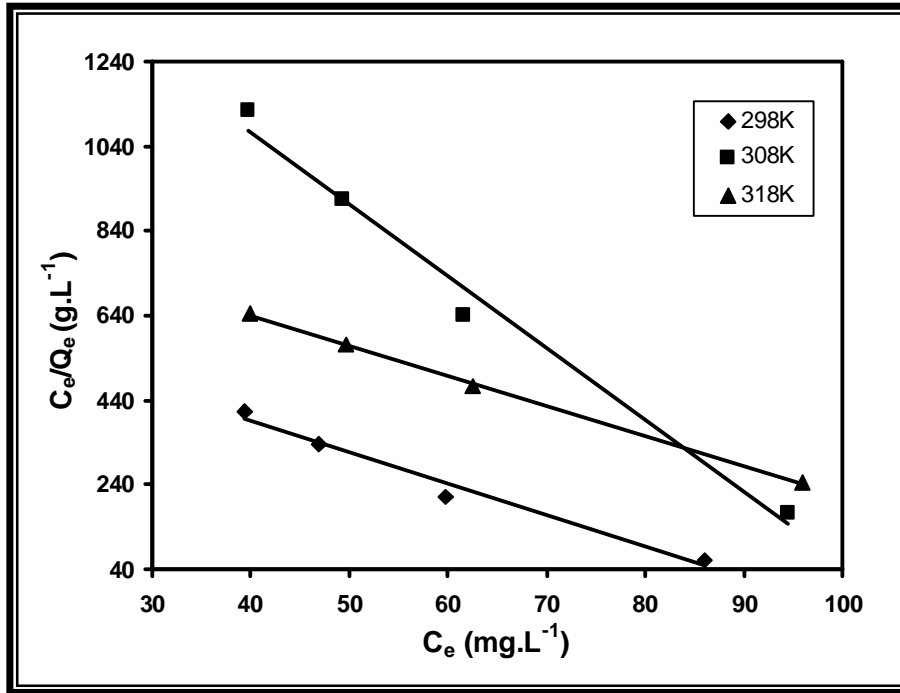


Fig.(3-2-3): Variation C_e/Q_e against C_e for the sorption of different PVA concentrations at different temperatures

Table (3-2-10) and Fig(3-2-4) shows plot of $\log Q_e$ against $\log C_e$.

Table (3-2-10): The values of $\log Q_e$ and $\log C_e$ for the sorption of different PVA concentrations at different temperatures

C_o	298 K		308 K		318 K	
	$\log C_e$	$\log Q_e$	$\log C_e$	$\log Q_e$	$\log C_e$	$\log Q_e$
40	1.59	-1.22	1.59	-1.61	1.60	-2.69
50	1.67	-0.50	1.69	-1.15	1.69	-1.45
75	1.77	0.18	1.78	0.12	1.79	0.08
100	1.93	0.14	1.64	-0.26	1.98	-0.40

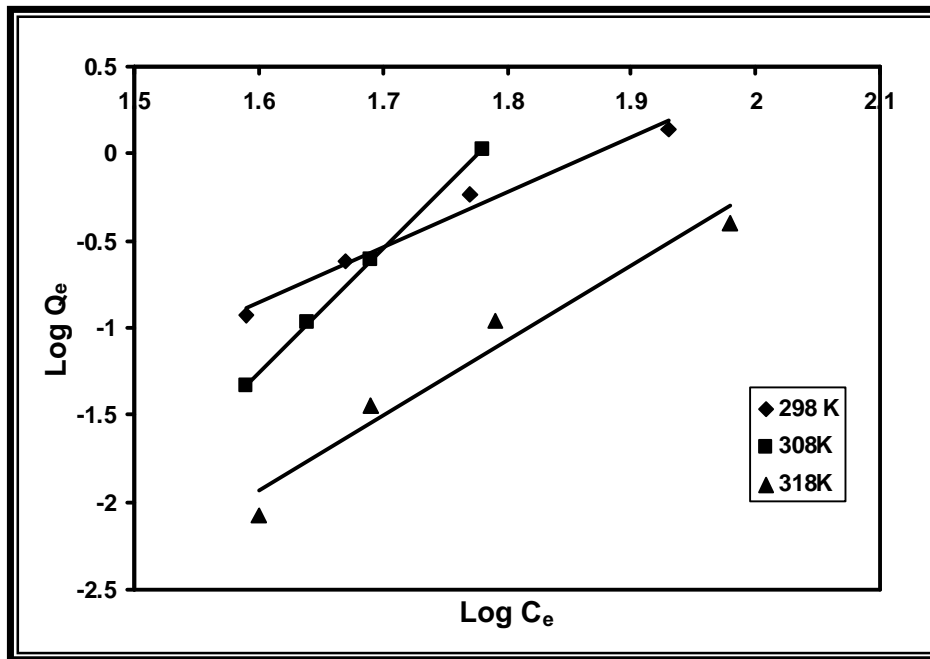


Fig.(3-2-4): The freundlich linear relationship between log Q_e and log C_e for the sorption of different PVA concentrations at different temperatures

The freundlich constants were calculated via applying freundlich equation (1-3) as show in Table (3-2-11).

Table (3-2-11): The freundlich and Langmiur constants for the adsorption of PVA on TiO₂ at different temperatures sorption isotherms

T	Langmiur			Freundlich		
	R ²	a	K _L	R ²	n	K _f
298	0.9798	-0.01	0.0014	0.9815	0.317	1.17×10 ⁻⁶
308	0.9847	-0.009	0.0005	0.9999	0.140	2.39×10 ⁻¹³
318	0.9992	-0.007	0.001	0.9574	0.233	1.2×10 ⁻⁹

3-2-4- Effect of Sorbent Quantity

Fig.(3-2-5) shows the effect of the does of sorbent TiO_2 on the sorption process.

The plot of (C_o-C_e) against sorbent quantity $m(\text{g})$, indicated that the sorption increased as the quantity of sorbent increased then exhibited a maximum uptake at 0.1g of sorbent, hence this does was chosen to be as an optimum amount of sorbent for all the sorption experiment alone lately.

Table (3-2-12): The value of (C_o-C_e) and m (quantity) of sorbent for 40 ppm PVA at 298 K

m (g)	(C_o-C_e)
0.05	0.25
0.1	3.1
0.2	1.18
0.3	1.24
0.4	1.07

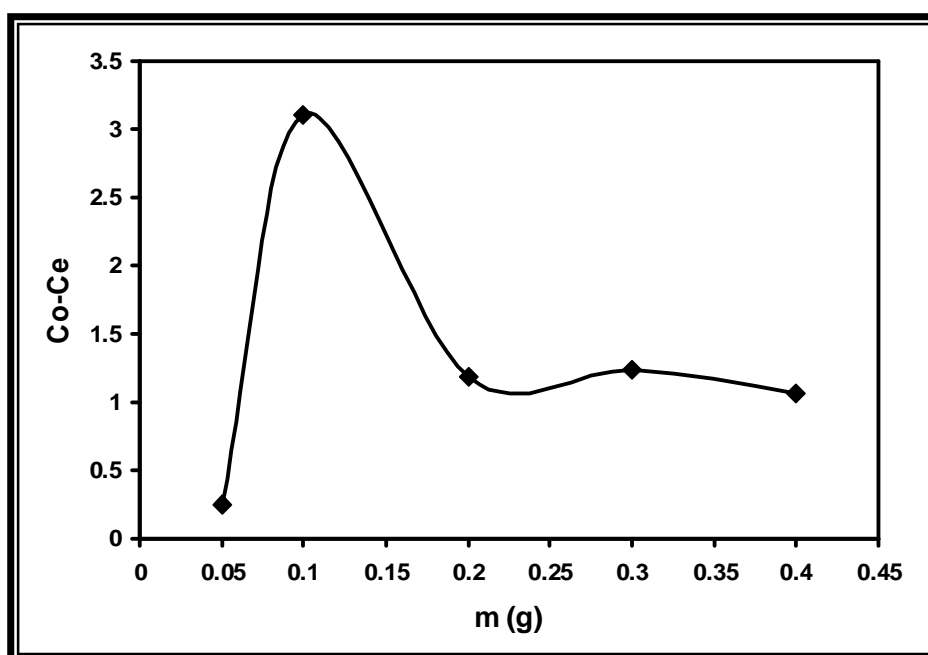


Fig.(3-2-5): The effect of TiO_2 on the sorption process for 40 ppm PVA at 298 K

3-2-5- Effect of Temperature on Sorption Percentage for

40 ppm PVA

Table (3-2-13) and Fig.(3-2-6) show that the sorption percentage decreases as the temperature increases.

Following the sorption percentage in Fig.(3-2-6), reveals that at 298-318K, the sorption percentage decreased, and then the proposed mechanism is adsorption, since it is an exothermic process.

Table (3-2-13): The sorption percentage and C_e values at different temperatures for 50 ppm PVA

T (K)	C_e (mg.L ⁻¹)	%Q
298	46.9	6.2
308	49.20	1.6
318	49.64	0.72

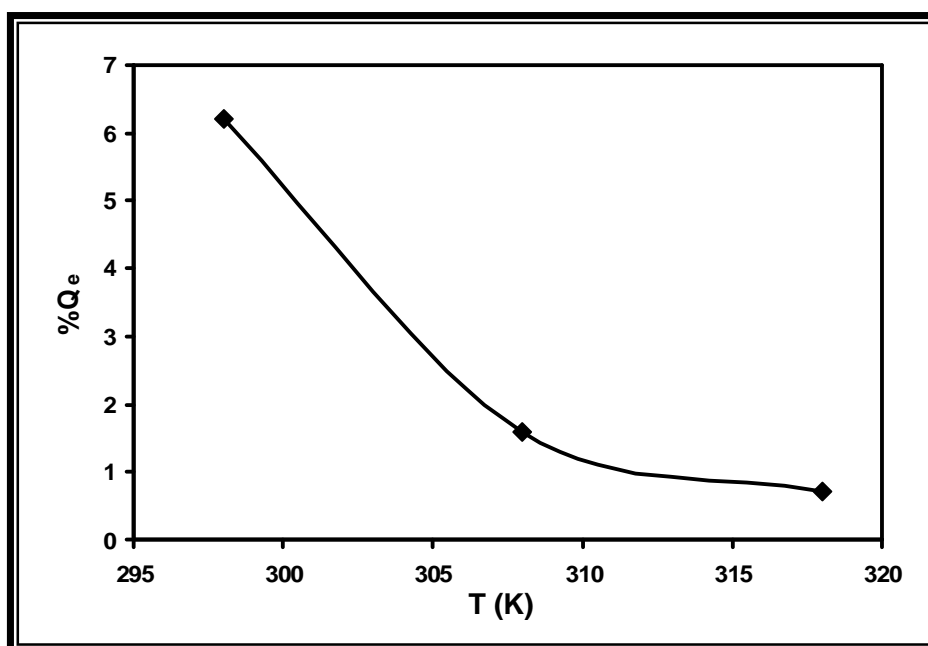


Fig.(3-2-6): The effect of temperature on the sorption percentage for 40 ppm PVA

3-2-6-Calculation of Thermodynamic Functions of Sorption of PVA

Table (3-2-14) and Fig.(3-2-7) showed a linear relationship and slope represents $-\Delta H/R$, where R is the gas constant ($8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$), and then $-\Delta H_s$ was calculated.

Table (3-2-14): Values of the reciprocal of temperature and ln b

T (K)	$\frac{1}{T} \cdot 10^{-3}$	b	ln b
298	3.35	0.06	-2.81
308	3.24	0.02	-3.91
318	3.14	0.002	-6.21

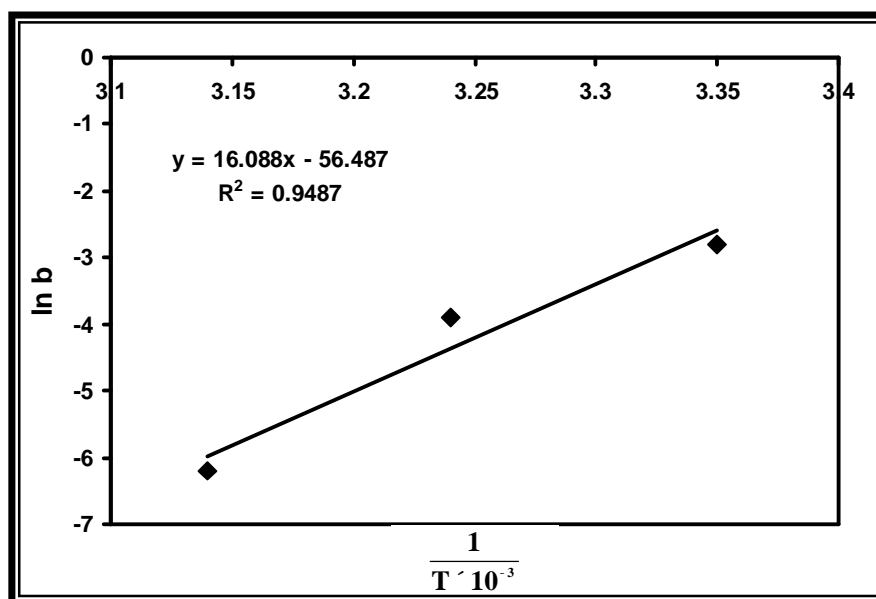


Fig.(3-2-7): The plot of ln b vs. the reciprocal of temperature

Table (3-2-15): Values of thermodynamic function for the sorption process

T (K)	DH (J.mol^{-1})	DG (J.mol^{-1})	DS ($\text{J.mol}^{-1}.\text{K}^{-1}$)
298	-1495.006	$+1.38 \times 10^5$	-469.63
308	-416.28	$+143.25 \times 10^5$	-469.72
318	-1312.52	$+157.43 \times 10^5$	-499.22

Table (3-2-15) shows a negative values of ΔH at 298, 308, and 318K. which due to dominate adsorption (exothermic process) more than absorption process (endothermic process), so the over all process of sorption gives negative ΔH values.

The process has been found to be aphysi-sorption due to its low heat sorption. Table (3-2-15) shows that all values of ΔG values were positive, so the sorption is a non spontaneous process⁽⁸⁴⁾.

Table (3-2-15) shows negative values of ΔS , and it was decreased in 318K.

3-2-7- Kinetic of Sorption Process

3-2-7-A- Lagergren Model

A linear relationship was obtained via plotting $\ln (q_e - q_t)$ versus t (min.) as show in Table (3-2-16) and Fig.(3-2-8).

Table (3-2-16): The parameters of Lagergren equation for different concentrations of PVA at 298 K

40 mg/L				50 mg/L			
t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$	t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$
5	0.56	0.5	-0.59	5	1.39	1.08	-0.07
10	0.51	0.45	-0.93	10	1.06	0.75	-0.28
20	0.25	0.19	-1.66	20	0.71	0.4	-0.91
25	0.014	-0.046	0	25	0.56	0.25	-1.38
75 mg/L				100 mg/L			
t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$	t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$
5	3.95	2.43	0.94	5	2.34	0.95	0.09
10	3.7	2.18	0.78	10	2.24	0.85	-0.23
20	3.75	2.22	0.47	20	1.97	0.58	-0.89
25	2.61	1.09	0.08	25	1.61	0.22	-1.51

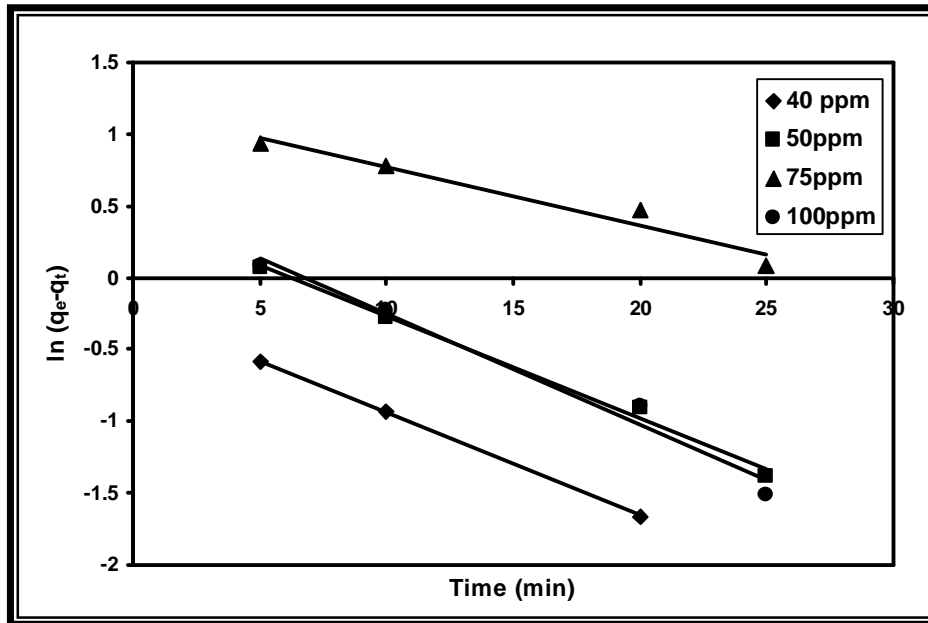


Fig.(3-2-8): The Lagergren kinetic model at 298 K

Table (3-2-17): The rate constant of adsorption process at 298 K

C_o	$k_{ad} \text{ (min.}^{-1}\text{)}$
40	0.004
50	0.0518
75	0.084
100	0.152

3-2-7-B- Morris-Weber Model⁽⁷⁴⁾

A linear relationship was obtained between q_t and \sqrt{t} Table (3-2-18) for 40 ppm PVA at 298 K as shown in Fig.(3-2-9).

Table (3-2-18): The Morris-Weber parameter for 40 ppm PVA

$t \text{ (min)}$	\sqrt{t}	$q_t \text{ (mg.g}^{-1}\text{)}$
5	2.23	3.55
10	3.16	3.7
20	4.47	3.75
25	5.0	3.8
30	5.4	3.85

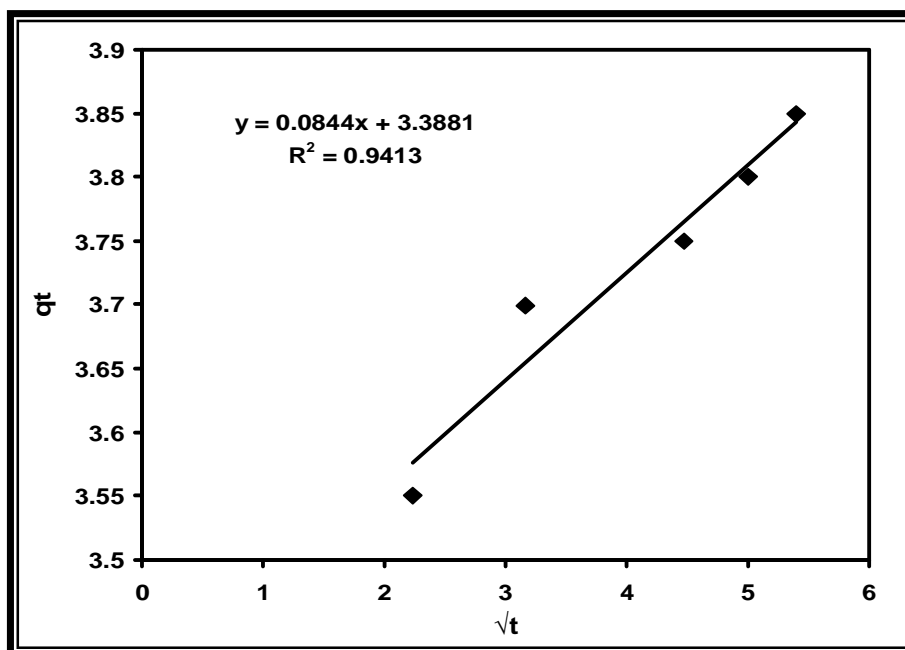


Fig.(3-2-9): The plot of q_t vs. $t^{1/2}$ for 40 ppm PVA at 298 K

The linear Morris-Weber relation indicated the following:

- 1- PVA were diffused from the bulk solution into the sorbent TiO_2 then adsorption process take place.
- 2- Penetration of PVA molecules and binding was done via Vander Waals forces.

3-2-7-C- Reichenbery Model⁽⁷⁴⁾

Plotting of time (min.) versus B_t revealed a linear relationship with relatively acceptable R^2 value and shown in Fig.(3-2-10).

According to this model, it characterized the rate determining mechanism which was a diffusion process for the PVA molecules in the bulk solution and absorption occurred.

Table (3-2-19): The change of Reichenbery parameters with time

B_t	t (min.)
-0.384	5
-0.372	10
-0.223	20

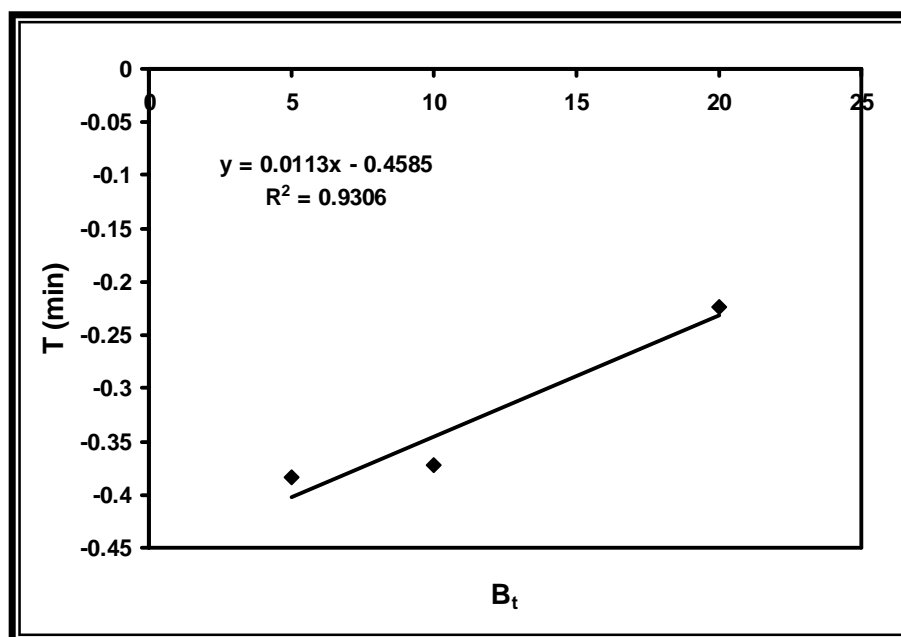


Fig.(3-2-10): The variation of B_t with time

3-3-1- Stability of LAS Solutions

3-3-1-A- Thermal Stability

The study of thermal stability of one concentration of LAS was achieved for a constant time (30 min.), which revealed that LAS is stable at temperature range (288-293) K.

Table (3-3-1) show the absorbance of LAS at different temperature after 30 min., the data obtained revealed that LAS is entirely stable over abroad range of temperatures and non-decomposable.

Table (3-3-1): The absorbance of 100 ppm LAS at different temperatures after 30 min at 234 nm

100 ppm LAS solution	
T (K)	Absorbance
288	1.097
289	1.079
291	0.997
293	1.064
298	1.123

3-3-1-B- Photo Stability of LAS

The photo stability of two concentrations of LAS revealed that LAS is stable after specific periods of irradiation by UV-light (290-320 nm), the data obtained proved that the LAS is non-decomposable even at a prolonged period of exposure to UV-light, and as shown below in Table (3-3-2).

Table (3-3-2): The absorbance of LAS after irradiation by UV-light (290-320)nm

C (ppm)	1 hrs.	2 hrs.	3 hrs.	24 hrs.
Absorbance				
100	0.345	0.344	0.345	0.345
1000	2.193	3.194	2.193	2.193

3-3-2- Contact Time

Table (3-3-3) and Fig.(3-3-1) shows the variation of Q_e with the contact time for a solution of 100 ppm LAS with 0.1g of TiO_2 , since it revealed that there was a slight change in the Q_e during the period of 5-30 minute, hence the probable mechanism the partitioning of LAS molecules from dispersion medium into a solid surface TiO_2 .

Table (3-3-3): The values C_e and Q_e for 100 ppm LAS at specific periods of time and 293 K

t (min)	C_e (mg.L ⁻¹)	Q_e (mg.g ⁻¹)
0	0	0
5	75.36	1.01
10	86.43	1.35
20	90.12	0.98
25	91.29	0.87
30	92.47	0.88

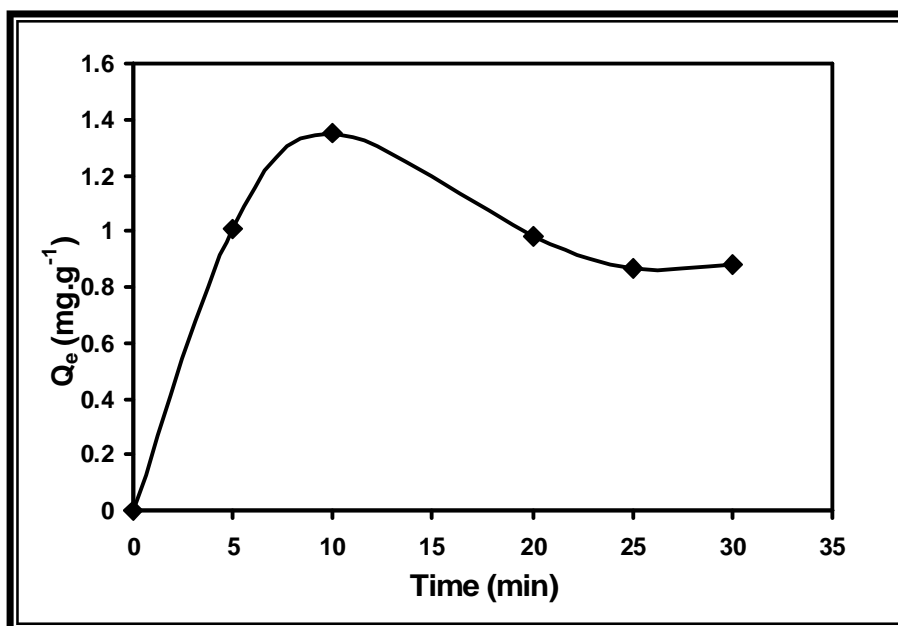


Fig.(3-3-1): Variation of Q_e against time for 100 ppm LAS at 293 K on TiO_2

For a comparison with study, Fig.(3-3-2) shows the time needed for the adsorption of LAS on the surface of bentonite clay⁽⁷⁷⁾, and it was 30 minutes, since the amount of adsorbate Q_e reached the steady state at the period 30 minutes, and thereafter the best agitation time was 30 min.

A higher agitation time may lead to adsorption process, which is unfavorable.

Table (3-3-4): The Q_e values for 250 ppm LAS on Bentonite at specific periods of time, and 298 K⁽⁷⁷⁾

t (min)	Q_e (mg.g ⁻¹)
0	0
10	6.21
20	8.59
30	9.25
45	9.03

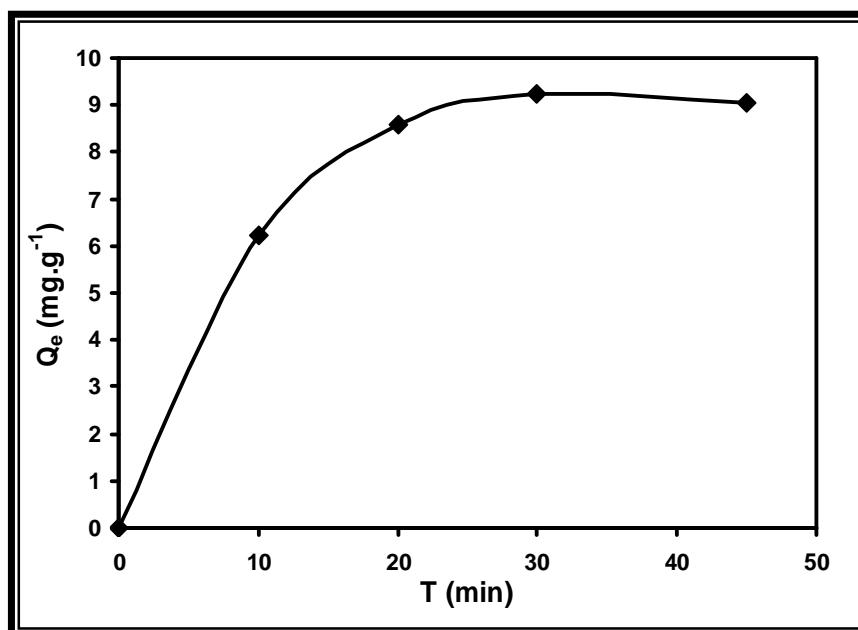


Fig.(3-3-2): The contact time of LAS on the bentonite at 298 K⁽⁷⁷⁾

3-3-3- Sorption Isotherms

3-3-3-A- Sorption Isotherms of 100 ppm LAS

Fig.(3-3-3) shows the variation between Q_e and C_e of freundlich type but according to the modern classification of isotherms, it's not atypical S-shaped isotherm. This may be due to a weak interaction between sorbate and sorbent, or could be attributed to the low concentration of sorbate⁽¹⁰⁾.

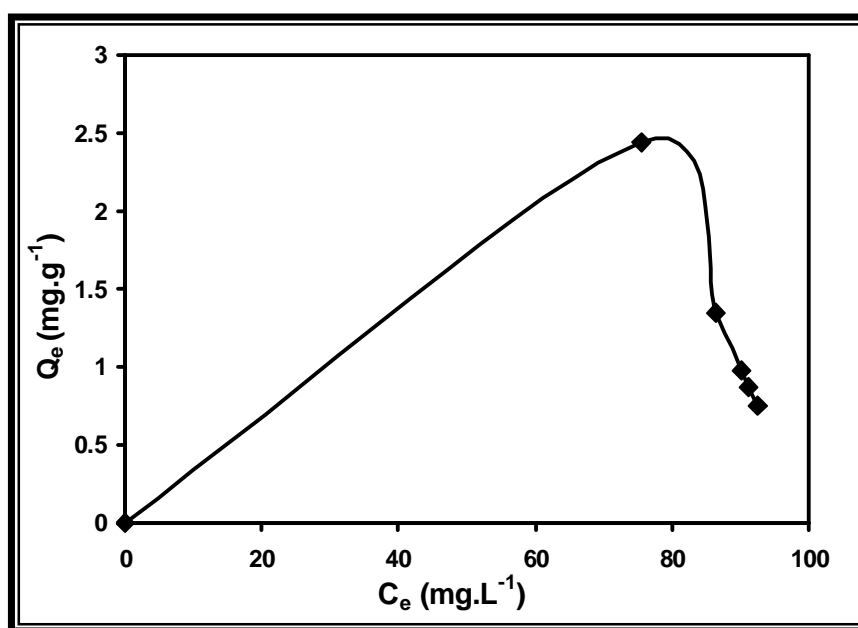


Fig.(3-3-3): The variation Q_e against C_e for 100 ppm LAS on TiO_2 at different contact time at 293 K

Table (3-3-5) and Fig(3-3-4) show the Langmiur linear relationship between C_e/Q_e and C_e of 100 ppm LAS solution.

Table (3-3-5): The values of C_e and C_e/Q_e for the sorption of 100 ppm on TiO_2 at 293 K

C_e ($mg.L^{-1}$)	C_e/Q_e ($g.L^{-1}$)
75.56	30.967
86.43	77.14
90.12	91.3
91.29	104.5
91.47	107.6

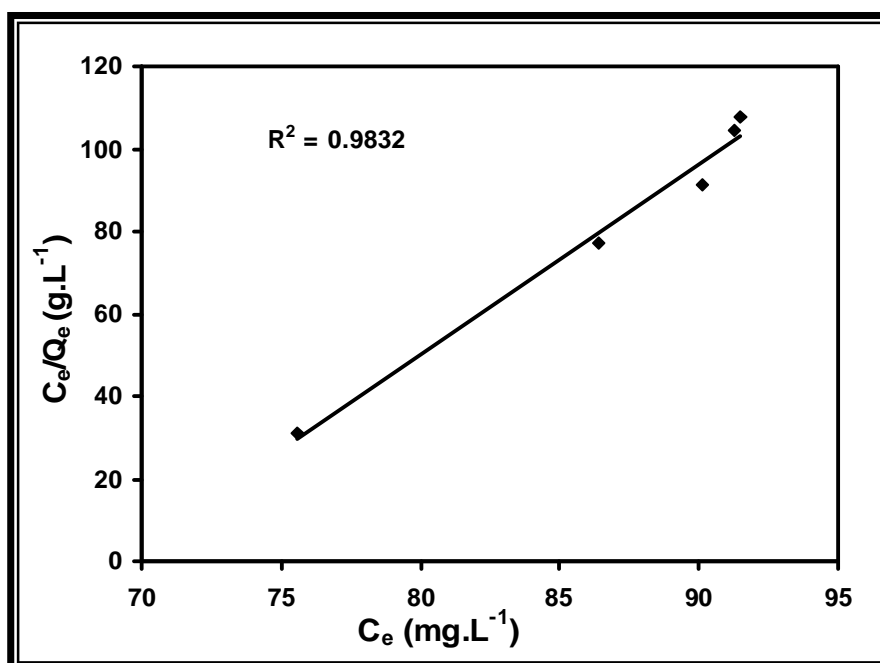


Fig.(3-3-4): The plot of C_e/Q_e against C_e for the sorption of 100 ppm LAS on TiO_2 at 293 K

3-3-4- Effect of Sorbent Quantity

Fig.(3-3-5) shows the effect of the does of sorbent TiO_2 on the LAS sorption process.

The plot of (C_o-C_e) against sorbent quantity $m(\text{g})$, indicated that the sorption increased as the quantity of sorbent increased, then exhibited a maximum up take at 0.1g of sorbent, hence this dose was chosen to be as an optimum amount of sorbent for all the sorption experiment done lately.

Table (3-3-6): The values of (C_o-C_e) and m (quantity of sorbent)

m (g)	(C_o-C_e) (mg/L)
0.05	7.26
0.1	13.57
0.2	10.5
0.3	9.32
0.4	9.79

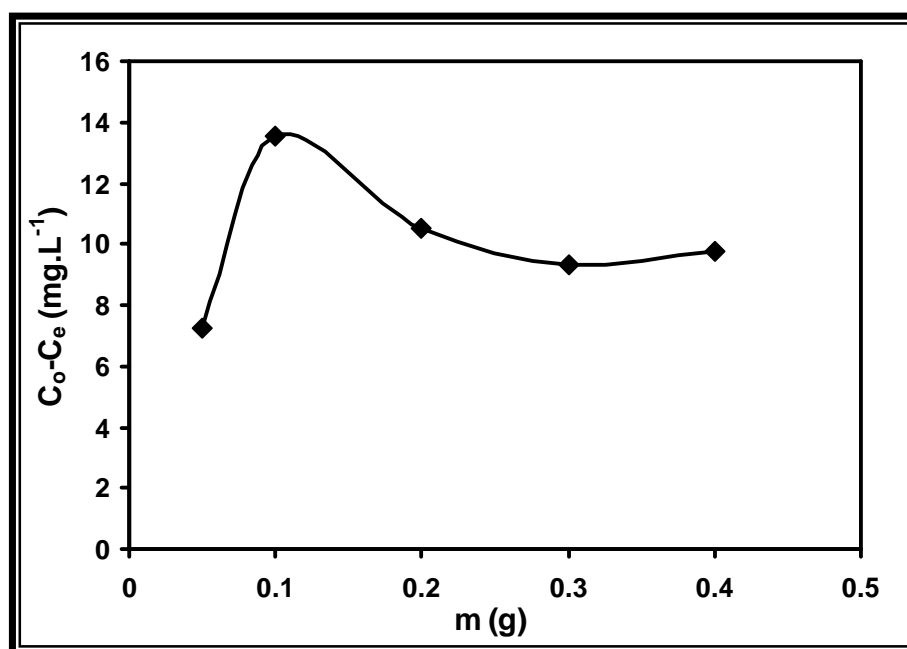


Fig.(3-3-5): The effect of TiO_2 dose on the sorption for 100 ppm LAS at 293 K

3-3-5- Effect of Temperature on Sorption Process

Table (3-3-7) and Fig(3-3-6) show that the sorption percentage increase as the temperature increase, knowing that the adsorption process is an exothermic process. However the sorption process could be exothermic or endothermic depending on the dominant process, in other words the adsorption or absorption or both of them.

Up to 291 K the sorption percentage reached a steady state, so the probable mechanism is absorption and up to 298 K the probable mechanism is adsorption, since the LAS molecules start to leave the surface of TiO₂.

As a consequence, the behavior of LAS molecules on the surface of TiO₂ with temperature raise could be explained as a comprehensive mechanism involving three, absorption, adsorption, and then desorption.

Table (3-3-7): The sorption percentage and C_e values at different temperatures for 100 ppm LAS

T (K)	C_e (mg.L⁻¹)	%Q_e
288	95.44	4.56
289	93.81	6.19
291	86.43	13.57
293	92.49	7.54
298	97.78	2.22

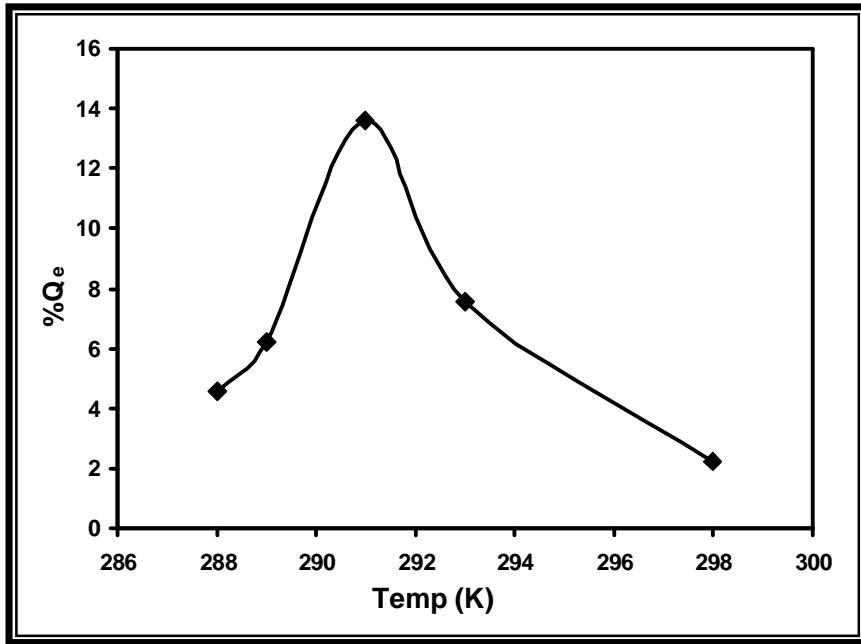


Fig.(3-3-6): The effect of temperature on sorption percentage for 100 ppm LAS

3-3-6- Calculation of Thermodynamic Function of Sorption

Table(3-3-8) and Fig.(3-3-7), showed a linear relationship and slope represents $-\Delta H/R$, where R is the gas, and the ΔH were calculated.

Table (3-3-8): Values of the reciprocal of temperature and $\ln b$

T (K)	$\frac{1}{T \cdot 10^{-3}}$	b	$\ln b$
288	3.47	0.55	-0.79
289	3.46	0.61	-0.49
291	3.43	0.70	-0.35
293	3.41	0.75	-0.28

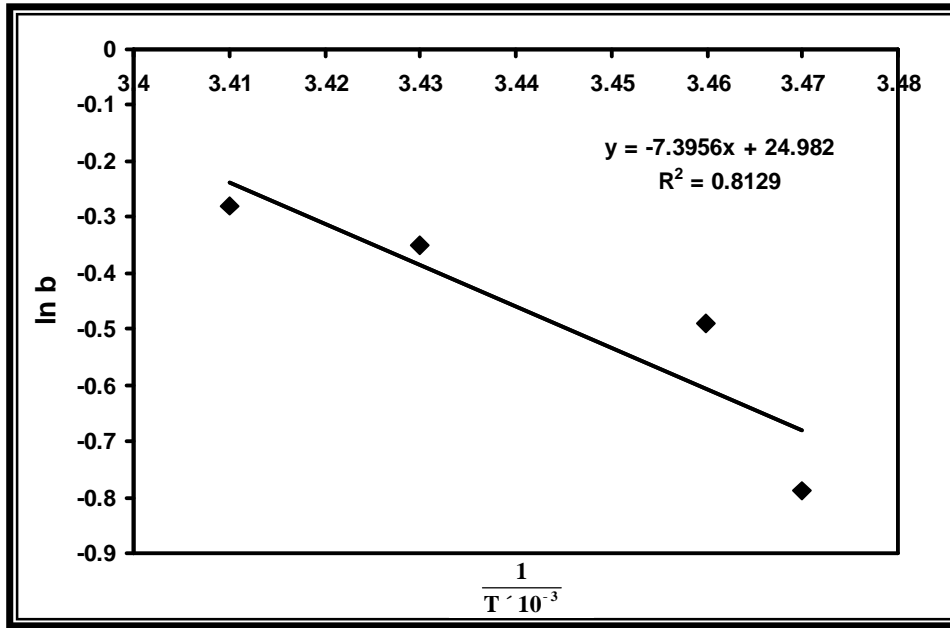


Fig.(3-3-7): Relation between $\ln b$ and the reciprocal of temperature

Table (3-3-9): The thermodynamic function of sorption process

T (K)	DH (J.mol ⁻¹)	DG (kJ.mol ⁻¹)	DS (J.mol ⁻¹ .K ⁻¹)
288	66.14	-1.21	4.43
289	59.01	-1.22	4.44
291	55.03	-1.37	4.9
293	53.14	1.38	13.21

Table (3-3-9) shows the positive values of the ΔH at temperature range (288-293)K indicated that absorption process is occur. ΔH values indicate the ideal and the maximum value of a physi-sorption process, never the less, the process has been found to be a physi-sorption due to the low value of ΔH .

Table (3-3-9) shows ΔG value was negative, so the sorption of LAS on the surface of TiO_2 was considered as spontaneous process.

3-3-7- Kinetics of Sorption Process

3-3-7-A- Lagergren Model

Values of Lagergren parameters are gives in Table (3-3-10), and a linear relationship was obtained via plotting $\ln(q_e - q_t)$ versus t (min.), and as shown below in Fig.(3-3-9).

Table (3-3-10): The parameters of Lagergren equation for 100 ppm at 293 K

t (min)	q_t	$(q_e - q_t)$	$\ln(q_e - q_t)$
5	0.68	-0.07	∞
10	1.35	0.63	-0.46
20	0.98	0.23	-1.46
25	0.87	0.12	-2.12

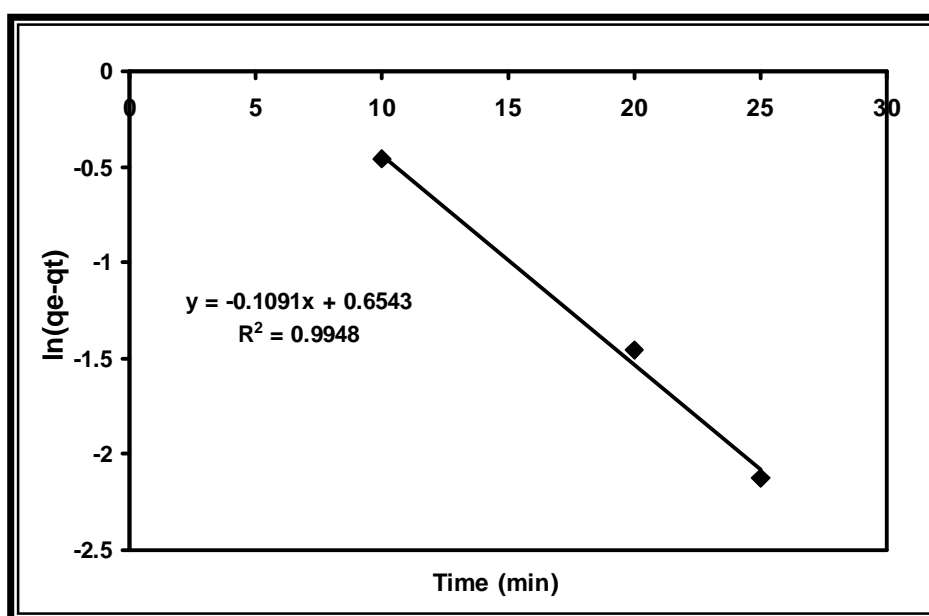


Fig.(3-3-8): Lagergren kinetic relation model at 293 K

3-3-7-B- Morris-Weber Model⁽⁷⁴⁾

Fig.(3-3-9) and Table (3-3-11) show a linear relationship q_t and \sqrt{t} for 100 ppm LAS at 293 K.

Table (3-3-11): The Morris-Weber parameters for 100 ppm LAS at 293K

t (min)	\sqrt{t}	q_t (mg.g ⁻¹)
5	2.23	0.68
10	3.16	0.78
20	4.47	0.98
25	5.0	0.99
30	5.4	1.02

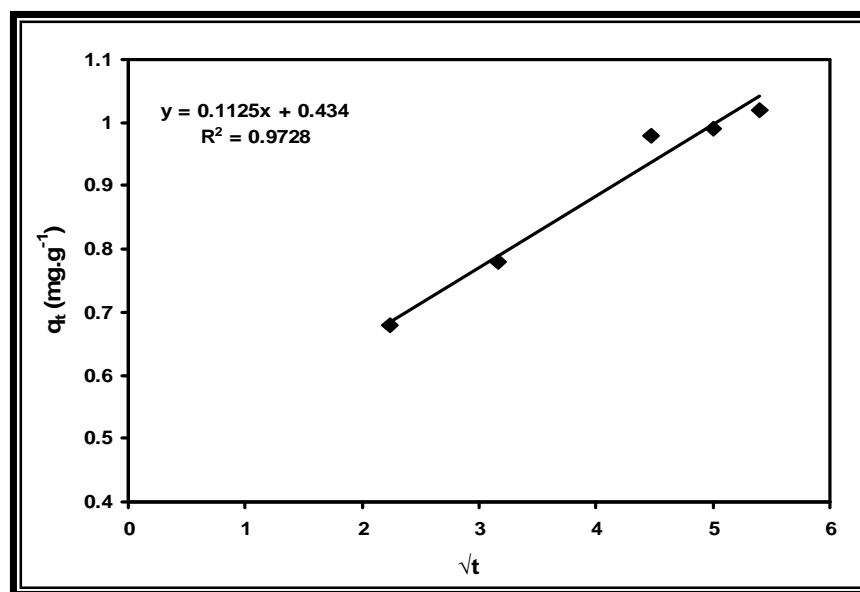


Fig.(3-3-9): The plot of q_t vs. $t^{1/2}$ for 100ppm LAS at 293 K

This linear relationship indicated that the rate limiting step was the diffusion of LAS molecules from the dispersion medium (solvent, H₂O) into the sorbent TiO₂ and penetration inside the pores of TiO₂ by the absorption process.

The linear Morris-Weber relation indicated the following:

- 1- LAS molecules were diffused from the bulk solution into the sorbent TiO₂ before absorption process.
- 2- Penetration of LAS molecules and binding was done via Vander Waals forces.

3-3-7-C- Reichenberg Model

Plotting of time (min.) versus B_t revealed a linear relationship with relatively acceptable R² value and shown in Fig.(3-3-10).

According to this model, it characterized the rate determining mechanism which was a diffusion process for the LAS molecules in the bulk solution and absorption occurred.

Table (3-3-12): The change of Reichenbery parameters with time

B _t	t (min.)
0.3	10
0.92	20
1.46	25

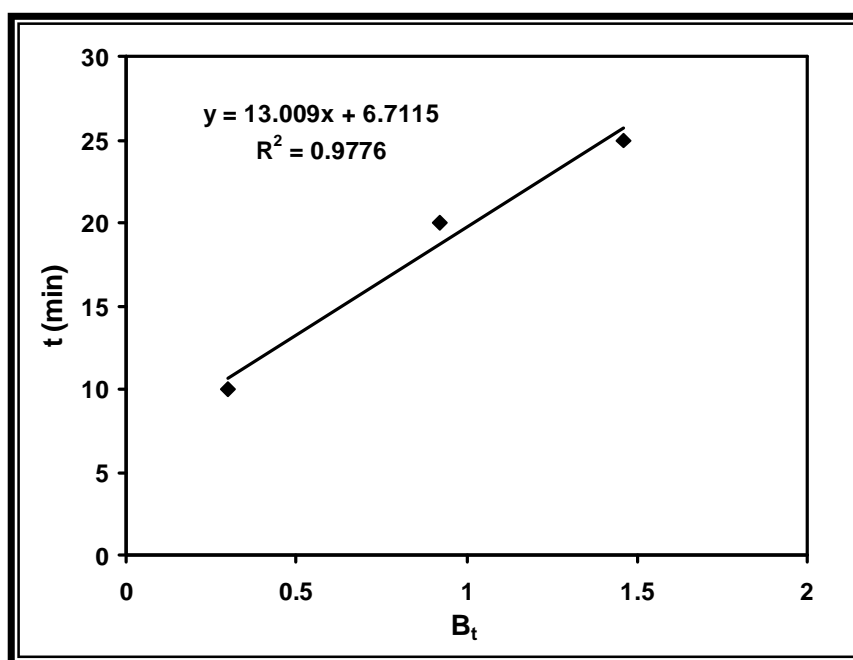


Fig.(3-3-10): The Variation of B_t with time

3-4- Pesticides

The adsorption of study pesticide was carried out. On the surface of TiO_2 , and the experimental results showed that there was no significant adsorption process occurs even at high concentrations and at high temperatures. This results may be due to the large pesticide molecules and its aversion to contact with TiO_2 surface because of the organic molecule nature and the absence of any charge in the pesticide structure.

3-5- Conclusions

A- Brilliant Blue Dye

- 1- Brilliant blue dye shows a good ability to adsorption on TiO_2 surface. This is due to its dye aromatic structure, and due to the existence of alkyl group (with drive electrons) on the dye aromatic rings. The second reason of a good ability of dye adsorption is due to its high molecular weight and large surface area. So the most dye molecules will be removed by TiO_2 surface.
- 2- the sorption of Brilliant blue dye on TiO_2 was of Langmuir type at low and very low concentrations, about $10\text{-}50 \text{ mg.L}^{-1}$, and this indicates that a monolayer of dye has been formed on the TiO_2 surface.
- 3- The positive value ΔH indicates that the adsorption process is dominating rather than the desorption, although that most of literatures assure that TiO_2 has a strong binding forces between its internal layers, the negative value of ΔG indicates that the sorption process is spontaneous and it was led to an increment in the disorder of dye arrangement on the TiO_2 surface. Since ΔS value was positive.

The detailed kinetic study has revealed the following observations:

- 1- Lagergren model has been employed to investigate the rate and order of the reaction, however the results showed a big match with this

equation, in the order words, the sorption process has followed a pseudo-1st order reaction kinetics, and the rate constant was calculated at four different temperatures (288, 289, 291, 293) K.

- 2- Arrhenius equation has been employed, and the rate of the sorption process didn't give a good match with this equation, the plot of $\ln k$ versus $1/T$ was anti-Arrhenins type. since the rate decreased as the temperature increased, which indicates that there was a change in the pattern of dye molecules in the solution which is due to the micelle formation⁽⁸⁶⁾.
- 3- Morris-Weber model has been employed and the results showed a good match with the straight line equations, so the rate limiting step is the diffusion of dye molecule from the bulk solution to the sorbent (TiO_2)⁽⁸⁶⁾.

B- Poly Vinyl Alcohol (PVA)

- 1- PVA molecule have an aromatic structure also, but its aromatic rings substituted with drawing alkyl group, so PVA molecules have not good centers to be adsorped on TiO_2 surface, so PVA show bad sorption on TiO_2 surface.
- 2- The sorption of PVA in TiO_2 was of freundlich type at high concentrations, about 40-100 mg.L^{-1} , and this indicates that a multi-layer of PVA has been formed on the TiO_2 surface.
- 3- The negative value ΔH indicates that the adsorption process is dominating rather than the absorption PVA ions may also enter inside the TiO_2 surface.

The negative value of ΔG indicates that the sorption process is anon spontaneous and it has led to an increment in the disorder of PVA arrangement on the TiO_2 surface. Since ΔS values was negative.

The detailed kinetic study has revealed the following observations:

- 1- Lagergren model has been employed to investigate the rate and order of the reaction, however the results showed a big match with this equation, in other words, the sorption process has followed a pseudo-1st order reaction kinetics, and the rate constant was calculated at four different concentrations (40, 50, 75, 100)K.
- 2- Morris-Weber model has been employed and the results showed a good match with the straight line equations, so the rate limiting step is the diffusion of PVA molecules from the bulk solutions to the sorbent TiO₂ before adsorption process.

C- Linear Alkylbenzene Sulfonate

- 1- LAS molecules have ionic part (SO₃⁻), this part can be connected with TiO₂ surface by sorption process. But the LAS molecular weight with existing of organic non polar tail, lead to decreased the sorption process.
- 2- The sorption of LAS on TiO₂ was of Langmuir type at low concentration, and this indicates that a monolayer of LAS has been formed on the TiO₂ surface.
But the sorption of LAS on bentonite was freundlich type at high concentration, about 250 mg.L⁻¹ and this indicates that multi-layer has formed.
- 3- The positive value ΔH indicate that the absorption process is dominating rather than the adsorption.

The negative value of ΔG indicates that the sorption process is spontaneous and it has led to an increment in the disorder of LAS arrangement on the TiO₂ surface, since ΔS value was positive.

The detailed kinetic study has revealed the following absorbations:

- 1- Lagergren model has been employed to investigate the rate and order of the reaction, however the results showed a big match with this equation, the sorption process has followed a pseudo-1st order reaction kinetics and the rate constant was equal to $(0.0037) \text{ min}^{-1}$ at 293 K.
- 2- Morris-Weber model has been employed and the results showed a good model with the straight line equation, which indicates that the rate limiting step of sorption is the diffusion, so the rate limiting step is the diffusion of LAS molecules from the bulk solution into the TiO_2 surface.

Titanium dioxide succeeded in removing; 95.54% of dye, 6.2% of PVA, 13.19% of LAS and failed in removing pesticides. The sorption process of dye and LAS gives a positive ΔH values, negative ΔG values and positive ΔS values, which indicates the spontaneous absorption process, which for the negative ΔH values, positive ΔG values and negative ΔS values are due to the non spontaneous adsorption process for PVA.

3-5- Future Work

It is worth while to forward some suggestions for the extension of the present work in future as in the following:

- 1- The present work has concentrated on only four organic pollutants [dye, polymer, pesticide and LAS (detagent)]. In order to draw more general conclusion on removing pollution, it is necessary to cover a number of other inorganic pollutants like heavy metals Cr (III, VI), Pb, Cu, Cd.

- 2- The adsorption of the four pollutants has been investigated on TiO_2 surface in the present work. It would be reasonable to investigate the adsorption of these pollutants on natural clay and some natural material like cotton, wood, tree leaves.
- 3- Developing other easy methods to follow the change in pollutants concentration, like construction of ion selective electrodes for each pollutant in order to minimize the cost, and to maintain accuracy.
- 4- Study the effect of these pollutants on metallic container to use these metals like Fe, Al as an electrodes to remove pollution by electrical method (oxidizing or reducing) for these pollutants.
- 5- Conducting a comprehensive comparison among the irradiation in the presence of other catalyst, using modified clays, biological methods and electrooxidation methods. The biological methods included biodegradation by some species of bacteria in the presence of a catalyst.



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الخلاصة

يتضمن موضوع الدراسة امكانية ازالة اربعاً من الملوثات العضوية باستخدام ثنائي التنتانيوم. هذه المركبات العضوية الاربعة تعتبر من الملوثات وهي (Birlliant blue ، Pesticide ، linear alkyl benzene sulfonate ، polyvinyl alcohol).

تمت دراسة الاستقرارية الحرارية والضوئية لهذه الملوثات في المحاليل المائية وتبين انها ثابتة عند المدى الحراري قيد الدراسة (288-318)K وكذلك ثابتة ضمن الطول الموجي للاشعة فوق البنفسجية عند المدى (290-320) nm.

نجح ثنائي اوكسيد التنتانيوم في ازالة 95.54% من الصبغ و6.2% من البوليمر و13.9% من المنظف وفشل في ازالة المبيد.

تم استخدام تقنية مطيافية الاشعة فوق البنفسجية لمتابعة تركيز الملوثات قبل وبعد اجراء عمليات الامتزاز وبعد اوقات زمنية مختلفة وقد تم الحصول على متساويات درجات الحرارة (ايزوثيرمات الامتزاز) من نوعها ايزوثيرمات Langmuir و Freundlich وبقيم معامل الارتباط تصل (1-0.9993) للصبغة، (0.9992-0.9574) للبوليمر، (-0.9503-0.9813) للمنظف، على التوالي.

اخذ شكل ايزوثيرم الامتزاز الصبغة شكل حرف S والذي يعود الى قوة ارتباط الصبغة بالسطح ثنائي اوكسيد التنتانيوم وبقيم ثرموداينميكية $\Delta H = +(5.962-26.57)J$ ، $\Delta S = +(3.45-9.1906)J$ ، $\Delta G = -(996-999)J$ للصبغة.

تم حساب القيم الثرموداينميكية لعملية امتزاز الملوثات عند المدى الحراري (288-318)K وكانت قيم $\Delta H = -(133.4-212.83)J$ ، $\Delta G = +(78-157.4)J$ ، $\Delta S = -(500)J$ للبوليمر. اما قيم $\Delta H = +(53.14-66.14)J$ ، $\Delta G = -(1.21-1.38)J$ ، $\Delta S = +(4-14)J$ للمنظف.

ان عملية امتزاز الصبغ والمنظف على سطح ثنائي اوكسيد التنتانيوم اعطت قيم ΔH و ΔS موجبة و ΔG سالبة بما يدل على ان العمل تلقائي ويطفي فيه الامتصاص على الامتزاز بينما اظهر البوليمر قيماً سالبة ΔH و ΔS وموجبة ΔG دلالة على كون العمل غير تلقائياً وتغلب فيه الامتزاز.

الدراسة الحركية للامتزاز الملوثات على سطح ثنائي اوكسيد التنتانيوم اعتمدت ثلاث معادلات حركية:

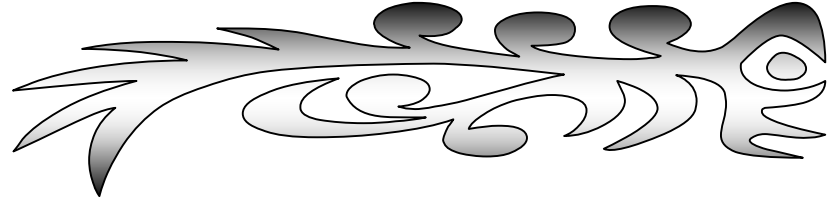
1 - Legergren equation: - والتي استخدمت معرفة مرتبة التفاعل الامتزاز وتبين النتائج انطباق جيد لهذه المعادلة بقيم معامل الارتباط (0.9477-0.9995) للصبغة و(0.956-0.9942) للبوليمر، (0.9948) للمنظف.

وهذه المعادلة تشير الى ان عملية الامتزاز تتبع معادلة من الدرجة الاولى ومن هذه العلاقة الخطية امكن حساب ثابت سرعة الامتزاز عند درجات حرارية مختلفة، تم حساب طاقة التنشيط الامتزاز والتي وصلت الى $39.011 \text{ kJ.mol}^{-1}$ بالنسبة للامتزاز الصبغة.

2 - Morris-Weber model: - حيث تم تطبيق هذا المؤيدل وأعطى علاقة مستقيمة بمعامل ارتباط (0.98-0.994) للصبغة و(0.9892) للبولمر و(0.9989) للمنظف هذه العلاقة تشير الى كون عملية انتشار المادة الملوثة من داخل المحلول الى السطح هي الخطوة المحددة للسرعة.

3 - Reichenberg model: - تم تطبيق هذا المؤيدل واعطا علاقة مستقيمة بمعامل ارتباط (0.9891) للصبغة، (0.9306) للبوليمر (0.9776) للمنظف.

هذه العلاقة تشير الى ان عملية الامتزاز تتضمن عملية امتصاص وابتزاز اذن مجمل العملية هي (امتزاز، امتصاص، ابتزاز).

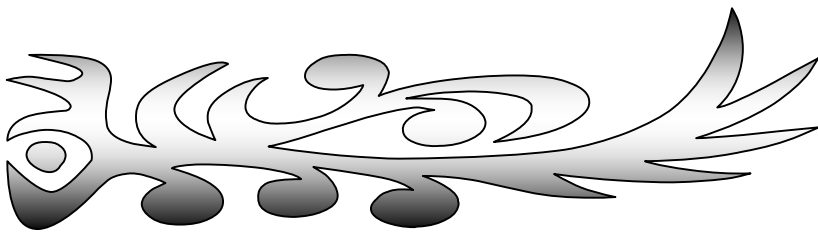


بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

{1} الرَّحْمَنُ {2} عَلَّمَ الْقُرْآنَ {3} خَلَقَ الْإِنْسَانَ
عَلَّمَهُ الْبَيَانَ {4} الشَّمْسُ وَالْقَمَرُ بِحُسْبَانٍ {5}
وَالنَّجْمُ وَالشَّجَرُ يَسْجُدَانِ {6} وَالسَّمَاءَ رَفَعَهَا وَوَضَعَ
الْمِيزَانَ {7}

صدق الله العظيم

سورة الرحمن (الآيات 1-7)





جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين - كلية العلوم
قسم الكيمياء

دراسة امتزاز وامتصاص بعض الملوثات العضوية على ثنائي اوكسيد التيتانيوم

رسالة مقدمة إلى كلية العلوم - جامعة النهرين وهي جزء من متطلبات نيل درجة الماجستير
في علوم الكيمياء / الكيمياء الفيزيائية

من قبل

قيس محمد عبد الحسين

بإشراف

الدكتورة ظلود عبد صالح السعدي

شباط 2009م

ربيع الاول 1430 هـ

