

Republic of Iraq
Ministry of Higher Education
& Scientific Research
AL-Muthanna University
College of Science
Department of Chemistry



Adsorption Study of Some Organic Dyes on the Astragalus Root Surface in Al-Muthanna Province

This thesis submitted in partial fulfillment of the requirement for the
Master's degree of science in chemistry

By

Sahar Ismail Naji

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Supervisor:

Assist. Prof. Dr. Khawla Kani Jassim

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

(يَرْفَعُ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا
الْعِلْمَ دَرَجَاتٍ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ)

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سورة المجادلة , الآية 11

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Signature:

Supervision: Assist Prof. Dr.KhawalaKaniJassim

Date / /2021

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

Signature:

Assist Prof. Dr.KhawalaKaniJassim

Head of Dept. of Chemistry/College of Science/ Al-Muthanna University

Date / / 2021

Dedication..

In the name of Allah, the Most Gracious, the Most Merciful

Dedicated to...

My school, the apple of my eyes, and the pulse of my heart ...

My mother

My angel, the days would never make me forget your memor...

My Father (may Allah have mercy on him)

My support in life ...My brothers and sisters

The enlightening lamp of science and the sea of knowledge ...

All my distinguished teachers

Comrades on the path of Knowledge... My dear colleagues..

Sahar

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Sahar

Abstract

In this study, locally available and inexpensive materials were used to produce the Astragalus root surface (AS surface), it was prepared by several steps, namely washing , drying the Astragalus root with a temperature of (53 °C), and grinding. The AS surface characteristics were diagnosed using (FTIR, SEM, TGA, BET, and XRD) techniques. The adsorption capacity of the prepared AS surface were studied, by adsorption of the three [Fuchsin (FU), Disperse Blue (DB), and Reactive Red (RR)] dyes from their aqueous solutions using the Batch Method. A number of different variables that affect the adsorption process were studied, such as equilibrium time, temperature, adsorbant weight and pH. The results indicated that the adsorption applied curve of type (S) according to Giles classification, the equilibrium time was (90 min). The effect of temperature was studied within the range of (25-45)°C. The results showed that the removal decreases with increasing temperature (exothermic processe). Results used to determine the adsorption isotherm of (Langmuir, Freundlich, and Timken) model. The results showed Freundlich isotherm was the most suitable with experimental data, it gives correlation coefficients (R^2) larger from Langmuir and Timken correlation coefficients. In addition results of thermodynamic studies showed that the adsorption process was spontaneous from the negative charge in change free energy (ΔG°), and the process is exothermic due to negative charge in enthalpy (ΔH°), while the change in entropy (ΔS°) was negative because of arrangement regulation of the adsorbat molecules on the AS surface. The results showed that the adsorption process affected by the pH, also, the adsorbent weight has an effect on the adsorption, as it increases with increasing the adsorbent dosage. The experimental adsorption data fitted with the pseudo-second order kinetic model.

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LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviation	Term
BET	Brunauer-Emmett-Teller
AS	The adsorbent surface prepared from Astragalus plant
FU	Fuchsin
DB	Disperse Blue
RR	Reactive Red
FT-IR	Fourier Transform Infrared
XRD	X-ray Diffraction
rpm	Revolutions per Minute
IUPAC	The International Union of Pure and Applied Chemistry
pH	The Hydrogen Function
R%	The percentage of removal
SEM	Scanning Electron Microscopy
min	Minute
TGA	Thermal Gravimetric Analysis
$^{\circ}\text{C}$	Degree Celsius
ΔG°	Change in free energy
ΔS°	Change in entropy
ΔH°	Change in enthalpy
cm	Centimeter
mL	Milliliters
PFO	Pseudo first order

PSO	Pseudo second order
R²	Coefficient of correlation
Fig	Figure
UV	Ultra Violet
V	Volume solution
P/Po	Relative Pressure
C.I	Colour Index
cal	calculated
exp	experimental
BDDT	Brunauer-Deming-Deming-Teller classification
BJH	Barrett-Joyner-Halenda Analysis

Chapter One

Introduction

1.1 Introduction

Pollution of the natural environment is the release of contaminants into the environment which results in harm or disorder in the global ecosystem [1]. Mainly pollution could be classified into three groups: air pollution, land pollution, and water pollution [2]. Pollution-related diseases have resulted in more mortality than AIDS, tuberculosis, and malaria combined. Chemical pollution is a major issue, as new chemical products continuously synthesized, and not all these chemicals have undergone safety or toxicity testing. As a result, these chemicals were responsible for disease, mortality, and environmental destruction [3]. An example of these chemicals, dyes, heavy metals, hormones, personal care goods, detergents, and pharmaceutical products [4]. Water considered polluted if some substances (pollutants) present in excessive amounts that the water is unusable for drinking, cooking, and bathing, or other uses [2]. Water is the most important natural resource for life, and a large number of water resources are polluted due to neglect and discharges of pollutants from industries, research laboratories, and hospitals. Therefore new technologies must be developed to provide clean water in the near future [4]. Because researchers have reported there are connections between water pollution and acute water-borne diseases, which include hepatitis, cholera, and diarrhea, also, increase the negative effects of the water pollution made people at risk of carcinogenic diseases [5]. In recent decades, the pollution of dye wastewater became a serious problem due to the increasing use of dyes to color the products, such as textiles, paper, plastics, and cosmetics, and the discharge of these highly toxic dyes. The dye pollution of the water stream is therefore a serious environmental problem, as It is widely recognized that dye-containing wastewater is hard to treat [6]. Dyes classified

into two groups: synthetic and natural compounds. Natural dyes, are colored materials extracted directly from natural sources such as leaves and flowers [7], and synthetic dyes are synthesized mainly from petrochemical sources, synthetic dyes characterized by wide availability of different classes and its economical price [8]. However, dyes usually have a complex aromatic molecular structure and a synthetic origin that makes the dyes more inert and very hard to biodegrade when releasing into water [9]. Various chemical, physical and biological methods are currently used to remove dyes. Adsorption is the cheapest and simplest of these methods. The most effective material for dye removal is activated carbon, but due to its high cost and loss of 10-15% during regeneration, unconventional adsorbents such as wood, silica, activated clay, and agricultural residues, etc, have attracted the attention of a number of investigations into the removal of dyes [10].

1.2 Adsorption

Adsorption is a new separation method [11] where molecules from the gas (or liquid) phase are taken up by a solid surface [12]. Adsorption is essentially a process that happens on the surface and consists of two elements: (1) the material that accumulates on the interface is called adsorbate and (2) the solid on which adsorption occurs is adsorbent [13]. Therefore, adsorption involves the contact of the adsorbent with a fluid containing specific pollutants [14]. The first quantitative study was reported by C.W Scheele in (1773) who used charcoal and clay to uptake gases [15]. In order to improve the design and operation of the adsorption system in wastewater treatment, it is important to study the adsorption equilibrium, and kinetics, which will give essential information on the adsorption [16]. The opposite process of adsorption is called

desorption, where a substance is released from the surface [13]. Among all the physico chemical treatment methods adsorption is found to be very effective [17]. Newly, adsorption techniques have gained wide attention due to their capacity in the elimination of pollutants. In addition, adsorption techniques have been found to be among the most capable and proven treatments of dye-loaded wastewater, as well adsorption is a relatively easy technique to perform [18]. Adsorption is controlled either by physical or chemical forces [12]. Thus, the adsorption can be divided into two main types physical adsorption and chemical adsorption:

1.2.1 Physical adsorption or physisorption, is a physical attraction resulting from non-specific, and relatively weak Van-der Waal's forces between adsorbate and adsorbent surface. Physical adsorption taking place on all surfaces when the temperature and pressure conditions are favorable. Being only weakly bound, physical adsorption is easily reversed [19].

1.2.2 Chemical adsorption or chemisorption is happened when strong chemical interactions are formed between molecules or ions of adsorbate to the adsorbent surface, which is caused by the exchange of electrons between the adsorbent and the adsorbed species [20], therefore it is generally irreversible and highly selective. Furthermore, the forces operating are chemical bonds (covalent or ionic bond), the resulting chemical bond is usually stronger than the derived from the physical adsorption and is consequently more stable at high temperature than physisorption [19] [21].

Adsorption was found to be superior to other strategies in terms of flexibility and the simplicity of design, initial expense, insensitivity to toxic pollutants, and ease of operation. Adsorption also fails to produce harmful substances [22].

1.3 Factors Affecting on Adsorption

The adsorption system is highly dependent on a number of important parameters that determine the amount of adsorbent on the surface, include pH, adsorbent dose, contact time, initial dye concentration [23], temperature, particle size, etc [24].

1.3.1 Effect of solution pH

The pH of the dye solution is one of the most important factors that regulated the adsorption process in wastewater treatment, in particular the adsorption capacity. Adsorption efficiency depends on the pH solution, as the pH variation contributes to variation in the degree of ionization of the adsorptive molecule, and the surface properties of the adsorbent [25].

1.3.2 Effect of initial dye concentration

Dye adsorption is highly dependent on the initial dye concentration. Generally, the percentage of dye removal decreases with an increase in the initial concentration of dye [26], and that because at low concentrations of the adsorbate (the dye), an excess of the active sites is available for a relatively low number of adsorbate species, therefore, an increased the percentage of dye removal is obtained at lower dye concentrations [27].

1.3.3 Effect of temperature

The adsorption process effected by the temperature because the changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [28]. If the adsorption increases with increasing temperature means the adsorption is an endothermic process. It may be due to an increase in the mobility of dye molecules and

an increase in the number of active sites for adsorption. While the decrease in adsorption capacity with increasing temperature means the adsorption is an exothermic process. It may be due to increase temperature, which will decrease the adsorptive forces between the dye and active sites on the adsorbent [29].

1.3.4 Effect of adsorbent dosage

This parameter is important to determine the adsorbent capacity [30]. Usually, dye removal rises with a rise in adsorbent dose, due to an increase in contact surface area of the adsorbent particles. Where the number of active sites increases by increasing the adsorbent dose. At a lower dose of adsorbent, there are insufficient active sites that can easily be filled by the adsorbate, but, at higher doses, active sites are more accessible for the adsorbate to occupy [31].

1.3.5 Effect of contact time

Dye removal was found to increase with an increase in contact time. The adsorption was very fast in the first, and then increased slowly, with the time until it reaches equilibrium time and with a maximum percentage of adsorption [32], and this percentage remains constant after equilibrium time [33]. The initial fast rate of adsorption may be due to the existence of adsorption sites in adsorbent surfaces. The later slow rate of adsorption may be due to electrostatic hindrance caused by already adsorbed material. In general, the initial rate of adsorption is rapid, followed by slower adsorption as the available adsorption sites gradually decrease. It is due to the fact that a significant number of unoccupied surface sites are available for adsorption during the initial stage and after an

increase in time the remaining unoccupied surface sites become difficult to occupy due to repulsive powers [31].

1.3.6 Difference in pore size

The size and distribution of pores directly influence their ability to work in a specific application [34], therefore, one of the parameters for which carbons are chosen for a given application was the variation in pore size that influences the adsorption capacity of molecules of various sizes and shapes [35].

A variety of methods have been suggested and widely used for the pore size evaluation. The invention of the Brunauer-Emmett - Teller (BET) method, which has become a common technique for estimating pore size, was a landmark in the estimation of different pore sizes [36]. Materials are classified and divide their pores depending on their width, i.e. the diameter of the cylindrical pore. So according to IUPAC, they are classified into the following groups [37]:

- macropores > 50 nm
- mesopores in the range of 2.0-50 nm
- micropores < 2.0 nm.

1.4 Adsorption Isotherms models

The adsorption isotherm is the curve that explains the phenomenon controlling the mobility of a material from aqueous porous environments to a solid-phase at constant pH and temperature. Adsorption equilibrium is defined when the adsorbate has been in contact with the adsorbent surface for enough time, and its adsorbate concentration in

the bulk solution remaining in a stable balance with the interface concentration [38]. Isotherm equations are mathematical relationships. That are derived or adapted to describe the system of adsorption in equilibrium and the type of the relationship between the adsorbed material and the surface of the adsorbent by taking into account a number of assumptions that have been taken into account when deriving a mathematical equation that varies with the different principle on which isotherm was based [39].

1.5 Classification and modeling of the isotherms

The adsorption isotherm is associated with the amount of adsorption uptake at a constant temperature with the equilibrium pressure. The equilibrium between the adsorbent and the adsorbate is represented by adsorption isotherms. Adsorption isotherms are essential for the determination of the adsorption mechanism. Brunauer introduced the first classification of adsorption isotherms, and in 1985, the IUPAC modified this classification by adding a sixth type to the original five types of Brunauer, the stepped isotherm (Fig. 1.1). Type I (Langmuir isotherm) is a model of microporous adsorbents and is characterized by monolayer adsorption. Type II isotherm has multilayer adsorption. Both forms (II) and (III) are models of non-porous adsorbents. Form IV and V are typical of mesoporous materials (these forms exhibit hysteresis loops). Type VI exhibits multilayer adsorption on a non-porous surface [40] [41] [42].

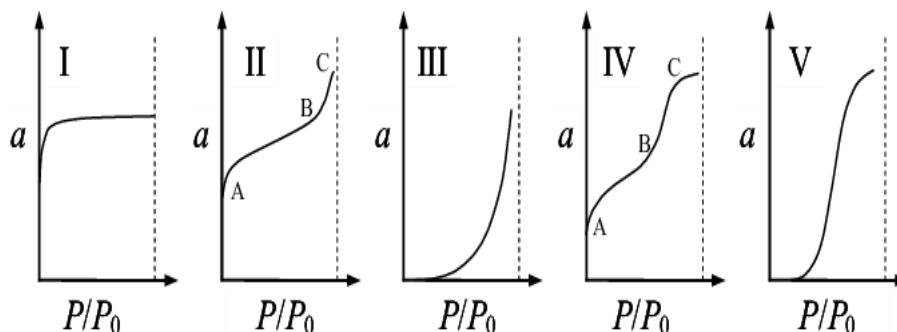


Fig. 1.1. Categories of adsorption isotherms (BDDT) [43].

Giles divides all the isotherms into four major classes S-curve, L (Langmuir type), H (high affinity), and C (constant partition) curves [44]. The (C) isotherm has a constant partition coefficient between substrate and solution, and the curve is a line of zero-origin. The coefficient of distribution decreases when the concentration of the solute increases, providing a concave curve in the (L) isotherm. Particles in the (H) curve tend to attract very high adsorption affinity. In the (S) isotherm, the curve is sigmoidal and therefore has an inflection point, furthermore, this type is always the result of the two opposite mechanisms [45].

Hysteresis phenomena are commonly seen in the characterization of porous solids by gas adsorption of polar and non-polar molecules, and are correlated with adsorption-desorption processes on porous solids, it commonly takes place because of the presence of capillary condensation of the adsorbed material on the pores of the adsorbent surface [46].

The classification of adsorption hysteresis loops suggested by the IUPAC in 1984 was based on experimental findings and on the implementation of the classical principles of pore filling (Fig. 1.2) [47].

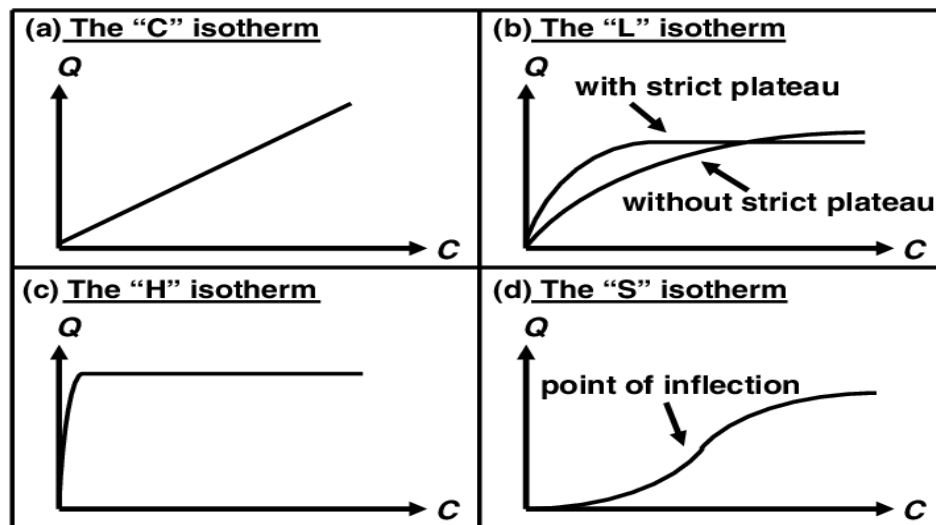


Fig. 1.2. The four main types of isotherms (after Giles et al., 1974). [45]

The class (H1) is mostly associated with porous materials according to the IUPAC classification Fig. 1.3. The (H2) refers to substance with a more complex pore structure. Whereas the class (H3) indicates the existence of non-rigid aggregates. The (H4) class is found with complex materials having both micropores and mesopores [48].

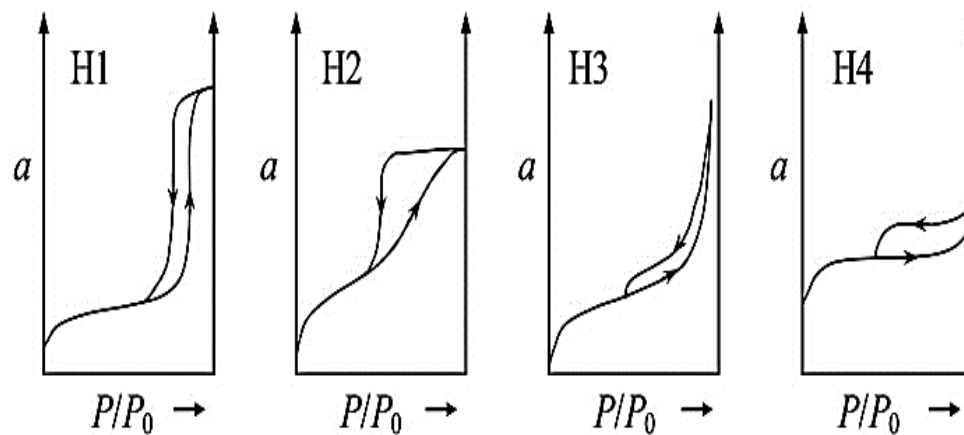


Fig. 1.3. Categories of gas adsorption loops (IUPAC). [43].

The distribution of adsorbate between the liquid phase and the solid phase, when the uptake was reached equilibrium, was assessed by different adsorption isotherms [49].

The parameters derived from the isotherms provide details on adsorption mechanisms, the surface properties, and affinities of the adsorbent. The most accepted isotherms are Langmuir and Freundlich. The correlation of the amount of adsorption and the concentration the liquid-phase, was tested with Langmuir, Freundlich, and Tempkin isothermal equations, also used to evaluate the best-fitting isotherm, and the applicability of isotherm equations is matched by evaluating the correlation coefficients [50].

1.5.1 Langmuir Adsorption Isotherm

The principle of Langmuir isotherm suggests a monolayer covering of adsorbate over a homogenous adsorbent surface. Graphically, the Langmuir isotherm is characterized by a plateau. Thus, at equilibrium, a saturation point is reached where no further adsorption can occur. The basic assumption is that sorption occurs at specific homogeneous sites within the adsorbent. When the dye molecule is in the site, no further adsorption can take place at that site [51]. The Langmuir isotherm is represented as the following form [52]:

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot b} + \frac{C_e}{q_m} \quad (1-1)$$

Where:

q_e : Is equilibrium quantity sorbed (mg/g).

C_e : The equilibrium concentration (mg/L).

q_m : The maximum capacity of the adsorption (mg/g).

b : The sorption equilibrium constant (L/mg).

1.5.2 Freundlich isotherm Adsorption Isotherm

Freundlich isotherm is the oldest known relationship that explains non-ideal and reversible adsorption, not limited to monolayer formation. This analytical model can be extended to multilayer adsorption with a non-uniform distribution of adsorption, heat and affinity over the heterogeneous surface [53]. The linear form of the isotherm may be expressed as follows [54]:

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (2-1)$$

Where K_F : is the Freundlich constant (mg/g), and $1/n$: is the adsorption intensity.

1.5.3 Tempkin isotherm Adsorption Isotherm

Tempkin isotherm was used to test the adsorption potential of the adsorbent. Tempkin and Pyzhev considered the influence of certain indirect adsorbate / adsorbate interactions on adsorption isotherms and proposed that, owing to these interactions, the heat of adsorption of all molecules in the layer would decrease linearly [51]. The Tempkin isotherm was implemented in the following linear form [55]:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (3-1)$$

where $B_1 = RT/b$.

R: is the universal gas constant $8.314 \text{ J (mol K)}^{-1}$

T: is the absolute temperature in Kelvin.

B_1 and K_T are Tempkin constants.

The constant B_1 is related to the heat of adsorption.

1.6 The adsorbent (*Astragalus* plant)

It is a widespread plant species throughout the temperate regions in the world for example Asia, South America, Europe, and mountains in Africa. Some species in the *Astragalus* genus are well recognized for their pharmacological properties, this plant has been used in traditional oriental medicine for a long time for many purposes, like stimulant, tonic, and diuretic [56]. It is among the largest flowering plant species in the Leguminosae family and widely distributed in temperate and arid regions. The genus estimated to contain 2000–3000 species and more than 250 taxonomic sections of the world. Some species are the source of an economically valuable natural substance, gum tragacanth. Although the most popular use of this species is as forage for cattle and wild animals, also used in cosmetics, as a substitute for tea or coffee, or as source of vegetable gums [57]. *Astragalus* has also used for treat a wide variety of diseases and corporal diseases. Among its diverse therapeutic uses, the possible use of this herb and its chemical constituents in the treatment of inflammatory diseases and cancers has been extensively studied in recent years. *Astragalus*-based therapies have demonstrated a major amelioration of the toxicity caused by other medications. The key components of *Astragalus* are polysaccharides, flavonoids and saponins. *Astragalus* is currently being used mainly for its immunomodulation, antioxidant, anti-inflammatory, and anti-cancer effects [58]. It is also possible to notice some toxic effects of this plant on the human body, as inhaling the root powder may lead to some respiratory problems and difficulty breathing. The plant is shown in Fig. 1.4.



Fig. 1.4. The Astragalus plant.

1.7 Dyes

The synthetic dye was widely available in 1856 [59]. Dyes are an important class of contaminants, and if they reach the water, it is no longer safe and often difficult to treat because dyes have a synthetic origin and a complex molecular structure, makes them more stable and hard to biodegrade [60]. Saving water to make the future safe is what the world need now. With the growth of humanity. Environmental disturbance with a major pollution problem is one of the consequences of this rapid growth, as the demand for water has increased for agricultural and industrial uses, which releasing large amounts of wastewater. Dye molecules consist of two key components: chromophores,

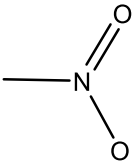
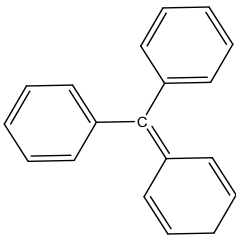
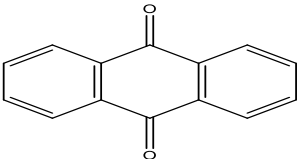
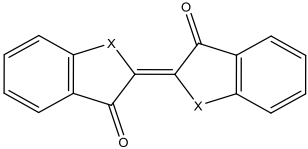
responsible for color production, and auxochromes, make the molecule soluble in water [61].

1.7.1 Classification of Dyes

Dyes are colored organic compounds dependent on functional groups such as chromophoric groups (NR_2 , NHR , NH_2 , COOH , and OH) and auxochromes (N_2 , NO , and NO_2) [62]. Dyes can be classified in several ways, according to their composition, color, and application methods, also by ionic charge when dissolution in water. Because the ionic classification of dyes highly affects the efficiency of dye adsorption [63]. As shown in Fig. 1.5. Dyes could be classified based on the method of application as reactive, dispersed, acid, basic, direct, and vat dyes [64]. Which has many uses example, acid dyes are commonly used for cosmetics, paper, and food. Basic dyes are used for polyacrylonitrile dyeing, and pharmaceutical industries. Disperse colorants are used with nylon, and cellulose fibers. Direct dyes are used with leather, cotton, and the paper industry. Reactive dyes are used on nylon, and wool. Vat dyes are used for rayon fibers. In addition, it is insoluble in water [62].

Dyes are also categorized as azo, anthraquinone, indigo, phthalocyanine, sulfur, nitro as well as nitroso dyes by their chemical structures Table 1.1. However, the classification of pigments as organic and inorganic pigments is also considered as an appropriate method [65].

Table 1.1: Classification of dyes according to the chemical structure [66, 67, 68].

Dyes	Chromospheres	Examples
Nitroso dyes	$\text{O}=\text{N}-$	Naphthol green B
Nitro dyes		Naphthol yellow S
Azo dyes	$- \text{N}=\text{N} -$	Acid orang 7
Triarylmethane dyes		Basic red 9
Anthraquinone dyes		Nuclear fast red
Indigoid dyes		Indigocarmine

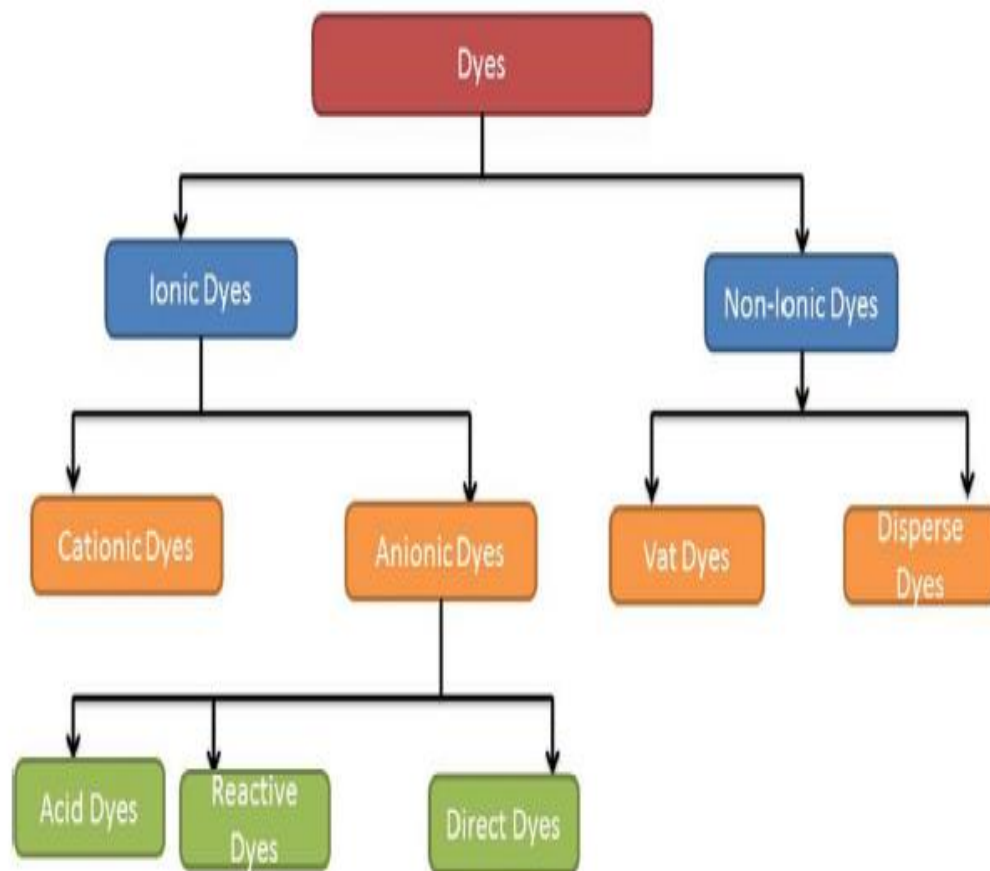


Fig. 1.5. Classification of dyes according to ionic charge. [63]

1.7.2 Toxicity effects of Dyes

The dye-using industries should handle harmful dye wastewater before it is released and contaminate the water. Dye effluents interrupt the cycle of self-purification of the water and create a visible film above the surface of the water. This prevent the penetration of the sunlight needed for photosynthesis and respiration. Dye effluent damage to the soil, and make the water a breeding ground for the bacteria and viruses. It also creates unpleasant smell, induces a sore eye for animals and humans, cause skin irritation and trouble breathing. Ingesting dyes can induce severe sweating, and irritation [69].

1.7.3 Present Treatment methods for Dye Removal

As for some of the more responsible dye-use industries, it is highly recommended that treated dye wastewater be reused in their dyeing processes instead of being disposed into the environment. This is a more economical idea than purchasing and using freshwater for dyeing processes frequently. Freshwater does not come cheap at the level required by dyeing industries, and cost-cutting is typically the desired factor for all industries [69]. Various treatment methods have been used to remove synthetic dyes from aqueous solution. On the basis of the principle mechanism behind the dyes removal, these processes can be divided into two classes: separation (physical and physicochemical) methods and degradation (chemical and biological) methods. A schematic diagram of the different methods used to remove dye is shown in Fig. 1.6 [70].

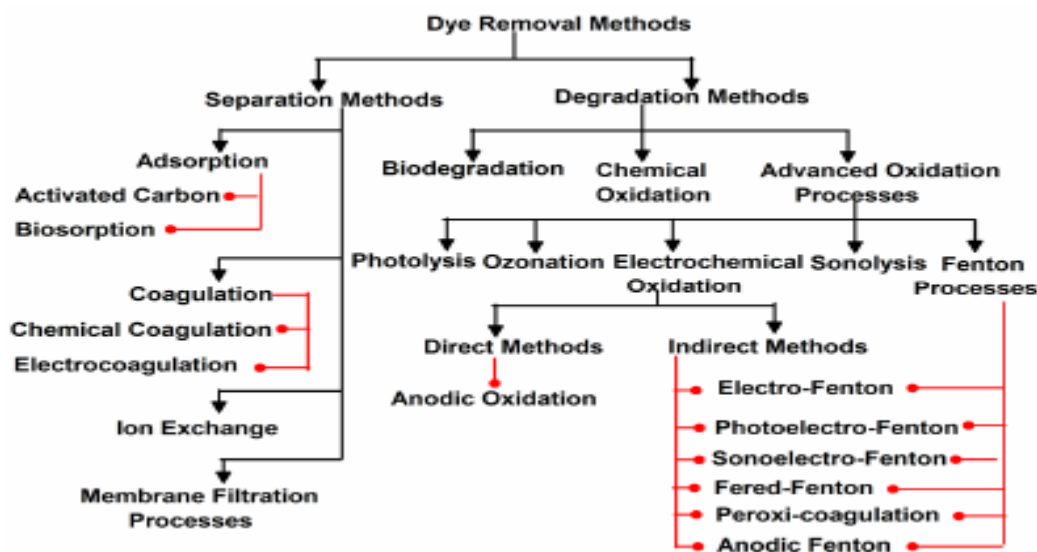


Fig. 1.6. Schematic representation of method used in dye removal from water. [70]

These methods have been discussed in three categories: chemical, physical and biological Table1.3 [71].

Table 1.2: Advantages and disadvantages of the dye removal methods [29, 71, 72].

Methods	Advantages	Disadvantages
Chemical treatments		
Fentons reagent	Effective decolourisation	Sludge generation
Ozonation	No change in effluent volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of by-products
NaOCl	Initiate azo-bond cleavage	Release aromatic amines
Electrochemical	No consumption of chemicals and no sludge build up	High cost of electricity
Oxidative process	Simplicity of application	(H ₂ O ₂) agent needs to activate by some means
Physical treatments		
Activated carbon	Good removal of wide variety of dyes	Very expensive
Peat	Good adsorbent	Surface area is low
Silica gel	Effective for basic dyes removal	Side reactions, prevent commercial application
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O ₂
Electrokinetic coagulation	Economically feasible	High sludge production
Biological treatments		
Decolourization by white-rot fungi	White-rot fungi are able to degrade dyes using enzymes	Enzyme production has also been shown to be unreliable
Other microbial Cultures (Mixed bacterial)	Decolorized in 24–30 h	Under aerobic conditions azo dyes are not readily metabolized
Adsorption by living/dead microbial biomass	Certain dyes have a particular affinity for binding with microbial species	Not effective for all dyes
Anaerobic textile- dye bioremediation systems	Allows azo and other water-soluble dyes to be decolorized	Anaerobic breakdown yields methane and hydrogen sulfide

1.8 Previous studies

(M.S. Chiou et.al, 2002) studied adsorption of the reactive dye (reactive red 189) from aqueous solutions using cross-linked chitosan beads. The Langmuir model matched with results. A decrease in pH solution leads to an important increase in adsorption capacity of dye RR 189. The data fit with the second-order kinetic model, except for the dried beads that match better with the first-order model [73].

(Mehmet Emin Argun et.al, 2008) studied the removal of Cd(II) and Pb(II) ions from aqueous solution by using an activated pine cone with a Fenton reagent. The changes in the surface properties of adsorbent materials were characterized by FT-IR and SEM analysis after pine cone activation. The pseudo-first-order reaction kinetics and the Langmuir adsorption isotherm is the best fit for the adsorption process. The process of adsorption was spontaneous and exothermic under natural conditions. Maximum removal efficiency was achieved at pH 7 at 91% and 89% at 90 and 105-min contact time for Cd(II) and Pb(II) [74].

(Saruchi et.al, 2016) studied the removal of rhodamine B dye and Pb^{+2} ions from aqueous solution using a synthesized hybrid ion exchanger. The results of pH and ionic strength have shown that hydrophobic-hydrophobic interactions may be the dominant attraction force for rhodamine B and lead ions to the synthesized hybrid exchanger system. The Langmuir model showed the best fit and the maximal adsorption capacity found to be 82.3 and 182.7 ($mg\ g^{-1}$) for lead ions and 76.4 and 156.8 ($mg\ g^{-1}$) for rhodamine B at 20 and 50°C, respectively. The findings showed that the pseudo-second-order kinetic model described the ion exchange kinetics for rhodamine B and lead ions [75].

(E.Ghasemian Lemraski et.al, 2016) prepared activated carbon using Persian mesquite grain by chemical activation method using phosphoric acid at with a ratio of 1-1 as an activation factor, activated at a temperature of 600°C for two hours and in a nitrogen atmosphere. Determine the physicochemical properties of activated carbon using BET, CHNS, XRD, FT-IR and SEM technologies. The adsorption capacity of the resulting carbon was studied by the adsorption of methyl orange (MO) and methylene blue (MB) dyes. Adsorption isotherm indicates that the Langmuir model is the best fitting model. Adsorption kinetics fitted to a pseudo second-order model [76].

(E. Khouya et.al, 2017) produced activated carbon from molasses, molasses are natural precursors of vegetable origin originating from the sugar industry. Via chemical activation processes with phosphoric acid as activation factor and 500 °C in the air. The resultant carbon properties have been characterized using BET and SEM technologies, presented a high surface area, and a high adsorption capacity for methylene blue and iodine. The removal of certain heavy metals, such as Cr^{6+} , Cu^{2+} and Pb^{2+} from aqueous solutions, has been studied. The affinity for the three ions was different as in the following order $\text{Cu}^{2+} > \text{Cr}^{6+} > \text{Pb}^{2+}$. The process is governed by the monolayer adsorption fitting with the Langmuir model [77].

(Rong-Zhong Wang et.al, 2018) Studied the adsorption behavior and relative distribution of Cd^{2+} sorption mechanisms to biochars. Bamboo biochars (BBCs), corn straw biochars (CBCs) and pig manure biochars (PBCs) were produced at 300–700 °C. The results revealed that PBCs had the highest adsorption potential for Cd^{2+} . Cd^{2+} - π interaction was the predominant mechanism for Cd^{2+} removal of biochars and the contribution ratio decreased significantly from 82.17% to 61.83 % as the ash content

increased from 9.40% to 58.08 %.The Langmuir isotherm model fitted the equilibrium data more than Freundlich model [78].

(Nazmul Abedin Khan and Sung Hwa Jung et.al, 2018) prepared a highly porous carbon from the pyrolysis of polyaniline (pANI) under appropriate conditions. To be used in the removal of three typical personal care products (PCPs), triclosan, oxybenzone and p-chloro-m-xyleneol, from water by adsorption. The carbons (named PDCs or pANI-derived carbons) demonstrated strong adsorption for the three PCPs. The kinetic constants, calculated by using a pseudo-second-order non-linear model, and the Langmuir isotherm was applied to explain the adsorption [79].

(Hatem A. Al-Aoh et.al, 2018) synthesized nickel oxide nanoparticles (NiO NPs) using a microwave-assisted method. The NiO NPs properties were determined using BET, TEM and XRD analysis. The Bromophenol blue (BB) adsorption was examined by using NiO NPs at different temperatures. The optimal laboratory conditions were found with an adsorbate concentration of 300 mg/L, a temperature of 333 K and a pH of 12 at 24 h. The results showed that the Langmuir isotherm is the best fit and that the data is well described by a second-order kinetic model. The adsorption of BB on NiO NPs is endothermic processes [80].

(Song Fang and Fanyu Kong et.al, 2019) analyzed the adsorption behavior of three widely used fungicides [hexaconazole (HEX), myclobutanil (MYC) and triadimenol (TRI)] on polystyrene (PS) using adsorption. The results showed that the adsorption kinetics and isotherm correspond to the Pseudo-second-order and Freundlich isotherm. Decreasing the PS particle size, changing the pH value of the solution, and increasing

the salt ion strength all leads to increasing the adsorption capacity. Hydrophobic and electrostatic reactions were the main mechanisms of adsorption [81].

The Aim of the study

1. Preparation of adsorption surface from agricultural waste, it was prepared from the root of the Astragalus plant.
2. Characterization and studying the properties of the adsorption surface using XRD, SEM, FTIR, TGA and BET techniques.
3. Study the activity and the adsorption capacity of the adsorbent surface by observing its removal of D Blue, R Red and dyes from their aqueous solutions. At different conditions (pH, contact time, temperature and adsorbent dosage) to obtained the optimum condition of adsorption.
4. Study the adsorption isotherms by the application of Langmuir, Freundlich, and Tempkin.

Chapter Two

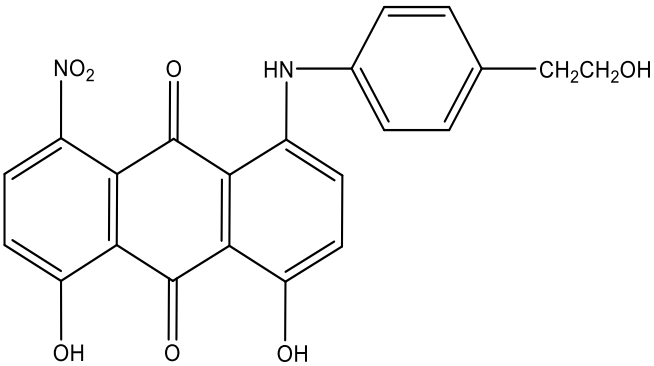
Experimental Part

2.1 The Adsorbate

Three industrial dyes (cationic, anionic and nonionic) have been used in the experiments. These dyes include:

I. Disperse Blue

This is a nonionic dye having the name C.I. Disperse Blue 27 (DB) Fig. 1.7. Disperse dyes (DDs) are the most common causes of textile-related allergic contact dermatitis. Are used in dyeing synthetic fabrics made from fibers. DDs don't use to dye natural fibers. They aren't chemically bound to the fibers, therefore the small, lipophilic molecules could migrate onto the skin of the human being wearing the clothes, particularly if the textile fastness is weak. DDs could removed by rubbing and by water. Most DDs are azo, or anthraquinone dyes [82]. Table 1.4 shows the description of Disperse blue used. **Table 2.1:** The physical and chemical properties of disperse blue.

Specification		Dye structure
MF	C ₂₂ H ₁₆ N ₂ O ₇	
MW	420.38	
Class	Anthraquinone	
Color	Dark blue	
Solubility	Water	
Company	Ciba	
$\lambda_{\text{max}}(\text{nm})$	553	1,8-dihydroxy-4-((4-(2 hydroxyethyl) phenyl) amino) -5-nitroanthracene-9,10-dione

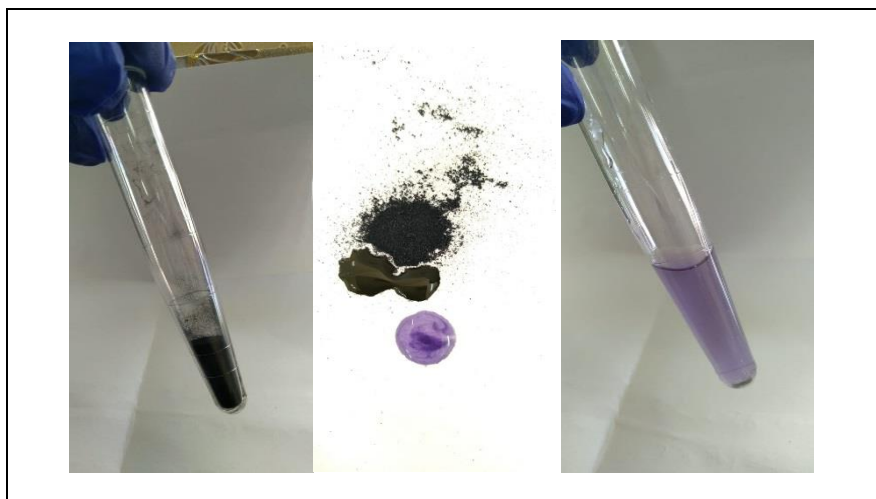


Fig. 2.1. The solid and aqueous solution of the Disperse blue dye.

II. Reactive Red

Anionic dye known as C.I. Reactive Red 15 (RR) Fig. 1.8. Table 1.5. It is one of the azo dyes, which is excessively used in a diversity of products, like textile, paper, and dye printing industry. Several of azo dyes show toxicity leading to the need for critical analytical procedures for the determination the little levels [83].

Table 2.2: The physical and chemical properties of Reactive Red.

Specification		Dye structure
MF	$C_{25}H_{14}ClN_7Na_4O_{13}S_4$	
MW	876.07	
Class	Azo dye	
Color	Dark red	
Solubility	Water	
Company	Ciba	Sodium 4-((4-chloro-6-((4-sulfonatophenyl)amino)-1,3,5-triazin-2-yl)amino)-5-hydroxy-6-((2-sulfonatophenyl)diazenyl)naphthalene-1,7-disulfonate
λ_{max} (nm)	540	

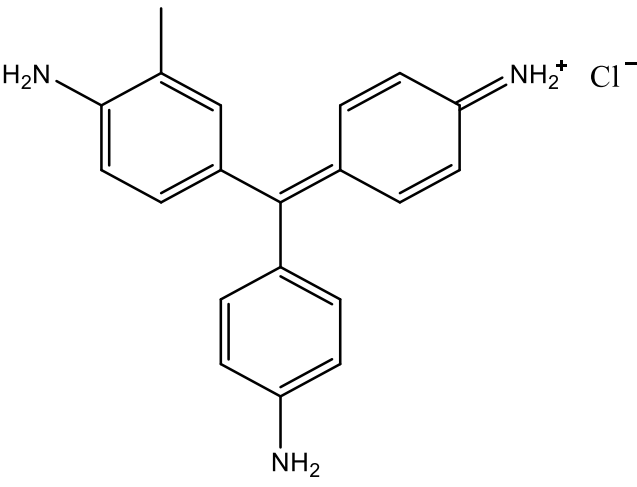


Fig. 2.2. The solid and aqueous solution of the Reactive Red dye.

III. Fuchsin

Fuchsin dye also called a Basic Fuchsin dye (FU) Fig. 1.9. It is a cationic dye, considered as triarylmethane class dyes, it is inflammable in nature and have an aesthetic, bactericidal, and fungicidal properties. It used as a coloring agent for textile, leather substances and in the staining of collagen, muscle, and mitochondria. Because of its possession of poor biodegradation, toxicity, carcinogenicity and unsightliness, Basic Fuchsin removal from wastewater is of great worry and should be tested and proceed immediately [84]. Table 1.6 shows the description of Basic Fuchsin used in the experiment.

Table 2.3: The physical and chemical properties of Fuchsin.

Specification		Dye structure
MF	$C_{20}H_{20}Cl^- N_3^+$	
MW	337.85	
Class	Basic dye	
Color	Dark green luster	
Solubility	Water	
Company	HIMEDIA	
λ_{max} (nm)	545	4-((4-amino-3-methylphenyl)(4-aminophenyl)methylene)cyclohexa-2,5-dieniminium chloride

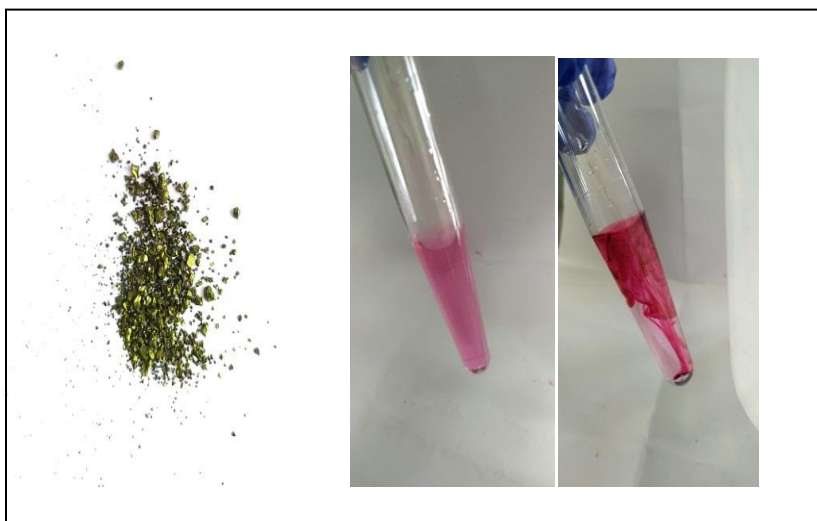


Fig. 2.3. The solid and aqueous solution of the Basic Fuchsin dye.

2.2 The Experimental part

2.3 Instruments

Some of the analytical were done at University of Tehran and, other analytical like (UV-Vis, FT-IR, and TGA) were done at Al-Muthanna University, Iraq.

2.3.1 Fourier-transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were measured using FT-IR spectrometer (Shimadzu-8400S) using KBr cm^{-1} disc and scanned at the wave number range of 4000–400 cm^{-1} in College of Science, Al-Muthanna University.

2.3.2 Nitrogen Adsorption-Desorption Analysis (BET)

Nitrogen adsorption was recorded using (Surface area analyzer BELSORP-mini II). The measurement was carried out in Chemical Sciences, University of Tehran, Iran.

2.3.3 pH Meter

Is used to measures the concentration of the hydrogen ions in the aqueous phase (Hanna 211 pH Meter C-A1), in College of Science, Al-Muthanna University, Iraq.

2.3.4 Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) were done to know the nature and porosity of the prepared surface, SEM images were taken using (Fesem Tescan Mira3 France) instrument. The measurement was done at, University of Tehran, Iran.

2.3.5 Thermogravimetric Analysis (TGA)

A thermogravimetric analyzer (TGA), instrument (Perkin Elmer-TGA-4000) model, was used for studying thermal stability of the surface prepared, it was carried out in College of Science, Al-Muthanna University, Iraq.

2.3.6 UV-Visible Spectroscopy

The scanning spectra were recorded by using UV-Visible spectrophotometer (1650 pc Shimadzu). The scanning was carried out in College of Science, Al-Muthanna University, Iraq.

2.3.7 Water Bath Shaker

Adsorption was carried out using (water bath shaker Lab Companion BS-11); it contains a temperature regulator, vibrator and time regulator, in College of Science, Al-Muthanna University, Iraq.

2.3.8 X-Ray diffraction (XRD)

Powder X-ray Diffraction (XRD) was obtained using (Xpert Phillips Holland) device. The measurement was done at University of Kashan, Iran.

2.4 Methods

2.4.1 Determination of maximum wavelength ($\lambda_{\max}$) and Calibration curve

Prepare a standard solution for the three dyes (DB, RR, and FU) at a specific concentration by dissolving a certain weight of the solid dyes in an amount of distilled water while stirring to complete the dissolution. Diluted solutions of the three dyes were also prepared after the necessary dilution of the standard solution was made, as required by the experiment. To determine the maximum wavelength ($\lambda_{\max}$) of the dyes.

The UV-visible absorption spectrum of the dye solution was recorded within the wavelength range of (800-400 nm). Where the maximum wavelength of the dye solution was determined from its highest absorbance in the UV-visible spectrum as shown in the Fig 2.1, 2.2, and 2.3 for the three dyes.

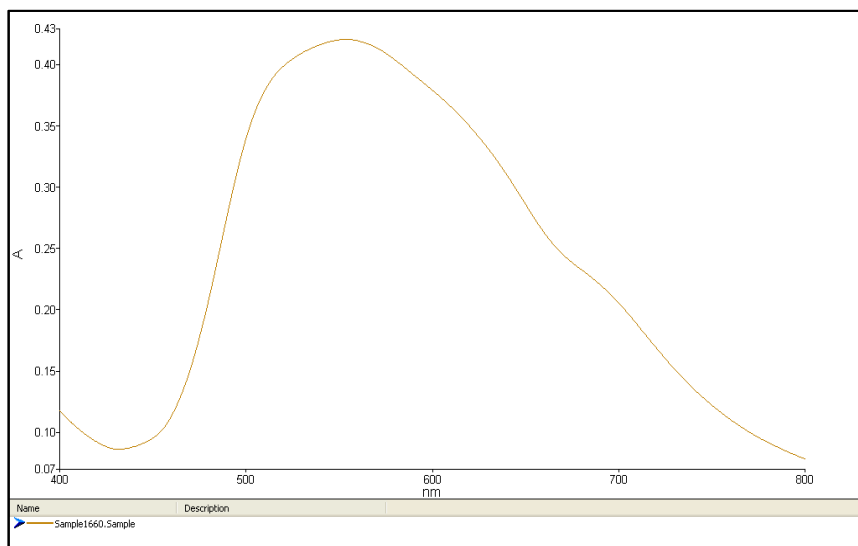


Fig 2.4. The scan spectrum curve of DB dye.

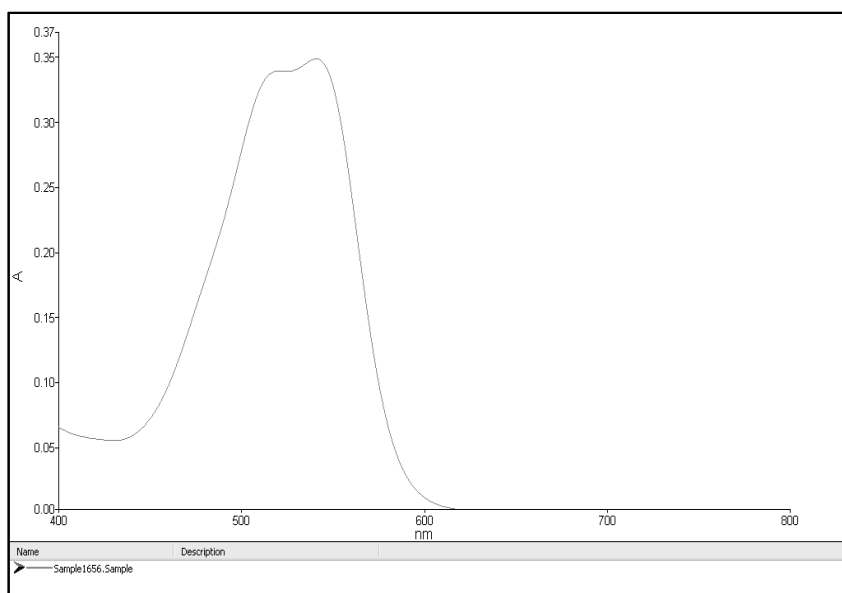


Fig 2.5. The scan spectrum curve of RR dye.

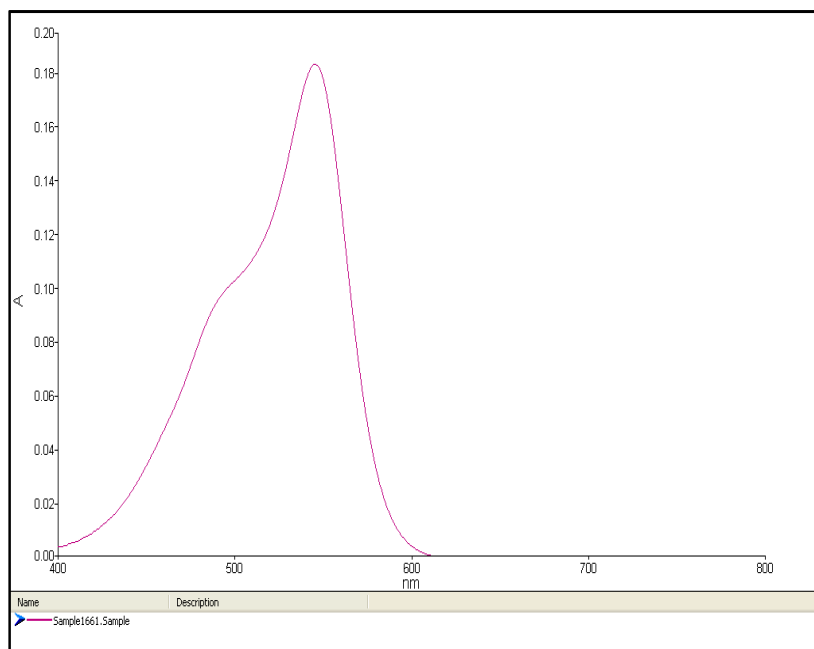


Fig 2.6. The scan spectrum curve of FU dye.

The maximum wavelength (λ_{max}) obtained for the three dyes (DB, RR, and FU) were listed in Table 2.1.

Table 2.4: The (λ_{max}) for DB, RR and FU dyes

The Dyes	$\lambda_{\text{max}}(\text{nm})$
Disperse Blue	553
Reactive Red	540
Fuchsin	545

To determine the calibration curves by install the (λ_{max}) for each dye. A series of solutions were prepared by successive dilution of the standard dye solution and with concentrations ranging from (0.3-100) ppm. Absorption was recorded and the calibration

curve appointed between concentration and absorption. Fig. 2.4 to 2.6 shows the calibration curves for DB, RR and FU respectively.

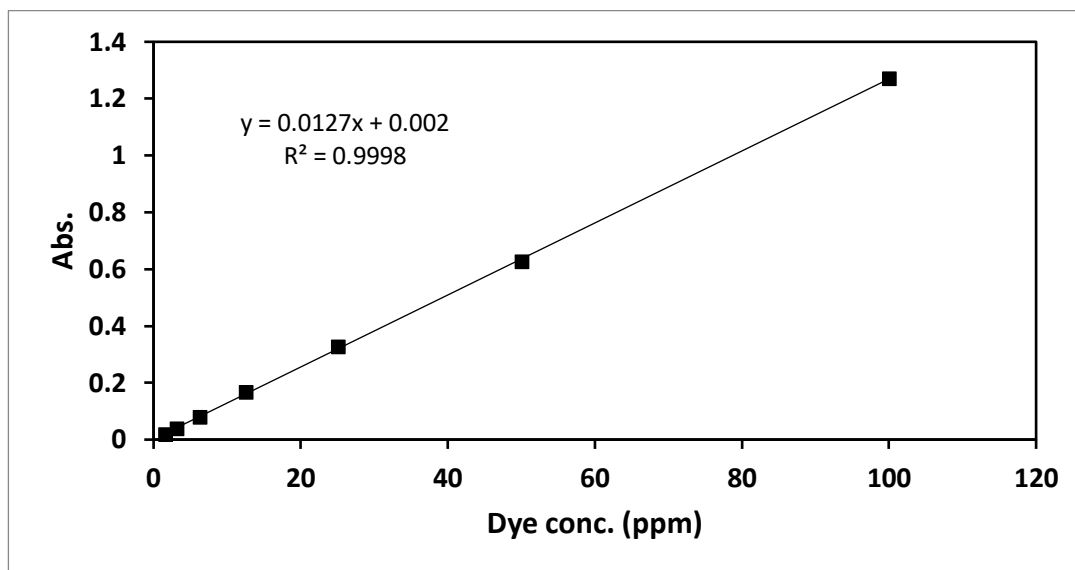


Fig. 2.7. The calibration curve of DB.

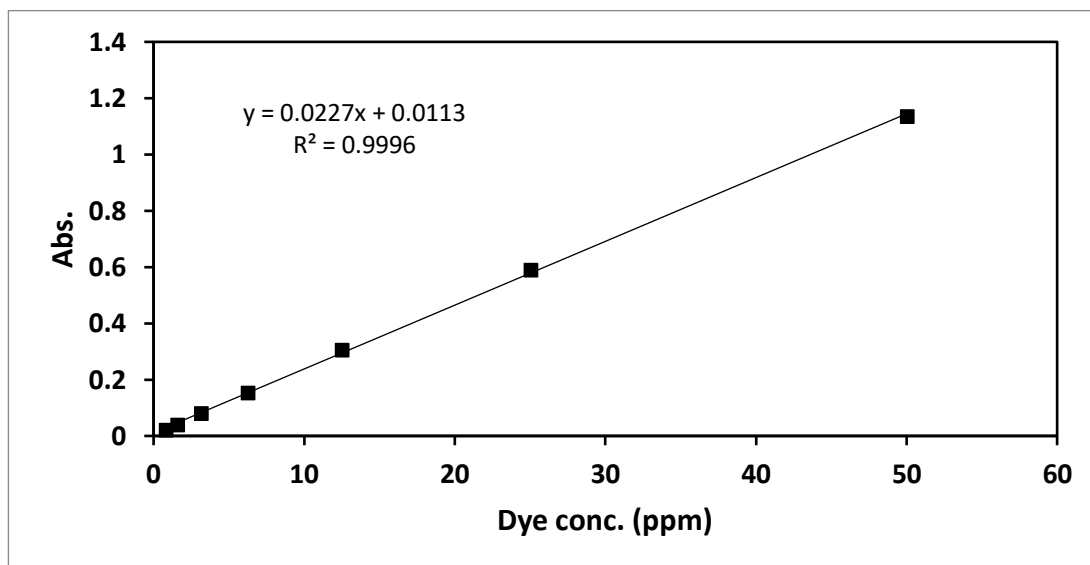


Fig. 2.8. The calibration curve of RR.

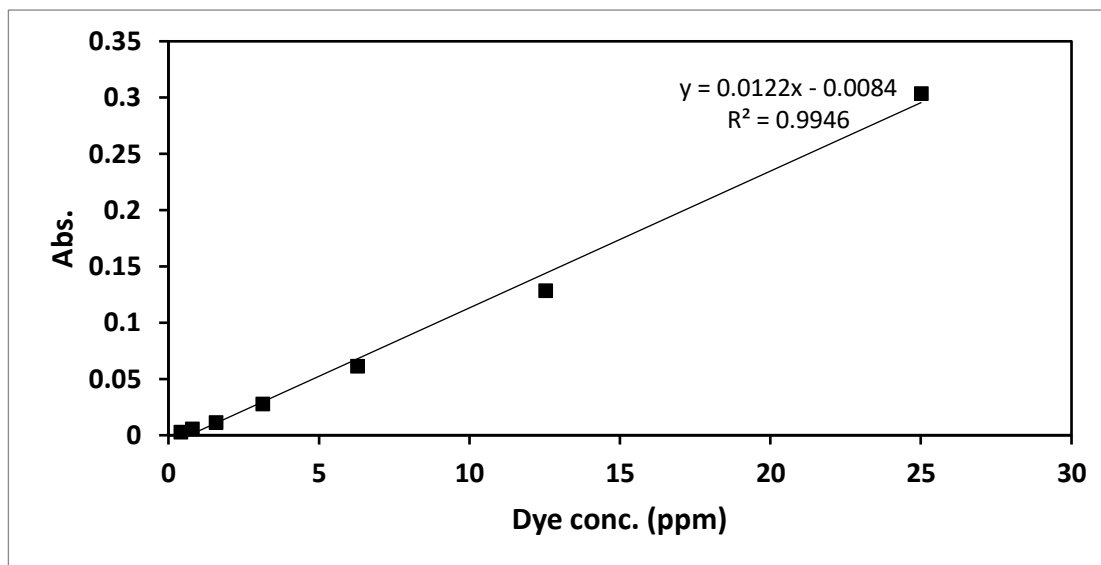


Fig. 2.9. The calibration curve of FU.

2.4.2 Preparation of adsorbent surface (AS)

- a) The samples of the root of the Astragalus plant were collected from the desert of Al-Salman district in Al-Muthanna Governorate, and the plant was air-dried.
- b) Then the roots were broken into small fragments of different sizes.
- c) The collected roots were thoroughly washed twice with running potable water first, for several times to remove dirt, dust, and any unwanted particles, followed by soaking in distilled water for 30 minutes until the washing liquid turned colorless.
- d) Placed in a drying oven and dried with a temperature of (53 °C) for 5 hours to complete drying.
- e) Then the material was ground with a home grinder into small-sized particles. Until it became almost powder. Then a sieve of (125µm) size sifted it. The preparation stages of the adsorbent surface are shown in Fig. 2.7 (a- f).

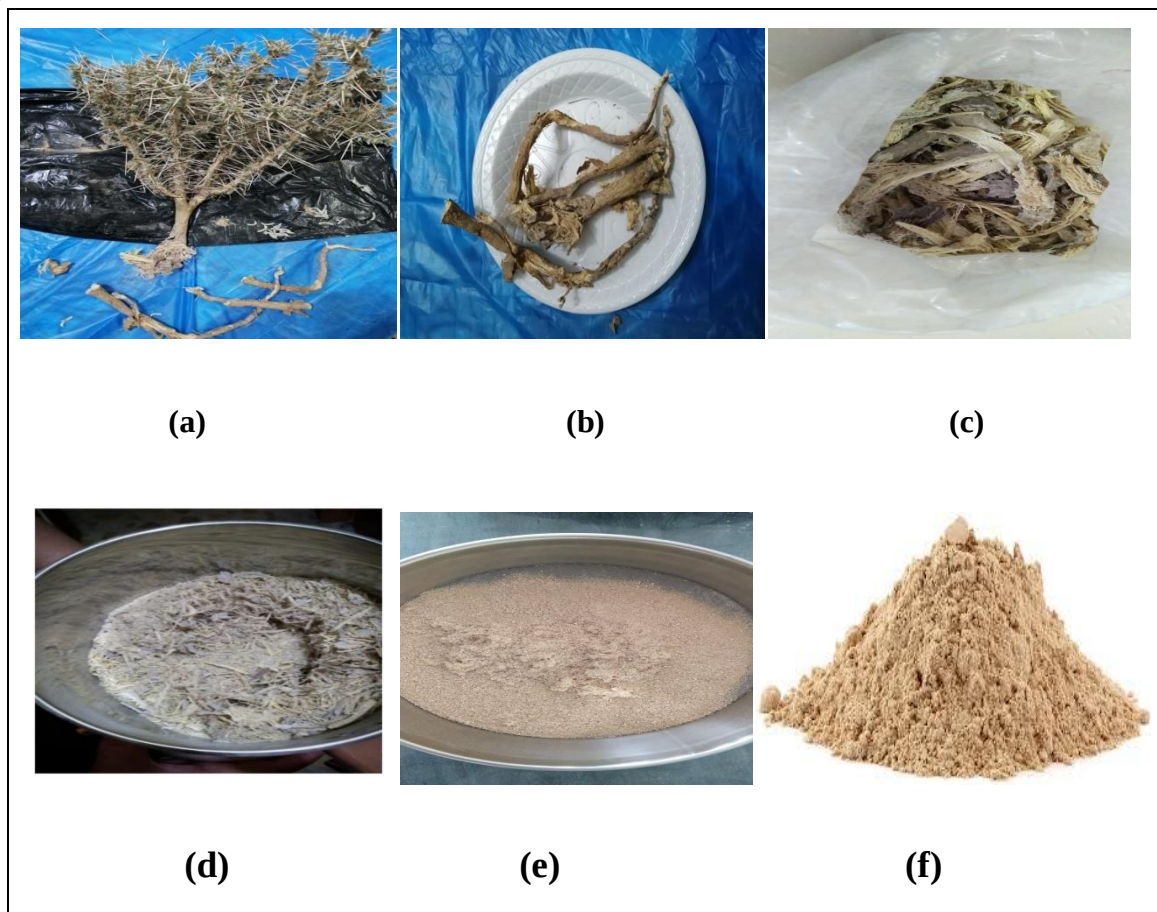


Fig. 2.10. Shows the preparation steps of adsorbent surface.

2.4.3 Preparation of Stock Solutions

Dyes stock solutions were prepared by dissolving the dyes in deionized water by using volumetric flasks. The dyes are minutely weighted in (0.25g), and dissolved in (500ml) conical flasks, and filled with water to prepare a concentration of (500ppm) for DB, RR and FU dyes. Then, from these concentrated solutions (the stock) for dyes, a series of diluted solutions were also prepared with different concentrations ranging from (10-80 ppm) and the solutions were stored [85]. The series of diluted solutions for the dyes are shown in Fig. 2.8, 2.9, and 2.10.



Fig. 2.11. Shows a series of diluted solutions for DB.



Fig. 2.12. Shows a series of diluted solutions for RR.



Fig. 2.13. Shows a series of diluted solutions for FU.

2.5 Study the factors effecting on adsorption process

2.5.1 Determination of the equilibrium time of Adsorption Systems

Determine the equilibrium time between adsorbent and adsorbate. Where all conditions are constant, the dye concentration, the weight, the pH, and temperature with the change of time factor. Different times (10, 30, 40, 50, 60, 90, and 300 min) were taken with (25ml, 50ppm) and the weight of the adsorbents surface was (0.5g). The pH of the dyes (DB, RR, and FU) solutions were not changed.

Volumetric flasks were placed in water-bath shaker at 25°C and 125rpm. After the time is up the sample was drawn from the water bath. Then placed in a centrifuge for (10 min) at 6000 rpm and filtered. After separation, the solutions were measure through UV-Visible spectrophotometer. By following the change in the percentage removal with time, the equilibrium time was determined, as the optimum time was 90 minutes, according to the following formula [86] [87]:

$$Removal(\%) = \frac{C_0 - C_e}{C_0} * 100 \quad (1-2)$$

Where C_0 and C_e are the initial and final concentrations(mg/L) of dye in solution, respectively. The adsorbed amount (mg/g) was calculated using the formulae:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2-2)$$

Where (C_0 and C_e) are the initial and equilibrium dye concentrations, respectively, (V) is the volume of the solution (L) and (m) is the mass of the adsorbent.

2.5.2 Effect of adsorbent mass

To study the effect of the adsorbent weight on the adsorption process, different weights have been taken (0.02, 0.05, 0.1, 0.2 and 0.5g) at 25°C, volume and concentration (25ml, 50ppm) for the three dyes were constant. The equilibrium time (90min) and the pH were also constant (It has not been changed). The conical flasks were placed in the water-bath shaker at 125rpm and then the samples were placed in the centrifuge for (10min) at 6000rpm. In addition, it was filtered through a filter paper, after that the solutions were measure through UV-Visible spectrophotometer [88].

2.5.3 Effect of Temperature

For determining the effect of temperature on the adsorption of the (DB, RR, and FU) dyes. Various solutions (10-80 ppm) were prepared from the three dyes. Also (0.5g /25mL) was added in the flasks. They were shaken in a water-bath shaker at 125rpm for 90 minutes, at three different temperatures (25, 35 and 45°C). The pH of the dyes solutions were not changed. The regulator of the water bath shaker controlled the temperature. After that, the samples were placed in the centrifuge for (10min) at 6000rpm. The solutions were measured using UV-Visible spectrophotometer [89].

2.5.4 Effect of pH

To study the effect of pH on the adsorption process, adsorption procedures were done at (3, 7 and 10) pH. Take a constant volume (25mL) of the three dye solutions with (10, 20, 30, 40, 50, 60, 70, and 80ppm) Concentrations. The pH value was adjusted by adding the required quantity of dilute (0.1N) hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions. The parameters such as adsorbent weight (0.5g), the temperature

(25°C) and contact time (90min) remains constant. Afterward, the conical flasks were placed in the water-bath shaker at 125rpm. Then the samples placed in a centrifuge for (10min) at 6000rpm. After equilibrium, the solutions were measured with the UV-Visible spectrophotometer [90].

2.5.5 Adsorption Isotherms

Eight solutions of each dye were prepared in volumetric flask 250 ml capacity with concentrations ranging from(10-80ppm). Then take (25ml) of each concentration and put in contact with (0.5 g) of adsorbent surface in conical flasks then placed in the water bath shaker at 125 rpm, and (25°C) for (90min). The pH of the dyes solutions were not changed. The adsorbate solutions were placed in the centrifuge for (10min) at 6000 rpm. After separation, the solutions were measure through UV-Visible spectrophotometer. After that, the amount of equilibrium adsorption, q_e (mg/g), was calculated using following equation [91]:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (3-2)$$

Where q_e : The amount of equilibrium adsorption (mg/g).

C_0 : The initial concentration of the dye in solution (mgL⁻¹).

C_e : The concentration of the dyes in solution at equilibrium time (mgL⁻¹).

V : The volume of the solution (L).

m : The mass of dry adsorbent (g).

Chapter Three

Result & Discussion

3.1 Characterization of the prepared surface (AS)

3.1.1 Fourier transform infrared spectroscopy (FTIR)

FTIR-spectroscopy development undergone great progress in recent years, which open a wide field of new applications. FTIR-spectroscopy used in the identification of functional groups of unknown compounds [92].

Fig. 3.1 shows the infrared spectrum of the prepared surface containing many adsorption peaks. The infrared spectrum peaks show the kinds of functional group presents. Each adsorbent might have a different functional group, therefore causes their adsorption capacity to be varied. The functional group could help or prevent the adsorption process [93].

The spectrum shows three broad and overlapping beams at wave numbers (3419.9, 3406.49, 3389.04 cm^{-1}) due to the vibration stretching of the hydroxyl group (H-O) . At frequency of 2924.18 and 2854.74 cm^{-1} , it shows there is C-H stretch. While at 1741.78 cm^{-1} , esters, saturated aliphatic functional group exist with C=O stretch. At 1637.62 cm^{-1} , there are C=C stretch. 1031.95 this could belong to the group the C–O That could be present [94] [95]. Table 3.1 shows the wave numbers and interpretation of the principal bands in FT-IR spectra.

Table 3.1: Wave numbers and interpretation of principal bands in FT-IR spectra of AS.

Assignment group	Wave numbers (cm ⁻¹)
O-H stretching	3419.9-3200
C-H stretching	2924.18 and 2854.74
C=O stretching in ester	1741.78
C=C stretch	1637.62
C-O stretch	1031.95

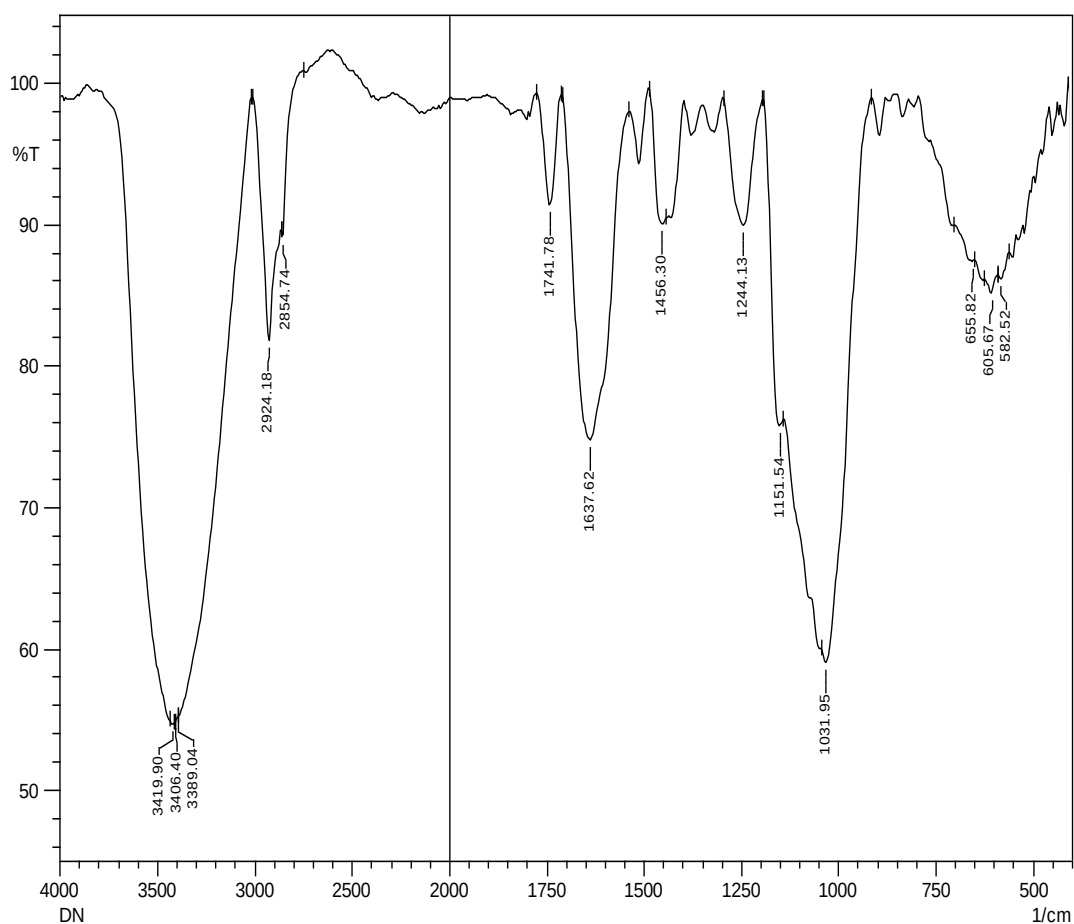


Fig. 3.1. The FT-IR Spectra of AS.

3.1.2 X-ray diffraction (XRD)

The crystalline structure of the prepared surface (AS) has been characterized using X-ray diffraction (XRD) technology, the spectrum (intensity versus 2θ) being shown in Fig. 3.2. The XRD diffraction pattern of AS showed two types of diffractions that indicate the presence of two phases. It shows poor crystallinity, and a broad diffraction band at 2θ angle of ca. 22° confirming the amorphous nature of the sample [96]. In addition, it can be observed that there are two sharp diffraction peaks appeared at $2\theta = 29.5^\circ$ and 50.2° indicate the presence of the second, crystalline phase. The mixture of amorphous and crystalline peaks reveals that the (AS) has semi-crystalline structure [97] [98]. There are diffraction peaks that became more widened when the size of the crystals is very small. The broadening of the diffraction peaks indicates the presence of these small particles. According to the literature, the crystalline size decreases when increasing the width of these peaks. The Fig. 3.2 shows a widening of the XRD diffraction peaks of particles (AS). This indicates the presence of small-sized particles [99]. The broadening of the X-ray diffraction peaks is due to four main factors: micro-strains such as lattice deformation, crystal faulting such as extended defects, domain size of the crystal, and the distribution of domain size [100] [101]. If the prepared crystals are neither are unstrained and non-faulted then the broadening in this case is attributed to crystalline domain size [102]. Bragg's law was used to calculate the interplanar distance

as shown in the following equation:

$$d = \frac{n \lambda}{2 \sin (\theta)} \quad (1-3)$$

where: n is an integer, λ is the wavelength of X-rays, d is the distance between the planes of the crystalline lattice and, θ is the angle between the incident rays and the scattering planes [103].

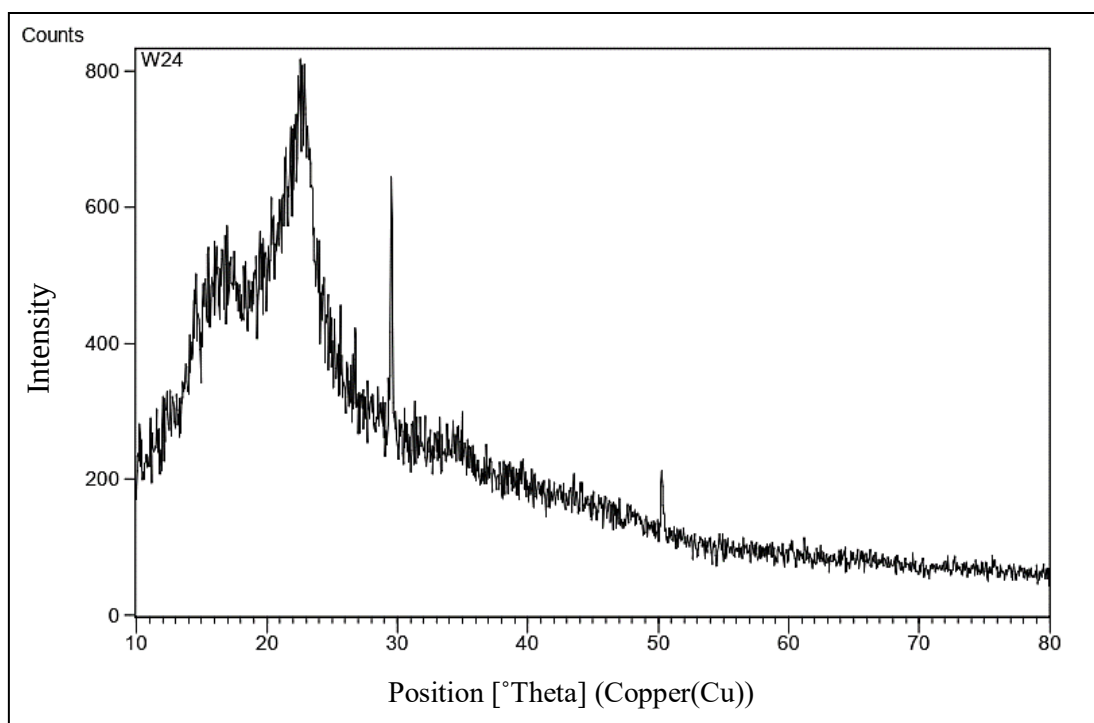


Fig. 3.2. The X-ray diffraction pattern for AS.

3.1.3 Scanning Electron Microscopy (SEM)

The use of SEM could help us better to understand the micromorphology on solid surface such as (shape, particle size and the nature of the surface) and to analyze the fracture forms and internal structure of materials [104]. Fig. 3.3 (a, b, c, d) shows the SEM micrographs of Astragalus root powder (AS), careful observation of the images at different levels of magnifications, revealed the presence of aggregate particles which might be correlated with its strongly porous nature resulting in nearly high surface area. As shown in micrographs, at low magnification Fig. 3.3 (a) and (b), shows surfaces with two different particles (Light and darker particles), and a very rough surface made up of granular particles. The granular particles are arranged randomly and with non-uniformity shape on the surface. In addition, the shape of the particles is rocky, irregular, and with different sizes. At the high magnification shown in Fig. 3.3 (c), the average particle size

ranges between (52-14 nm). While Fig. 3.3 (d) shows a big rock shape [98] [105,106, 107].

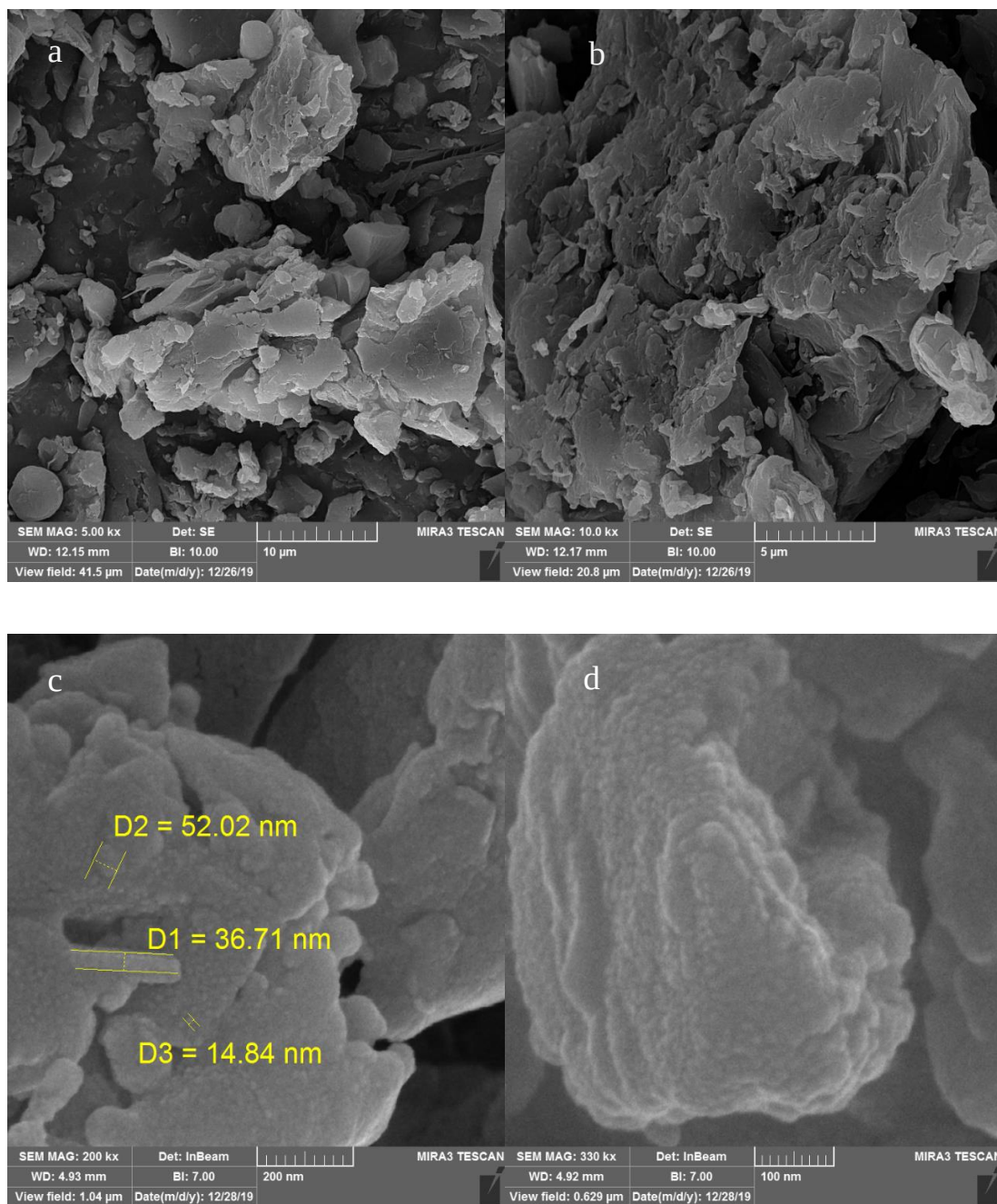


Fig. 3.3. SEM micrographs of AS at magnifications of (a) 5000 magnification, (b) 10000 magnification, (c) 200000 magnification, (d) 330000 magnification.

3.1.4 Surface Area Analysis (BET,BJH)

In BET surface area analysis, nitrogen (N_2) is usually used due to its availability in high purity and also its strong interaction with most solids. The interaction between gaseous and solid phases is commonly weak, therefore the surface is cooled by liquid nitrogen (N_2) to obtain a detectable amounts of adsorption [108]. The surface properties were studied in terms of surface area, pore volume and average pore diameter of the prepared surface particles (AS) using BET (adsorption-desorption) isotherms. Fig. 3.4 illustrates BET isotherms for nitrogen (N_2) adsorption and desorption on the surface of (AS) particles, and Fig. 3.5 shows the pore size distribution by (BJH) method. The form of the isotherm is reversible and convex and the relative pressure axis corresponding to (type III) isotherm according to the nomenclature of (IUPAC). This type is often encountered with macroporous materials, and which refers to a multilayer adsorption [109] [110]. The results showed that the total surface area of the (AS) surface reach ($13.84 \text{ m}^2/\text{g}$), where the pore volume is ($0.016 \text{ cm}^3/\text{g}$), and the average pore diameter (4 nm).

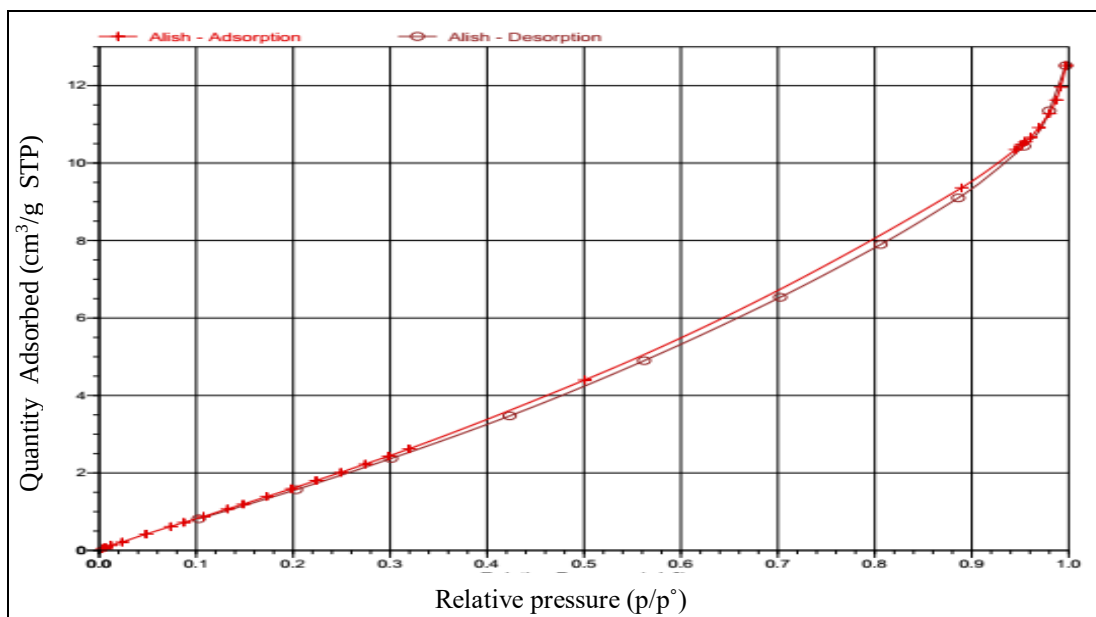


Fig. 3.4. The (N_2) adsorption-desorption isotherms of AS.

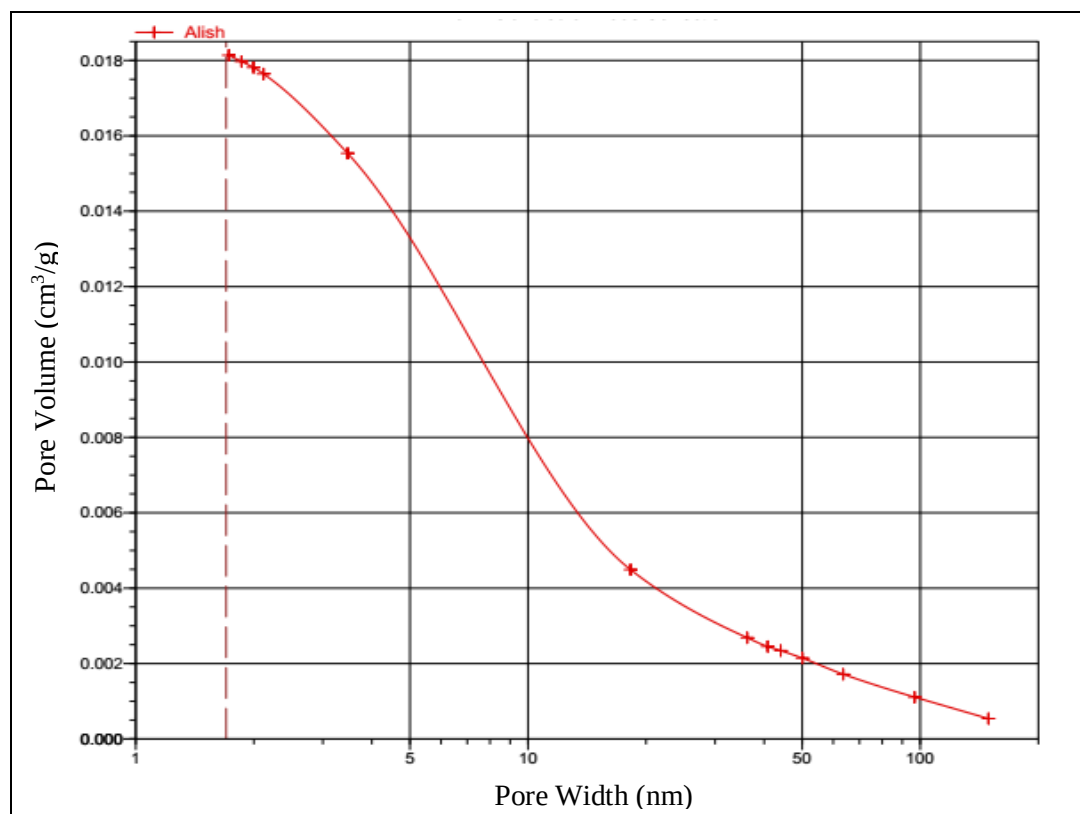


Fig. 3.5. Pore size distribution of AS particles according to the BJH method.

The size distribution of pores on the surface of (AS) particles in the (BJH) method showed that the surface possesses one type of pores, mesopores, whose sizes in the range of (2-50 nm) [48].

3.1.5 Thermogravimetric analysis (TGA)

Thermogravimetric analyzer (TGA) is used to determine the thermal degradation behavior of materials. It is proved to be one of the best processes to study and understanding the kinetics of pyrolysis, also it has been broadly used at low heating rates and temperatures up to 900°C [111]. Several information obtained from the TGA analysis such as the remaining mass percentage, the percentage of mass loss, and

determines the temperatures in which all the decomposition occurred. In the range of 40–900°C.

The results of the TGA analysis of the (AS) surface were shown in Fig. 3.6, which shows the corresponding mass loss with an increase in temperature. The results shows that the percentage of the remaining mass of AS sample was 0.000% of the original weight and three characteristic decomposition stages were shown. The first step of weight loss (5.39 %) was observed between 40–182°C, with a maximum of 100 °C. Due to the loss of absorbed water and the residual organic groups onto the surface because these are volatilized at low temperatures.

The highest amount of mass loss was found during the second stage (63.2 %) occurred between 182–439°C, with a maximum at 381 °C, assigned to the decomposition of the bonds of some groups onto the AS surface such as carbonyl and hydroxyl groups. The third mass loss (31 %) between 439–840°C, where the total weight loss for AS sample was 100%, which shows that the AS sample contains only organic compounds [112].

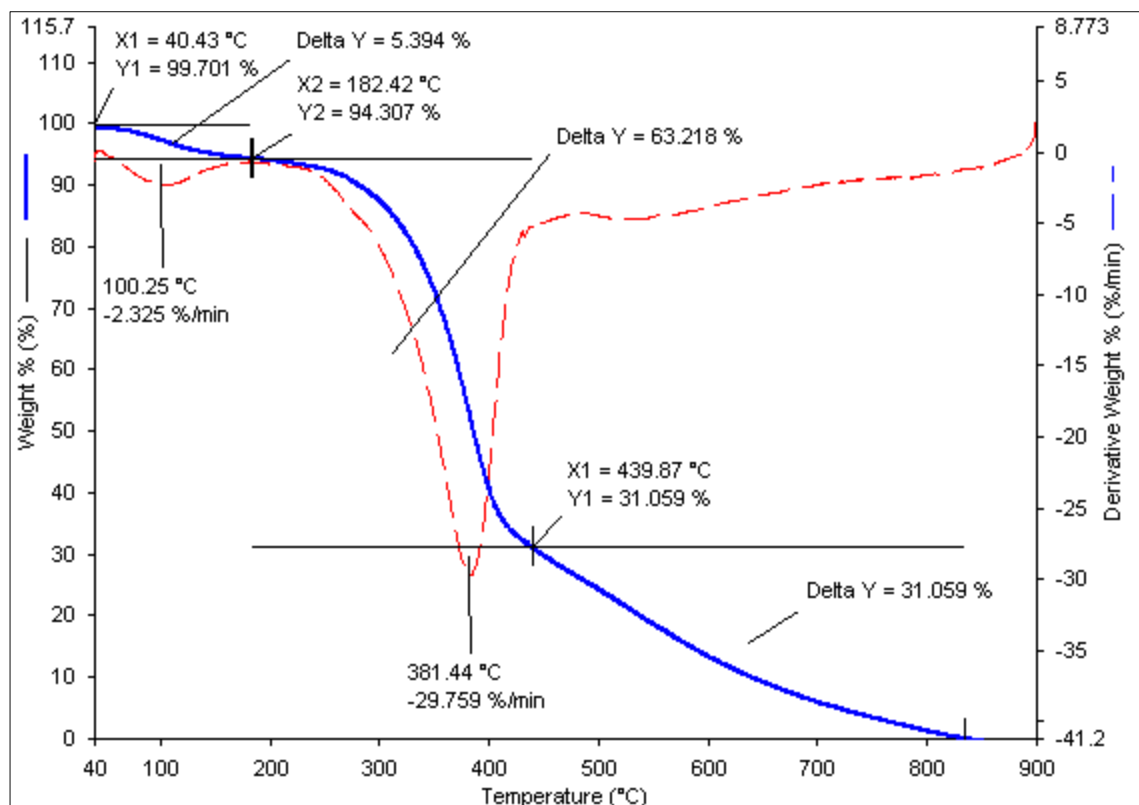


Fig. 3.6. The TGA analysis of AS surface.

3.2 Effect some parameters on adsorption of AS

3.2.1 Influence of contact time

Batch experiment to evaluate relationship between contact time and adsorption of three dyes (DB-RR-FU) on the surface of AS, studying the contact time required to achieve equilibrium time for the solution of dyes on the surface of AS at period time (10,30,40,50,60,90 and 300 min) with constant concentration (50ppm), temperature (25°C) and pH nature of dyes solution. Table 3.2 shows the time required to reach the equilibrium for the three dyes is 90 min and the percentage of removal rate (R %) also shown in the Table. Fig. 3.7 shows the percentage of removal for the three dyes. Which

increases with an increased in time at different rates in the first 80 min, and then remains stable after 90 min.

All of that depending on the chemical and physical nature of dyes and saturation of active sites on the surface. The percentage removal of the dyes increases with time because initially unoccupied active sites are available more for the adsorption of the dyes and as the time increase, the active sites are used up and a stable state has resulted, an equilibrium state. Where the sites are reached fully saturated [113]. The shaking time of 300 min was used to ensure full equilibration.

The percentages of dye removal (R%) calculated as follows:

$$R\% = \frac{C_0 - C_e}{C_0} * 100 \quad (1-3)$$

Where C_0 and C_e are respectively the concentrations of initial and equilibrium for dyes in solution (mg/L).

Table 3.2: Show the R% of the dyes (DB-RR-FU) by AS at different times.

Tim(min)	DB	RR	FU
	R%	R%	R%
10	53	47.1	49.2
30	53.2	51.5	58.7
40	62.3	55	67.3
50	64.8	57.3	68.9
60	73.2	60	79.6
90	75.7	60.7	80.2
300	75.9	61.1	80.5

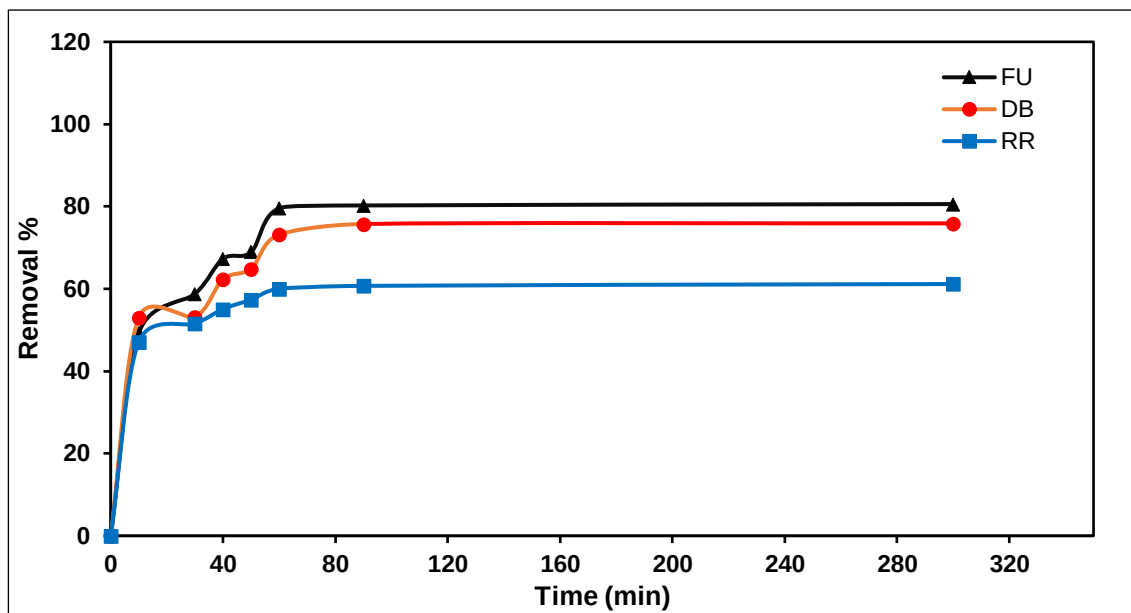


Fig. 3.7. The effect of contact time on the adsorption of the three dyes for AS.

3.2.2 Influence of adsorbent dosage on adsorption

This experiment has been conducted to observe the influence of varying adsorbent weight on the adsorption of dyes solutions with keeping contact time (90min) and the initial concentration for the dyes (50 ppm) constant, the adsorption was done with different adsorbent weights (0.02, 0.05, 0.1, 0.2 and 0.5 g, per 25 ml) at 25 °C. Fig. 3.8 shows the effect of AS adsorbent dosage on removal of the three dyes (DB-RR-FU). Table 3.3 shows the results where the percentage of removal for three dyes increases with the increases of adsorbent weights of AS. This is maybe to the greater availability of sorption sites and an increased surface area where the adsorption occurred. The results indicate that it is possible to increase the percentage of removal for the three dyes on the AS surface and reach a high percentage by increasing the weight of the adsorbent under the same experimental conditions. The increase in the percentage of removal with the increase in the adsorbent weight is due to the increase in the number of active sites

on the AS surface that are available to adsorb the dyes, so the efficiency of the dye removal will increase with the increase in surface mass [114]. In this study, the suitable weight of, AS is 0.5 g for the dyes adsorption.

Table 3.3: The values of R% and Quantity of adsorbent for AS.

Quantity of adsorbent (g)	DB			RR			FU		
	Ce mg/l	qe mg/g	R%	Ce mg/l	qe mg/g	R%	Ce mg/l	qe mg/g	R%
0.02	34.3	19.5	31.3	38.1	14.8	23.7	31.1	23.5	37.6
0.05	31	9.4	37.9	37.1	6.4	25.6	24.5	12.7	50.9
0.1	27.9	5.5	44	34.8	3.7	30.3	21.5	7.1	56.8
0.2	22.5	3.4	54.9	30.3	2.4	39.2	17.9	4	64
0.5	12.1	1.8	75.7	19.6	1.5	60.7	9.8	2	80.2

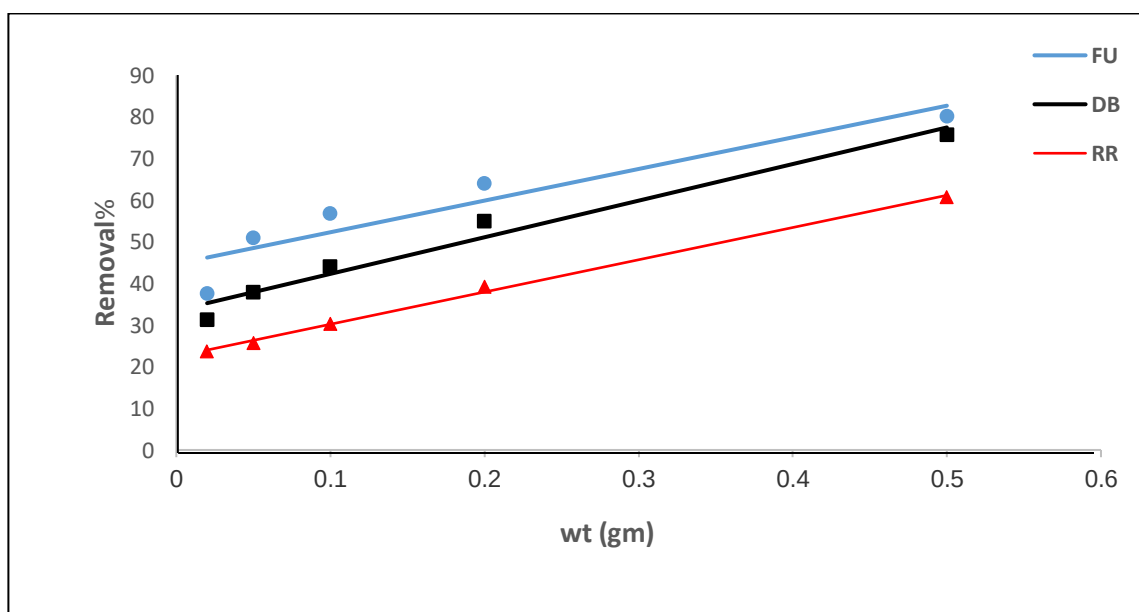


Fig .3.8. Effect of adsorbent dosage on removal of the three dyes for AS.

It is obvious from the Table 3.3 that the lower surface mass showed the highest adsorption capacity. The reason for this is that this surface has high adsorption efficiency, and therefore the adsorbed amount (q_e) is relatively high for the lower weight compared to the rest of the weights used.

3.2.3 Influence of solution pH

The values of the solution pH affect both, the binding sites of the adsorbents surface and the aqueous chemistry of the dye [115]. Many studies have proved that the pH of an aqueous solution is an important parameter in the whole adsorption process [116] [117], as it significantly influences on surface charge of the adsorbent, the adsorption mechanism, as well as the ionization degree of the functional groups of the adsorbate, and the adsorption capacity [118]. To investigate the effect of pH on (FU, RR, and DB) dyes adsorption onto the surface of AS were studied under the pH (4, 7 and 10) in 25°C with keeping contact time (90min) and the weight of adsorbent (0.5g) are constant. The results showed that the pH affects the absorption efficiency of the three dyes.

Fig. 3.9 and Table 3.4 show the effect of pH for FU onto the AS surface, the adsorption of FU dye is a phenomenon where is strongly affected via the pH of the solution. The obtained results indicate that the percentage of removal for FU on the surface of AS was increased with increasing the pH of solution. The adsorbed amount increases with the change of the solution pH in the following order: $10 > 7 > 4$.

At lower pH, H^+ may competing with the cationic dye (FU dye) for the adsorption sites of the AS surface, therefore inhibiting the adsorption of the FU dye, and thus restricts the approach of FU (positively charged) toward the surface of AS resulting in decreased

adsorption of FU dye at acidic solution [119]. In addition, at alkaline pH the system shows high sorption of the cationic dye because when the pH increases, the amount of negatively charged sites increases and the amount of positively charged sites decreases. Therefore, the negatively charged surface sorption site on the adsorbent favor the adsorption of FU dye due to the electrostatic attraction [120].

Either the maximum percentage of removal for RR dye was obtained at (pH= 4) while the minimum percentage of removal at (pH=10) as the following order: $4 > 7 > 10$, as shown in Fig 3.10 and Table 3.5. In aqueous solution, the RR dye is dissolved and sulfonate groups of the RR dye are dissociated and converted into anionic ions, at lower solution pH values, and due to the presence of H^+ ions, the dye ions will attracted to the positive charge of the AS surface due to increasing the electrostatic attraction forces. While lower adsorption of the anionic dye (RR dye) at basic pH could be attributed to the abundance of OH^- ions which will competing with the RR dye anions for the same sorption sites, causing a decrease in the adsorbed amount of the dye [121] [122].

The results in Fig. 3.11 and Table 3.6 shows that the adsorbed amount increases with the change of the pH of the solution in the following order: $4 > 7 > 10$. When decreasing the pH values of the solution, then the positive charges control the AS surface (adsorbent), and then an electrostatic attraction exists between the positively charged surface of the adsorbent and the DB dye. In this case, slight interaction dipole-charge-like can be suggested, taking into consideration both the negatively delocalized charge presents on anthraquinone residue and also, the dipole of ketons.

This attractive force increases the dye molecules adsorption onto the adsorbent surface. While when the pH of the system further increased, the adsorbent surface tended to

become negatively charged, and avoiding adsorption of the DB dye because of the electrostatic repulsion. Still, the adsorption could be considered good, suggesting that electrostatic interactions were not the only class of interaction forces involved in the adsorption phenomenon. The presence of Van der Waals, hydrophobic interactions and H-bonds can be considering predominant [115].

Table 3.4: The effect of the pH on the adsorption of FU dye to the AS.

	pH = 4		pH = 7		pH = 10	
C₀	C_e	Q_e	C_e	Q_e	C_e	Q_e
10	4.7	0.26	1.26	0.43	0.77	0.46
20	8	0.59	2.98	0.85	1.59	0.92
30	11.7	0.91	4.04	1.29	1.91	1.4
40	16.8	1.15	5.52	1.72	3.14	1.84
50	19.6	1.51	6.18	2.19	3.55	2.32
60	24.2	1.78	7.9	2.6	4.04	2.79
70	26	2.19	10.5	2.97	5.68	3.21
80	32.5	2.37	12.08	3.39	6.01	3.69

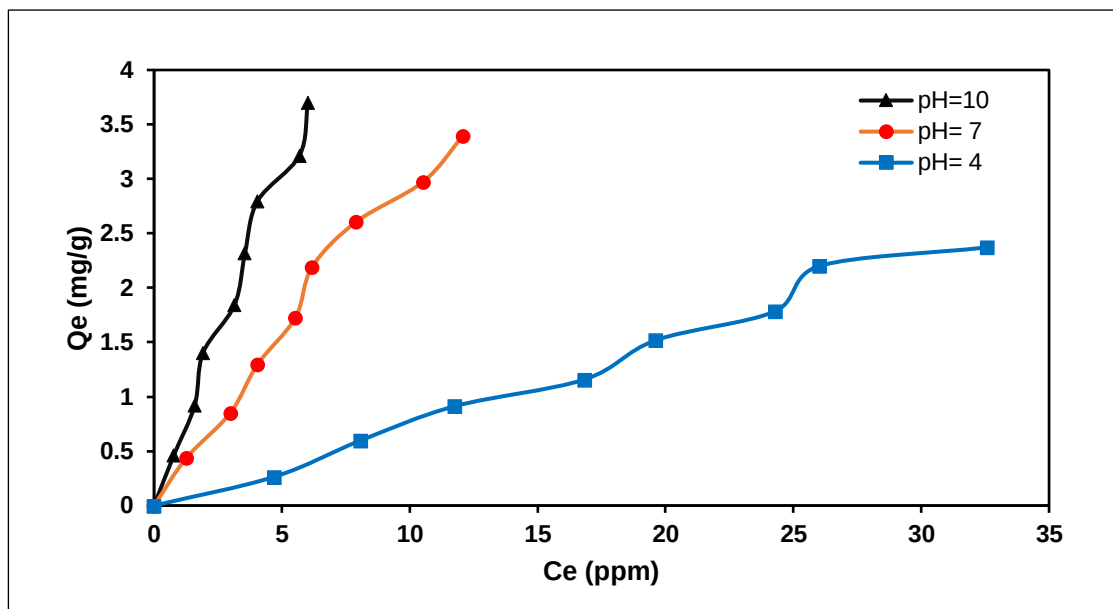


Fig. 3.9. Effect of pH on the adsorption of FU into AS.

Table 3.5: The effect of the pH on the adsorption of RR dye to the AS.

	pH = 4		pH = 7		pH = 10	
C ₀	Ce	Qe	Ce	Qe	Ce	Qe
10	1.26	0.43	3.86	0.3	5.71	0.21
20	2.18	0.89	6.63	0.66	8.22	0.58
30	3.46	1.32	8.53	1.07	16.7	0.66
40	3.95	1.8	14.7	1.26	21	0.94
50	8.44	2.07	17	1.64	27.6	1.11
60	7.51	2.62	21.4	1.92	35.6	1.21
70	8.79	3.06	26.4	2.17	38.8	1.55
80	12.2	3.38	31.6	2.41	43.4	1.82

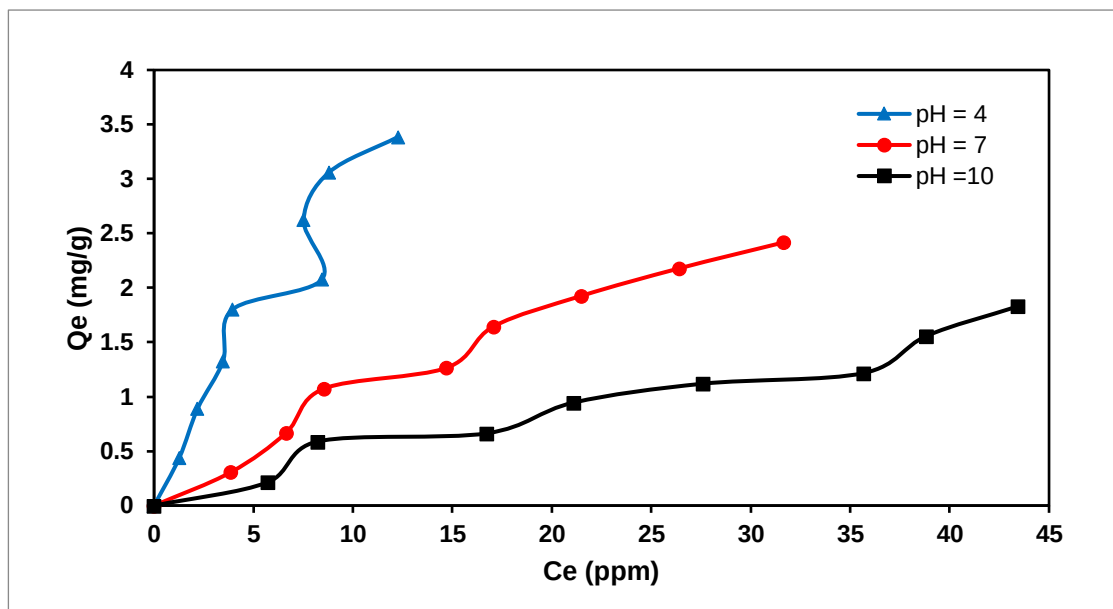


Fig. 3.10. Effect of pH on the adsorption of RR into AS.

Table 3.6: The effect of the pH on the adsorption of DB dye to the AS.

	pH = 4		pH = 7		pH = 10	
C ₀	Ce	Qe	Ce	Qe	Ce	Qe
10	1.49	0.42	2.44	0.37	3.14	0.34
20	2.75	0.86	4.17	0.79	6.37	0.68
30	5.51	1.22	6.85	1.15	10.7	0.96
40	5.66	1.71	8.5	1.57	12.5	1.37
50	7.95	2.1	12.2	1.88	15.4	1.72
60	8.42	2.57	12.3	2.38	20.2	1.98
70	9.37	3.03	15.1	2.74	21.6	2.41
80	11.4	3.42	19.8	3	25.7	2.71

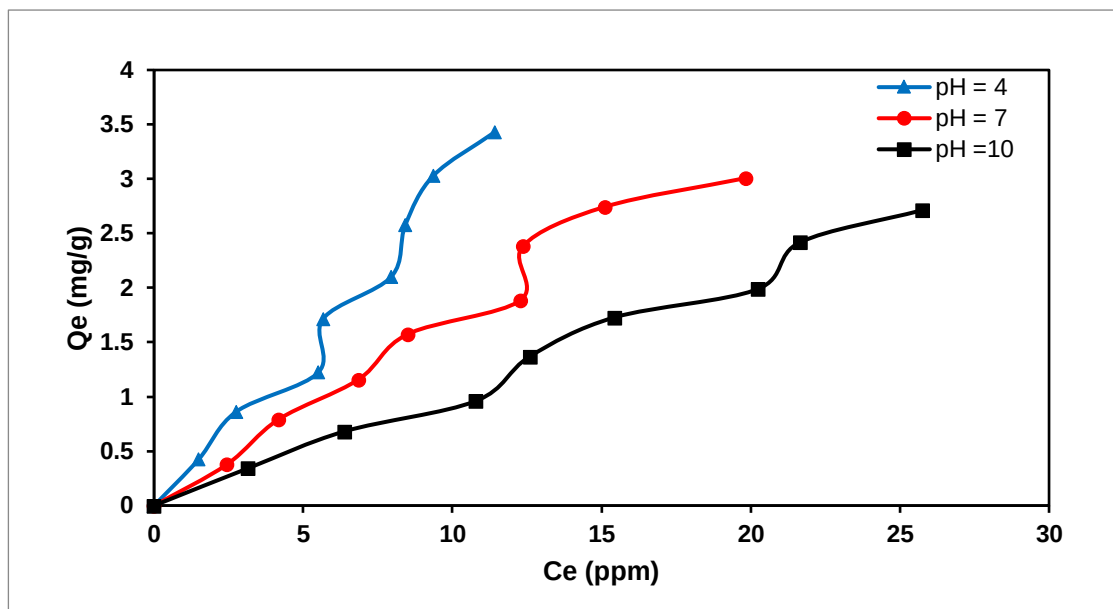


Fig. 3.11. Effect of pH on the adsorption of DB into AS.

3.2.4 Influence of temperature

To study the effect of the temperature on the adsorption of (FU, RR and DB) dyes from their aqueous solutions onto the AS surface, were carried out at three different temperatures (25, 35, and 45)°C with keeping the contact time (90min), pH(7) and the adsorbent weight (0.5g) constant. The adsorbed amount (q_e), Corresponding to each equilibrium concentration value (C_e), was calculated from the following equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2-3)$$

From Tables 3.7, 3.8, and 3.9 note the effect of temperature on the adsorption, was a decrease in the adsorbed amount of FU, RR, and DB dyes with increasing the temperature.

This indicate that the interaction between the adsorbent (AS) and the adsorbate (FU, RR, and DB) is exothermic process in nature. Fig. 3.12, 3.13, and 3.14 show the decrease in the (q_e) of the three dyes with increasing temperature. This could be due to increasing in the mobility of the adsorbate molecules with increasing in temperature of the solution. Which leads to the tendency of dye molecules to separate from the solid phase to the solution with increasing in the solution temperature [123] [124].

Table 3.7: The effect of temperature on (q_e) FU dye for AS surface.

C_0	25°C		35°C		45°C	
	Ce	Qe	Ce	Qe	Ce	Qe
10	1.83	0.4	3.06	0.34	4.04	0.29
20	4.21	0.78	5.85	0.7	8.14	0.59
30	6.18	1.19	7.73	1.11	12.5	0.87
40	6.67	1.66	9.62	1.51	15.2	1.23
50	9.86	2	13.5	1.82	17.7	1.61
60	13.5	2.32	15.5	2.22	23.8	1.8
70	14.2	2.78	17	2.65	24.5	2.27
80	16.5	3.17	22.5	2.87	29.9	2.5

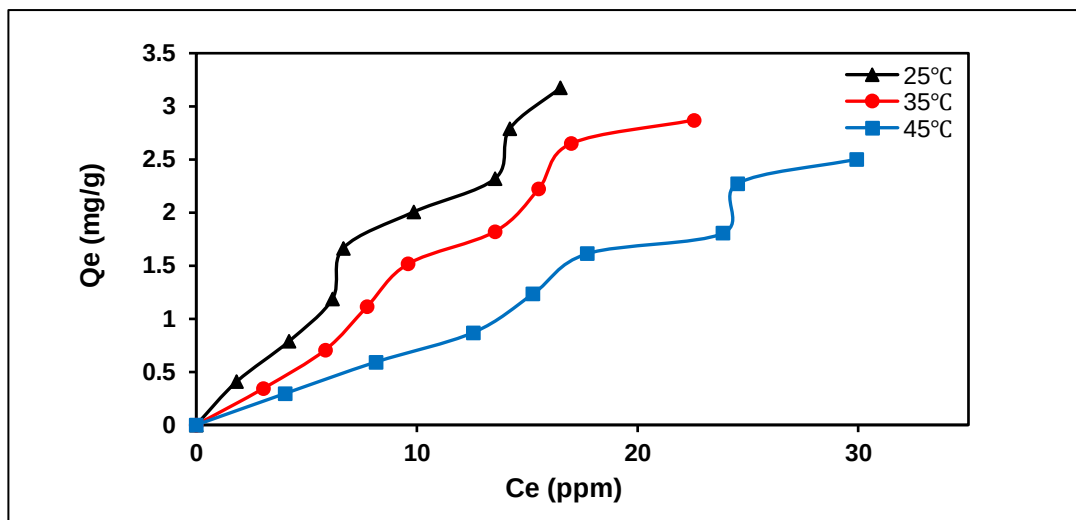


Fig. 3.12. Effect of temperature on the adsorption capacity of FU dye for AS.

Table 3.8: The effect of temperature on (qe) RR dye onto AS surface.

C_0	25°C		35°C		45°C	
	Ce	Qe	Ce	Qe	Ce	Qe
10	3.51	0.32	5.44	0.22	6.77	0.16
20	8.22	0.58	12.1	0.39	15	0.24
30	13	0.84	14.5	0.77	19.9	0.5
40	15.4	1.22	20.7	0.96	29.5	0.52
50	19.6	1.51	23.8	1.3	33.1	0.84
60	20.9	1.95	28.4	1.57	43.4	0.82
70	30	1.99	38	1.59	46.8	1.15
80	32.5	2.37	42.4	1.87	59.7	1.01

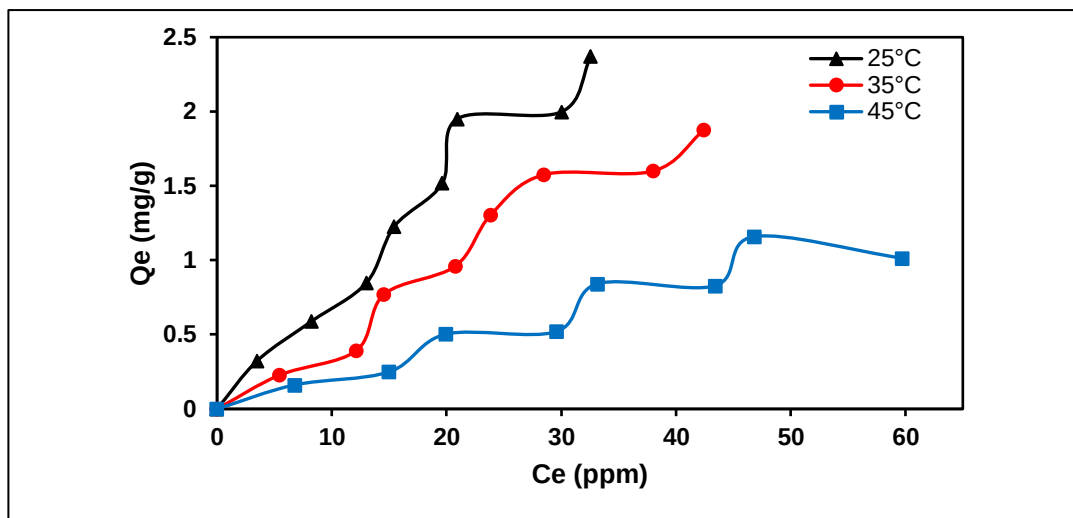


Fig. 3.13. Effect of temperature on the adsorption capacity of RR dye for AS.

Table 3.9: The effect of temperature on (qe) DB dye onto AS surface.

C_0	25°C		35°C		45°C	
	Ce	Qe	Ce	Qe	Ce	Qe
10	2.2	0.38	3.93	0.3	5.43	0.22
20	6.14	0.69	7.79	0.61	9.84	0.5
30	8.5	1.07	11.8	0.9	14.9	0.75
40	9.8	1.5	16.8	1.15	21.7	0.91
50	12.1	1.89	18.8	1.55	24	1.29
60	18	2.09	24	1.79	29.4	1.52
70	21.8	2.4	30.4	1.97	38.8	1.55
80	23.7	2.81	33.4	2.32	40	1.99

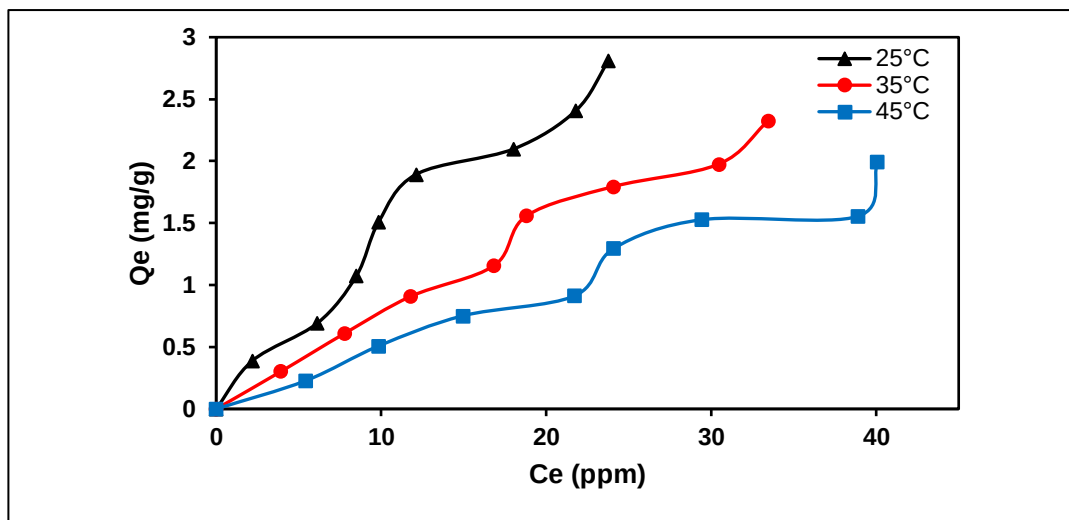


Fig. 3.14. Effect of temperature on the adsorption capacity of DB dye on AS.

3.2.5 Adsorption isotherm

The adsorption isotherm suggests how the adsorption particles distribute between liquid phase and solid phase, when the adsorption process reaches the equilibrium state. The isotherm data analysis by fitting them in different isotherm models, it is an important step to find the most suitable model. The Adsorption isotherm is mainly important to describe how the solutes will interact with the adsorbents, and is critical in the improvement of the use of adsorbents [125].

This study employed three isotherm models: the Langmuir, Freundlich, and Temkin isotherm models. The adsorption is carried out at concentrations (10-80 ppm) and at (25°C) for (90 min). The general form of adsorption for (FU, RR, and DB) dyes on the AS surface gives the general form of adsorption isotherms as shown in Fig. 3.15. The Figure was S-type according to the Giles classification of adsorption isotherms [126]. The S type isotherm curves occur when the adsorbent has a very high affinity for the solvent, thus, competing strongly with adsorbate molecules for the sorption sites [127].

The S-type isotherm indicates that the adsorbent is tend to stack vertically in regular arranging on the surface [128].

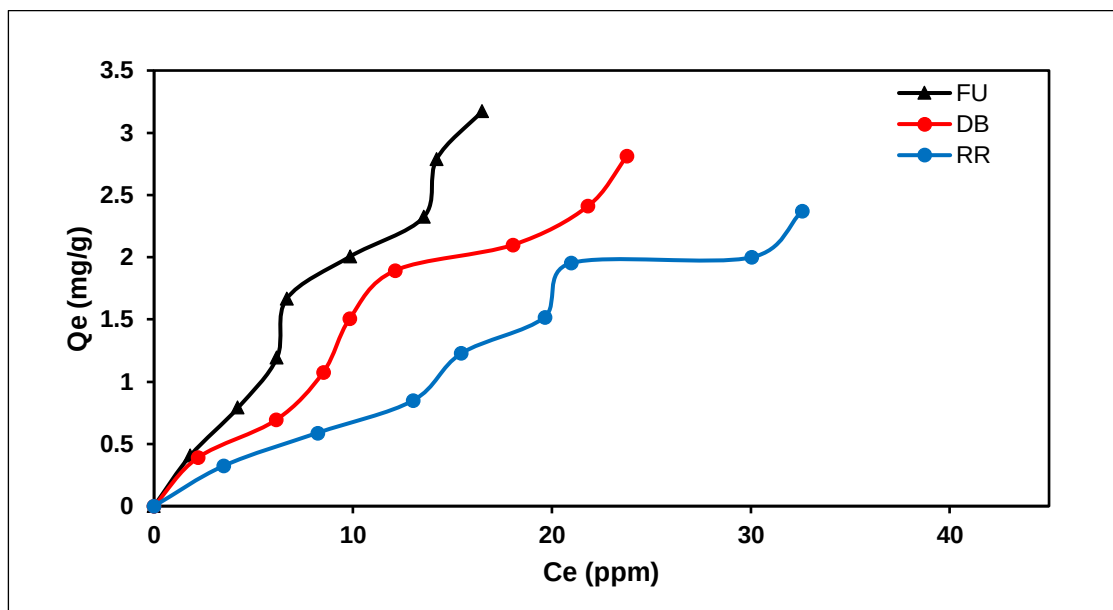


Fig. 3.15. Adsorption isotherms of the three dyes on AS.

The data obtained are used to study the adsorption nature of the three dyes on the AS surface and are analyzed according to Langmuir equation (1-1). The values of C_e/q_e and C_e are listed in the Tables 3.10, 3.11, and 3.12. Fig. 3.16 shows the linear plots of Langmuir equation of the adsorption for the three dyes on the AS surface. The values of Langmuir constant (b), coefficient of correlation (R^2) and maximum adsorption capacity (q_m) have been calculated as shown in Tables 3.13, 3.14, and 3.15.

The data obtained in Tables 3.13, 3.14, and 3.15 are analyzed according to the Freundlich equation (2-1), and Fig 3.17 shows the linear plots of the Freundlich equation for AS surface at different concentrations. The values of constants ($1/n$ and K_f) are calculated from the linear plot of $\log C_e$ against $\log q_e$. Where (K_f) is useful for knowing the amount of adsorption, ($1/n$) is ranging between (0-1), is a measure of the adsorption

intensity or the surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [128]. Therefore, the K_f and n values are presented in Tables 3.16, 3.17, and 3.18.

The data obtained in Tables 3.16, 3.17, and 3.18 are analyzed according to the Tempkin equation (3-1), and Fig. 3.18 shows the linear plots of Tempkin equation for AS surface at different concentrations. The values of constants (B_1 and K_T) are calculated from the linear plot of q_e against $\ln C_e$.

Table 3.10: Values of the parameters of Langmuir equation for FU into AS.

Ce mg/l	qe mg/g	Ce/qe	qm(mg/g)	be(L.mg ⁻¹)	R ²
1.83	0.4	4.49	20.242	0.0108	0.218
4.21	0.7	5.33			
6.18	1.1	5.18			
6.67	1.6	4			
9.86	2	4.91			
13.5	2.3	5.83			
14.2	2.7	5.09			
16.5	3.1	5.20			

Table 3.11: Values of the parameters of Langmuir equation for DB into AS.

Ce mg/l	qe mg/g	Ce/qe	qm(mg/g)	be(L.mg ⁻¹)	R ²
2.20	0.38	5.65	9.718	0.0161	0.369
6.14	0.69	8.86			
8.50	1.07	7.91			
9.84	1.50	6.52			
12.1	1.89	6.40			
18	2.09	8.59			
21.8	2.40	9.05			
23.7	2.81	8.45			

Table 3.12: Values of the parameters of Langmuir equation for RR into AS.

Ce mg/l	qe mg/g	Ce/qe	qm(mg/g)	be(L.mg ⁻¹)	R ²
3.51	0.32	10.8	17.636	0.0046	0.107
8.22	0.58	13.9			
13	0.84	15.3			
15.4	1.22	12.5			
19.6	1.51	12.9			
20.9	1.95	10.7			
30	1.99	15			
32.5	2.37	13.7			

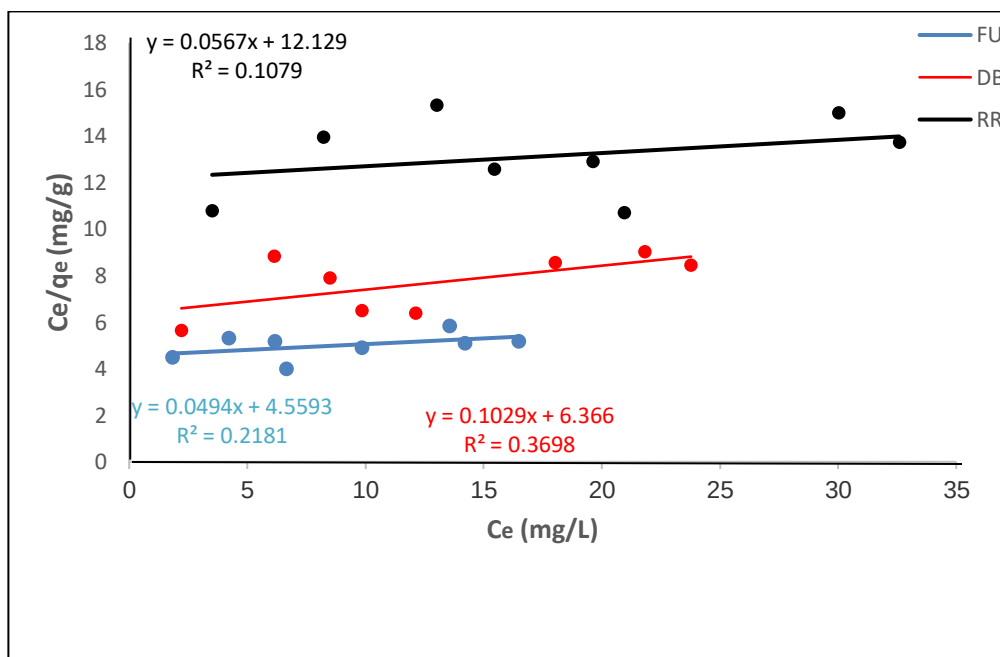


Fig. 3.16. The linear of Langmuir equation of three dyes for AS.

Table 3.13: Values of the parameters of Freundlich equation for FU into AS.

log Ce	log qe	n	K _f (mg/g)	R ²
0.26	-0.38	1.073	0.230	0.978
0.62	-0.10			
0.79	0.07			
0.82	0.22			
0.99	0.30			
1.13	0.36			
1.15	0.44			
1.21	0.50			

Table 3.14: Values of the parameters of Freundlich equation for DB into AS.

Log Ce	Log qe	n	K _f (mg/g)	R ²
0.34	-0.40	1.174	0.186	0.960
0.78	-0.15			
0.92	0.03			
0.99	0.17			
1.08	0.27			
1.25	0.32			
1.33	0.38			
1.37	0.44			

Table 3.15: Values of the parameters of Freundlich equation for RR into AS.

log Ce	log qe	n	K _f (mg/g)	R ²
0.54	-0.48	1.079	0.093	0.967
0.91	-0.23			
1.11	-0.07			
1.18	0.08			
1.29	0.18			
1.32	0.29			
1.47	0.30			
1.51	0.37			

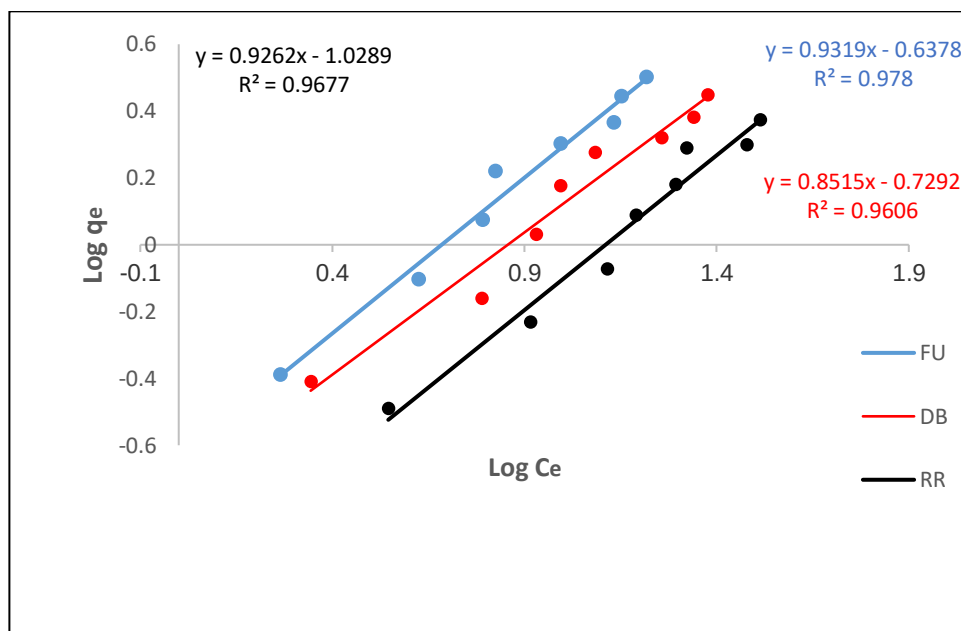


Fig. 3.17. The linear of Freundlich equation of three dyes for AS.

Table 3.16: Values of the parameters of Tempkin equation for FU into AS.

$\text{Ln } C_e$	q_e	$K_T(\text{L.g}^{-1})$	B_1	R^2
0.60	0.40	0.266	1.245	0.907
1.43	0.78			
1.82	1.19			
1.89	1.66			
2.28	2.00			
2.60	2.32			
2.65	2.78			
2.81	3.17			

Table 3.17: Values of the parameters of Tempkin equation for DB into AS.

LnCe	qe	$K_T(L.g^{-1})$	B_1	R^2
0.79	0.38	0.173	1.023	0.893
1.81	0.69			
2.14	1.07			
2.28	1.50			
2.49	1.89			
2.89	2.09			
3.08	2.40			
3.16	2.81			

Table 3.18: Values of the parameters of Tempkin equation for RR into AS.

LnCe	qe	$K_T(L.g^{-1})$	B_1	R^2
1.25	0.32	0.056	0.932	0.870
2.1	0.58			
2.56	0.84			
2.73	1.22			
2.97	1.51			
3.04	1.95			
3.4	1.99			
3.48	2.37			

When compare the coefficient of correlation (R^2) values for Langmuir, Freundlich, and Tempkin isotherms, the Freundlich's R^2 values is greater than the other values. Therefore, the Freundlich equation is more suitable for the adsorption processes of the three dyes in aqueous solutions onto the AS surface. Therefore, the adsorption is more than one layer (multilayer adsorption) [130].

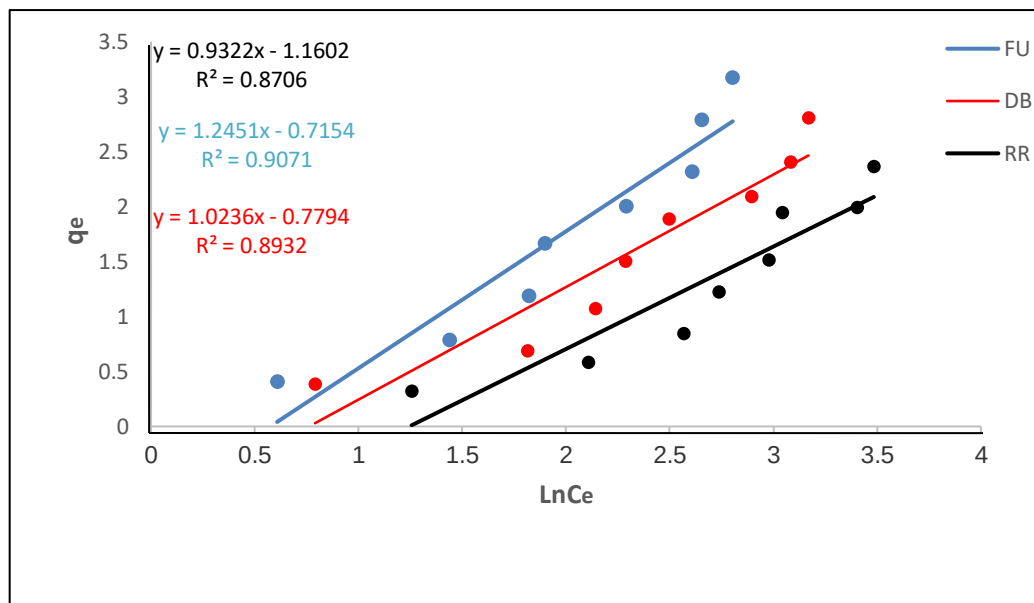


Fig. 3.18. The linear of Tempkin equation for three dyes for AS.

3.3 Thermodynamics of adsorption process

Adsorption of FU, DB and RR dyes by the AS surface was studied by thermodynamic point of view to better understand the nature of the adsorption process under specific conditions. Therefore, it is important for studying the Thermodynamics parameters at 298 to 318 K of the adsorption involve entropy (ΔS^0), Gibbs free energy (ΔG^0) and change in standard enthalpy (ΔH^0). Gibbs free energy change can be calculated from the following equation [131]:

$$\Delta G^0 = - R T \ln k \quad (3-3)$$

Since ΔG^0 is the Gibbs free energy change (KJ.mol^{-1}), R is the universal gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$), T is the absolute solution temperature (in Kelvin) and K is the thermodynamic equilibrium constant to the adsorption. Therefore, the value of (k) has been calculated based on the following equation [10]:

$$K = (qe\ m)/(Ce\ v) \quad (4-3)$$

Where the change in standard enthalpy (ΔH^0) has been calculated by plotting the values of $\ln k$ against $1/T$ according to Van't Hoff - Arrhenius equation [131]:

$$\ln k = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5-3)$$

The values of $(\Delta S/R)$ and $(-\Delta H/R)$ have been calculated from the intercept and slope of the linear plots. Where, the data obtained from the intercept and slope are listed in the Table 3.19 and are plotted in the Fig. 3.19.

Table 3.19: Values of the equilibrium constant (K) and thermodynamic parameters of adsorption the three dyes onto AS.

Dyes	T (C°)	T (K)	1/T (K ⁻¹)	K	lnk	-ΔG° (J.mol ⁻¹)	-ΔH° (KJ.mol ⁻¹)	-ΔS° (J.mol ⁻¹ .K ⁻¹)
FU	25	298	0.003355	4	1.38	2524.393	31.229	93.249
	35	308	0.003246	2.68	0.98			
	45	318	0.003144	1.81	0.59			
DB	25	298	0.003355	3.12	1.13	1293.033	42.082	131.968
	35	308	0.003246	1.65	0.50			
	45	318	0.003144	1.07	0.07			
RR	25	298	0.003355	1.54	0.43	232.993	43.668	142.294
	35	308	0.003246	1.09	0.09			
	45	318	0.003144	0.50	-0.67			

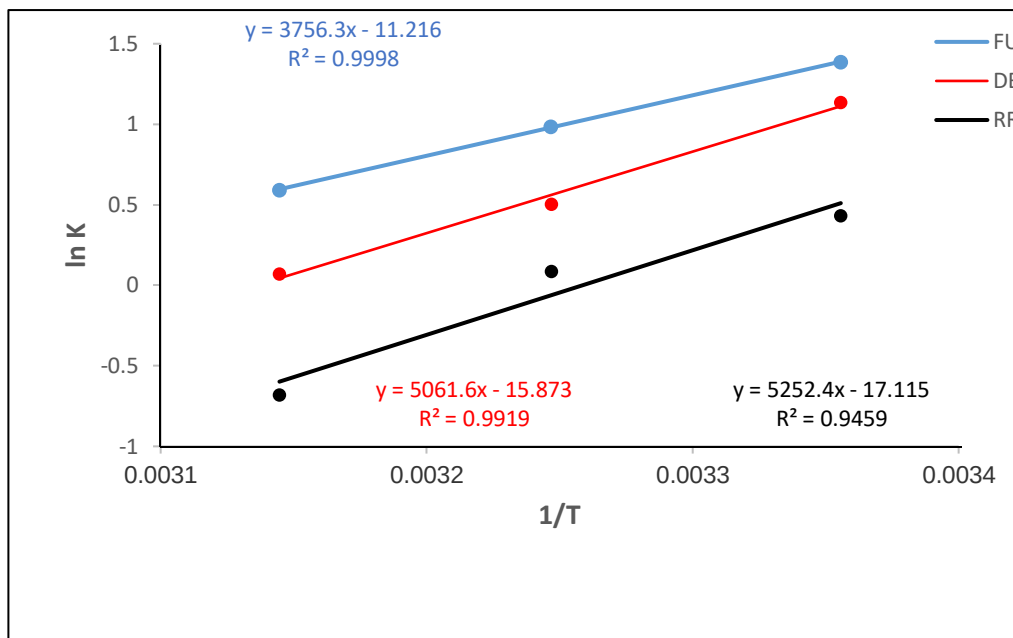


Fig. 3.19. Values of $\ln K$ versus $1/T$ of adsorption for the three dyes onto AS.

The results obtained in the Table 3.19 shows that:

1. The negative values of enthalpy (ΔH°), means that the adsorption of (FU, DB, and RR) dyes onto AS surface was an exothermic process [132]. This could be because that the dyes molecules tend to separate from the solid phase (the adsorbent), to the bulk phase (the solution) with an increase in the temperature of the solution [123]. Therefore, the adsorption of the three dyes onto the AS surfaces decreases with increasing temperature as presented in Table 3.19.
2. The negative values of ΔG° indicate that adsorption process of (FU, DB, and RR) dyes onto AS surface was spontaneous process [133].

3. The negative values of the entropy (ΔS°), means that the randomness of the adsorbed particles is decreases at the (solid–solute) interface during the adsorption process [134].

3.4 Adsorption Kinetics

Kinetic modeling is important to explain and to understand the adsorption mechanism and also to determine the rate constants of sorption, by applying two kinetic models, the pseudo first-order (PFO) kinetic and pseudo second-order (PSO) kinetic (two linear forms for each of them) [134].

3.4.1 Pseudo-First order kinetic model

The first-order equation (PFO) depends on the difference between the (q_e) and the (q_t) at a certain time (t), the equation is as follows [135]:

$$\ln(q_e - q_t) = \ln q_e - k_1 * t \quad (6-3)$$

Where (q_e) and (q_t) are the amounts of the three dyes adsorbed per gram of AS surface (mg/g of AS) at equilibrium and at time (t). The k_1 is the PFO rate constant (min^{-1}) and t is the contact time (minute) for the adsorption. The q_t value has been calculated using the following equation:

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (7-3)$$

The values of k_1 and q_e have been calculated by plotting $\ln(q_e - q_t)$ against time (min) and determined R^2 from the linear plots which should match with the experimental values as Fig 3.20.

3.4.2 Pseudo-Second order kinetic model

Pseudo-Second order equation (PSO) is based on the adsorption capacity of the adsorbent, but not on the concentration of adsorbate. The PSO kinetic equation can be expressed as follow [137]:

$$\frac{t}{q_t} = \frac{1}{k_2 * q_e^2} + \frac{1}{q_e} * t \quad (8-3)$$

The values of k_2 (rate constant of PSO) and q_e have been calculated by plotting t/q_t against time (min) and determined R^2 from the linear plots which should match with the experimental values as Fig 3.21.

The results obtained from the PFO model in Table 3.20 show the values of the calculated adsorption capacity $q_e(\text{cal})$ from the linear plots, do not match with experimental adsorption capacity $q_e(\text{exp})$. Also, the values obtained from the PSO model in the Table 3.21 shows that the calculated adsorption capacity $q_e(\text{cal})$ are close to experimental adsorption capacity $q_e(\text{exp})$.

Also, the value of correlation coefficient (R^2) for (PSO) is greater than R^2 for (PFO). Therefore, the adsorption of FU, DB, and RR dyes onto AS surface follows PSO kinetics. These results are identical to some studies [138].

Table 3.20: Values of kinetic parameters for the three dyes onto AS obtained from PFO equation.

Dyes	Time (min)	qt (mg/g)	qe(exp) (mg/g)	Ln(q _e -q _t)	qe(cal) (mg/g)	k ₁ (1/min)	R ²
FU	10	1.231	2.006	-0.255	0.1279	0.0655	0.689
	30	1.469		-0.621			
	50	1.723		-1.263			
	60	1.990		-4.110			
	90	2.006		0			
DB	10	1.326	1.893	-0.567	0.6502	0.0397	0.725
	30	1.330		-0.574			
	50	1.622		-1.303			
	60	1.830		-2.764			
	90	1.893		0			
RR	10	1.179	1.518	-1.081	0.6211	0.055	0.854
	30	1.289		-1.473			
	50	1.434		-2.480			
	60	1.500		-4.038			
	90	1.518		0			

Table 3.21: Values of kinetic parameters for the three dyes onto AS obtained from PSO equation.

Dyes	Time (min)	qt (mg/g)	qe(exp) (mg/g)	t/qt	qe(cal) (mg/g)	k ₂ (mg. l ⁻¹ .min ⁻¹)	R ²
FU	10	1.231	2.006	8.117	2.260	0.037	0.984
	30	1.469		20.412			
	50	1.723		29.006			
	60	1.990		30.148			
	90	2.006		44.852			
DB	10	1.236	1.893	7.537	2.092	0.043	0.977
	30	1.330		22.544			
	50	1.622		30.825			
	60	1.830		32.774			
	90	1.893		47.525			
RR	10	1.179	1.518	8.481	1.601	0.121	0.997
	30	1.289		23.270			
	50	1.434		34.853			
	60	1.500		39.982			
	90	1.518		59.277			

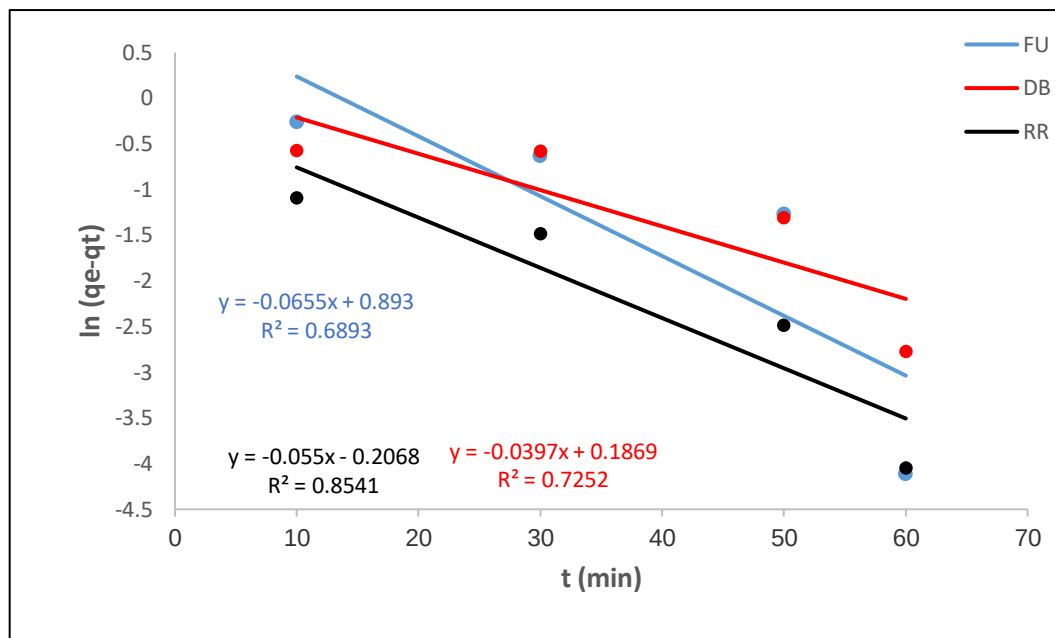


Fig. 3.20. The PFO kinetics of the three dyes onto AS.

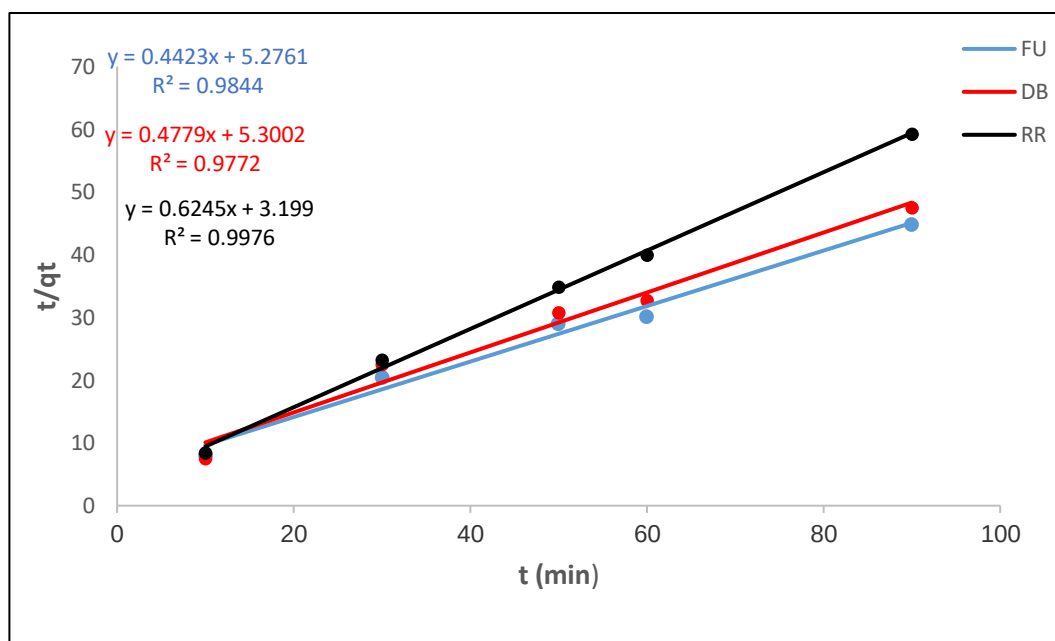


Fig. 3.21. The PSO kinetics of the three dyes onto AS.

Chapter Four

Conclusions & Recommendations

4.1 Conclusions

1. The possibility of using locally available materials, such as the root of the Astragalus plants available in large quantities in the southern region of Iraq to produce a good adsorbent surface at a low cost and with high efficiency.
2. The adsorption isotherms of the three dyes (FU, DB, RR) on the AS surface are of the (S-type) according to the Giles classification, and that the adsorption is more fit to the Freundlich equation.
3. The thermodynamic study showed that the adsorption process of the three dyes was spontaneous from the negative values of the Gibbs free energy (ΔG°), and that the adsorption process of the three dyes was exothermic from the negative values of the enthalpy (ΔH°).
4. The study showed that the acidic function (pH) has an effect on the percentage removal (R%) of the three dyes.
5. The study showed that the percentage of removal of the three dyes from their aqueous solutions on AS surface were in the following order: FU > DB > RR.
6. The study showed that the weight of the adsorbent material has a great effect on the removal process, as the percentage of removal increases with the increase in the amount of adsorbent material.
7. The kinetic study of adsorption of the three dyes on the AS surface has been shown that is most fitting with the pseudo second-order equation.

4.2 Recommendations

1. due to the increase in the level of pollution in the world in general and in Iraq in particular, it would be useful to conduct extensive studies of the adsorption capacity of the AS surface, that prepared from the root of the Astragalus plant used in this study to many toxic heavy elements, dyes, and some organic materials that are present in rivers water such as industrial wastes, pesticides and residues Petroleum industries and other industries.
2. The possibility of carry out other studies in which the AS surface modification and the preparation of activated carbon using a number of oxidizing and reducing agents such as zinc chloride, sodium borohydride and nitric acid in activating the AS surface, that is prepared from the root of Astragalus plant to increase the surface area and increase the adsorption efficiency of the resulting activated carbon.
3. Conducting more studies to test the AS surface efficiency in removing dyes, several elements such as copper, mercury, iron, manganese, radioactive elements, some organic compounds and other water pollutants.
4. The ability of the AS surface, the prepared from the root of the plant Astragalus to adsorb the dyes, indicates the possibility of using this surface in the construction of inexpensive wastewater treatment Stations.

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الخلاصة

استخدمت في هذه الدراسة مواد متوفرة محلياً ورخيصة الثمن لإنتاج سطح نبات القات AS. حيث حُضر سطح AS بعدة خطوات هي غسل وتجفيف جذر نبات الأستراغالوس بدرجة حرارة (53 °C), ثم الطحن و تم الحصول على سطح AS . وشخصت خصائص سطح AS المحضر باستخدام تقنيات (SEM , TGA , BET , FTIR , XRD). تم دراسة قابلية سطح AS المحضر كمادة مازة, وذلك عن طريق امتزاز الصبغات الثلاثة (الفوشين FU و (reactive red RR) و (disperse blue DB) من محاليلها المائية بطريقة الوجبات (Batch Method). تم دراسة المتغيرات المختلفة التي تؤثر على سعة الامتزاز مثل زمن الاتزان ودرجة الحرارة والدالة الحامضية و وزن المادة المازة ، ووضحت النتائج ان امتزاز الصبغات الثلاثة هو من نوع (S) حسب تصنيف جيلز (Giles)، فكان زمن الاتزان هو (90 min) للصبغات الثلاثة. وتم دراسة تأثير درجة الحرارة ضمن المدى °C (45-25) في عملية امتزاز الصبغات الثلاثة على سطح AS , وقد اوضحت النتائج ان سعة الامتزاز للصبغات الثلاثة تقل بزيادة درجة الحرارة ، اي أن الامتزاز باعث للحرارة. استخدمت النتائج التي تم الحصول عليها في دراسة المعادلات الرياضية لايزوتيرمات الامتزاز لانكمير (Langmuir) وفريندليش (Frenudlich) و تمكن (Timken) للحصول على البيانات العملية للامتزاز. فكانت معادلة فريندليش اكثر انطباقا ، فقد اعطت علاقة خطية بمعاملات ارتباط (R^2) اعلى من معاملات ارتباط لانكمير ويمكن. بينت الدراسة الترموديناميكية ان عملية الامتزاز للصبغات الثلاثة كانت تلقائية وذلك من القيم السالبة للطاقة الحرة (ΔG°) ، وان عملية الامتزاز للصبغات الثلاثة هي باعثة للحرارة من القيم السالبة للانثالبي (ΔH°) ، بينما دلت القيم السالبة للانتروبي (ΔS°) على الانتظام وعدم العشوائية في عملية ازالة الصبغات الثلاثة. كما اوضحت الدراسة ان للدالة الحامضية تأثير على النسبة المئوية لإزالة الصبغات الثلاثة ، وبينت الدراسة ايضا ان لوزن المادة المازة دور كبير في عملية ازالة الصبغات الثلاثة ، حيث تزداد النسبة المئوية للامتزاز مع زيادة كمية المادة المازة . درست كذلك حركية امتزاز الصبغات الثلاثة من خلال تطبيق أنموذجي معادلتى المرتبة الاولى الكاذبة والثانية الكاذبة . وظهرت نتائج الدراسة الحركية ان معادلة المرتبة الثانية الكاذبة اكثر ملائمة للنظام المدروس لإزالة الصبغات الثلاثة على سطح (AS) حيث تنطبق بصورة افضل على البيانات العملية .



جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة الموصل / كلية العلوم

قسم الكيمياء

دراسة امتزاز بعض الصبغات العضوية على سطح جذر نبات القثاء في محافظة الموصل

رسالة مقدمة كجزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل الطالبة

سحر اسماعيل ناجي

بكالوريوس علوم كيمياء 2012-2013

بإشراف

أ.م.د. خوله كاني جاسم

2021 م

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