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Synthesis Characterization of Soot Chitosan Nanocomposite and its Application as Adsorbent

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

((وَقُلْ اَعْمَلُوا فَسَيَرَى اللَّهُ عَمَلَكُمْ وَرَسُولُهُ وَالْمُؤْمِنُونَ ۖ

وَسَتُرَدُّونَ اِلَىٰ عَالِمِ الْغَيْبِ وَالشَّهَادَةِ فَيُنَبِّئُكُمْ بِمَا كُنْتُمْ تَعْمَلُونَ))

صَدَقَ اللَّهُ الْعَلِيُّ الْعَظِيمُ

سورة التوبة ، الآية 105

Certification of The Supervisor

I certify that this thesis entitled “**Synthesis Characterization of Soot Chitosan Nanocomposite and its Application as Adsorbent**” was done by “**Russl Mohammed Abdul Zahra**” under my supervision in the Department of Chemistry/College of Science/ Al-Muthanna University, in partial fulfilment of the requirements for the Master’s degree in Chemistry.

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Date / / 2021

Dedication..

**In the name of God, the most gracious, the most merciful
intended for...**

Heaven on earth and my whole life, dear mother...

**To the star of happiness in the darkness of darkness, dear
father...**

**To the apple of the eye and the beat of my heart, my brothers
and sisters...**

To all friends

To my support in life.. my dear husband

**To enlightening lamp and the sea of knowledge,
all my outstanding teachers**

To Comrades, on the path of knowledge, my dear colleagues.

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RussL

ABSTRACT

This thesis is concerned with preparing the soot and chitosan nanocomposite (ACS_1) and diagnosing the prepared compound using different techniques. The surface of ACS_1 was prepared by several steps; the soot was extracted from the paraffin candle by it is collected clean, dry flask, adding chitosan to it in a ratio of 1:2, then treating it with acetic acid and drying at 60 °C. ACS_1 was treated with 10% nitric acid to obtain the soot- chitosan activated nanocomposite (ACS_2). The structural, chemical and surface properties of surfaces nanoparticles (ACS_1 & ACS_2) were diagnosed and studied using (FT-IR, BET, SEM, XRD) techniques. Then study the adsorption efficiency of the prepared nanocomposites ACS_1 and ACS_2 in terms of the adsorption capacity of Alizarin Red S (AR), crystal violet (CV) and dispersed red (DR) dyes from their aqueous solutions using several methods, followed by studying the factors affecting on the adsorption, such as the equilibrium time, weight of the material Absorbent, temperature and pH result from the adsorption process. The results indicated that the adsorption process was S-type according to Giles classification and the equilibrium time was 20 min for AR, CV, and DR on ACS_1 & ACS_2 . Similarly, the analyses showed that the measurements of adsorption for the three dyes decreased with increasing temperature at equilibrium, which means that the adsorption was exothermic. Langmuir and Freundlich isotherms were used, and the results showed that the (model Freundlich isotherm) is fit with the experimental data, as it gives correlation coefficients (R^2) greater than Langmuir's correlation coefficients. Thermodynamic analysis showed that the adsorption of the three AR, CV and DR dyes on ACS_1 and ACS_2 surfaces were spontaneous from the negative charge of free energy ΔG° and the exothermic process from the negative charge of ΔH° , while the negative values of ΔS° were due to the regulation of the arrangement of adsorbent molecules on the surface. The pH values showed that the optimal pH for adsorbance was 4 for AR, DR dyes and 10 for CV dye. In contrast, the uptake information showed that the percentage of removal of three dyes rises with higher weights of the adsorbents for both ACS_1 and ACS_2 . The study showed that the adsorption kinetics of AR, CV and DR dyes fit well with first-order and second-order kinetic models. Hence, the experimental adsorption data showed that the adsorption of the three AR, CV and DR dyes on the surfaces (ACS_1, ACS_2) is consistent with the pseudo-second-order kinetic model.

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List of Symbols and Abbrevtions

Abbreviation	Term
ACS ₁	Soot & chitosan
ACS ₂	Activated soot & chitosan
AR	Alizarin Red S
BDDT	Brunauer-Deming-Deming-Teller classification
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda Analysis
cm	Centimeter
CV	Cristal Violet
cal	Calculated
DR	Disperse Red
exp	Experimental

FT-IR	Fourier Transform Infrared
IUPAC	The International Union of Pure and Applied Chemistry
min	Minute
mL	Milliliters
pH	The Hydrogen Function
P/P₀	Relative Pressure
PFO	Pseudo first order
PSO	Pseudo second order
rpm	Revolutions per Minute
R%	The Percentage of Removal
R²	Coefficient of Correlation
SEM	Scanning Electron Microscopy
UV	Ultra Violet
V	Volume Solution
XRD	X-ray Diffraction
C°	Degree Celsius
ΔG°	Change in Free Energy
ΔS°	Change in Entropy
ΔH°	Change in Enthalpy

Chapter One

Introduction

1.1 Introduction

The problem of environmental pollution with industrial pollutants has become one of the most important problems facing the world in general and the Arab countries in particular, due to the industrial development that accompanied the industrial revolution since the early twentieth century. As a result of the increased use of natural resources and chemicals previously unknown to the environment, fumes and poisonous gases erupted from many factory chimneys, polluting the air and dumping toxic waste into rivers and sewers. Among the types of environmental pollution: air pollution, water pollution, soil pollution, food pollution, radioactive pollution, and others. One of the important properties of pollutants is that they interact with each other or with other materials to produce synergistic effects, making environmental pollution more complex. The accumulation of these pollutants together may be more severe than what is expected from the effect of each pollutant separately [1]. Mainly, Pollutants are classified into three groups.; The introduction of particles and chemicals into the environment is referred to as air pollution, Surface runoff, liquid spills, wastewater discharge, and groundwater leaks are all examples of land contamination [2][3], where water is a highly prized natural resource [4]. As a result, wastewater contamination has a negative impact on municipal water sources, and can result in health issues such as diarrhea. Water contamination is one of the most important environmental challenges that needs to be addressed right now [5]. The majority of the focus has been on removing dyes and heavy metals, which are both commonly found in industrial effluents and are especially dangerous [6]. Many processes are being investigated for the removal of these pollutants, including chemical precipitation [7], coagulation [8], ion exchange

[9], chemical reduction [10], membrane separation [11], biological treatment [12], and adsorption [13] ,the advantage and disadvantage this technologys were shown in table(1-2). Pollutants are divided into two categories: natural and man-made. Natural contamination is shown by a rise in water temperature [14]. Increased salinity and suspended materials Chemical contamination, on the other hand, includes wastewater pollution, oil leakage, and agricultural pollution wastes such as pesticides and fertilizer [15]. Where, since dye waste is filled with toxic and unfavorable dyes all over the world, there are many methods for handling contamination caused by dye waste, including photocatalytic degradation., son chemical degradation [3], Ultrafiltration with micellar water, cation exchange membranes, electrochemical degradation, chemical-biological integration, and absorption [16]. A large volume of colored pigments, metals, and dangerous dyes have recently been discharged into the water system from textile factories, dye processing industries, as well as the paper and pulp industries [17]. Owing to the increased use of dyes to paint items such as textiles, paper, plastics, and cosmetics, and the leakage of these highly toxic dyes, dye wastewater contamination has become a serious problem in recent decades as in table (1-1) it shown the effect of different types of dyes on human. Dye contamination of the water supply is therefore a major environmental problem, as dye-containing wastewater is notoriously difficult to handle [18]. Synthetic and natural compounds are the two types of dyes. Natural dyes are colored substances derived from natural sources such as leaves and flowers [19], Synthetic dyes are made primarily from petrochemical sources, and they are distinguished by their large availability of different groups and low cost[20].When dyes are released into water, however, they are often inert and difficult to

biodegrade due to their complex aromatic molecular structure and synthetic origin [20]. To extract dyes, a variety of chemical, physical, and biological methods are currently used. The simplest and cheapest of these methods is adsorption. While activated carbon is the most effective material for dye removal, it is expensive and loses 10-15% of its effectiveness during regeneration, so unconventional adsorbents such as wood, silica, activated clay, and agricultural residues, among others, are used instead have drawn the attention of a variety of dye removal inquiries [21]. Biological and physicochemical methods are the most popular methods for removing dyes and dye wastes.

Table (1-1) Shows the impact of various dyes on human

Dye group	Disadvantages
Azo groups	Toxic amines are formed in the effluent as a result of their reductive cleavage of Azo linkages
Basic dyes	It has a lot of brilliance and color intensity, and even at low concentrations, it's highly noticeable
Acidic dye	It stays colored in wastewater for a longer time, because it is the most resistant to oxidation

The physicochemical approach involves multiple processes such as precipitation, membrane filtration, and coagulation-flocculation [22].

Biological processes including anaerobic and aerobic processes are often used to remove dyes. Since there is no technically or commercially viable approach, two or more methods are often combined to achieve the desired degree of color removal

[23]. Furthermore, the advantages and disadvantages of each method are given in Table (1-2). The technology of adsorption on activated surface (soot & chitosan) was chosen for this study because it is more efficient and less expensive than other methods for removing dyes [24].

Table (1-2)The advantages and disadvantages of techniques used for dyes removal.

Technology	Advantages	Disadvantages
Photochemical	No sludge production and reduced a lot of fould odors.	Formation a lot of by-products
Ion exchange	Regeneration, efficient recovery of colors, no adsorbent loss, and commercially available.	Not efficient for all dyes, although high cost for regeneration
Membrane Filtration	Remove all dyes of wide types	Concentrated sludge is produced, high cost.
Adsorption on Activated carbons	Great capacity, good removal of dye and the most effective adsorbent.	Ineffective against reactive and direct dyes. Also, the regeneration is avery expensive and non-destructive process
Ozonation	When ozone is applied as a gas, it does not add to the sludge or wastewater volume.	Shorter half-life (20) min.
Cucurbituril	High sorption capacity for different dyes.	The high cost

Electrochemical Destruction	Breakdown some compounds are no dangerous.	The high cost of electricity and high flow rate
Oxidation	Rapid process.	Height energy costs and the formation of by- products

1.2 Adsorption

Adsorption is one separation method [25] where a molecules from the (gas or liquid) phase are taken up by a solid surface [26]. Adsorption is essentially a process that happens on the surface and consists of two elements: (1) Adsorbate is the substance that accumulates on the interface, and (2) adsorbent is the solid on which adsorption occurs [27]. As a result, adsorption involves contacting an adsorbent with a fluid containing pollutants [28]. The first quantitative study was published by C.W Scheele in (1773) using coal and clay to absorb gases [29]. The process opposite to adsorption is called desorption, It involves the separation of the adsorbent material from the adsorption surface and this requires the return of the released energy to the system. The adsorption is usually accompanied by a change in the free energy of the surface (ΔG) What happens is adsorption, and it is accompanied by a decrease in entropy (ΔS) because the molecules that undergo adsorption become restricted due to their attachment to the adsorption surface and thus lose some of their temperatures compared to the state in which they were before adsorption, A simultaneous decrease in free and entropy energy results in a decrease in enthalpy (Heat content ΔH) according to the following relationship [30]:

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots(1.1)$$

Among all the physicochemical treatment methods adsorption is found to be very effective[31]. Adsorption techniques have recently gained much attention due to their ability to remove pollutants. Moreover, adsorption technology has been discovered to be one of the most capable and verified treatments for dye-laden wastewater, as well as being a simple and easy-to-implement technology [32]. In terms of simplicity of design, initial cost, ease of operation and insensitivity to harmful substances, it has also been shown to outperform alternative mechanization of wastewater treatment[33][29]. Adsorption is controlled either by physical or chemical forces [26]. As a result, adsorption can be divided into two main parts namely physical adsorption and chemical adsorption.

1.2.1 Types of Adsorption

Adsorption can be classified based on the type of association between the adsorbent molecules, atoms or ions with the adsorbent surface and the temperature that accompanies the adsorption process into two parts:

1.2.1.1 Physical adsorption:

There is no interchange of electrons between the adsorbate and the adsorbent, which is known as (physisorption) [5]. Furthermore, non-specific and physical weak powers such as hydrogen bonding and Van der Waals and multimolecular layers are created with the itself heat of adsorption, and the heat of adsorption is low temperature. When the temperature and pressure circumstances are favorable, adsorption can occur by increasing the temperature, and it occurs on all surfaces. Furthermore, this procedure is reversible [34].

1.2.1.2 Chemical adsorption:

Chemisorption occurs when strong chemical interactions arise between adsorbate molecules or ions and the adsorbent surface as a result of electron exchange between the adsorbent and the adsorbed species [35] . As a result, it's usually permanent and quite selective. In addition, the forces at work are chemical bonds (covalent or ionic bonds), and the resulting chemical link is frequently stronger than that obtained through physical adsorption, making it more stable at high temperatures [34]. Adsorption was found to be better to other strategies in terms of flexibility and the simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation. Adsorption also fails to produce harmful substances [36].

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 [37]. Therefore, some studies are performed on the importance of physical factors, like molecular conformation and the effects of pore composition for compounds [38], the chemical besides interactions involved in the adsorption of dyes a fundamental understanding of the physical factors is critical to predicting the fate and transport of the dyes in the environment [39]. Where, factors that influence the adsorption capacity include contact time, adsorbent dose, pH, initial dye concentration [37], temperature, particle size etc [40].

1.3.1 Effect of Solution pH

The degree of ionization of the adsorbates and the surface charge density of the adsorbent are influenced by the pH of the solution from which adsorption occurs. Cause hydrogen and hydroxide ions are firmly adsorbed and efficiently compete with metal ions for bound sites [41]. One of the most critical elements regulating the adsorption process in wastewater treatment, in particular the adsorption capacity, is the pH of the dye solution. 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 [42].

1.3.2 Effect of Initial Dye Concentration

The initial dye concentration has a big impact on dye adsorption. Generally, the percentage of dye removal decreases with an increase in the initial concentration of dye [43], 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 percentage of dye removal is obtained at lower dye concentrations [44].

1.3.3 Effect of Temperature

The adsorption process is affected by the temperature because changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [45]. If the adsorption increases with increase 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 adsorption is exothermic when the adsorption capacity decreases with increasing temperature. It may be because the increase temperature, will decrease the adsorption forces between the dye and active sites on the adsorbent [46].

1.3.4 Effect of Adsorbent Dosage

The adsorbent weight also affects the adsorption process. Sometimes, high adsorbent dosages yield higher uptakes and higher percentage removal $R\%$ [47]. Therefore, An increase in adsorbent dosage generally increases the amount of solute adsorbed that due to the increase in surface area which increases the number of active sites [48]. When the adsorbent dosage is increased, the number of active sites increases. There are inadequate active sites that can easily be occupied by the adsorbate at lower doses of adsorbent, while active sites are more accessible for the adsorbate to occupy at greater doses [49].

1.3.5 Effect of Contact Time

Dye removal was found to be increased with the increase in contact time. The adsorption was very fast in the first, and then increased slowly, with the time until it reach equilibrium time and with a maximum percentage of adsorption [50], and this percentage remain constant after equilibrium time [51]. 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 [49].

1.3.6 Difference in Pore Size

The size and distribution of pores directly influence their ability to work in a specific application [52], As a result, the variation in pore size that determines the adsorption capability of molecules of varied sizes and shapes was one of the characteristics for which carbons were chosen for a certain application [53]. Different methods have been suggested and widely used for the pore size evaluation. The invention of the Bruner-Emmett - Teller (BET) method, which has become a common technique for estimating pore size, was a land mark in the estimation of different pore sizes [54]. As a result, porosity is divided by IUPAC into three different classes of pore sizes. they [55]:

- Microspores: width less than 2 nm
- Mesoporous: width between 2 and 50 nm
- Macropores: width greater than 50 nm

1.4 Thermodynamic

A number of different adsorption isotherm equations have been applied to describe adsorption behaviour at equilibrium. In the study of adsorption thermodynamics, the equilibrium constants derived from various isotherms, such as the Langmuir and Freundlich isotherms as well as from some specially defined formulas, have often been used for calculation of changes in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) of adsorption. It is obvious that determination

of the equilibrium constant is a key toward correct estimates of ΔG° , ΔH° , and ΔS° , whereas the equilibrium constant for adsorption is related to the isotherm equation employed. In the sense of reaction thermodynamics, ΔG° can be determined according to the unit less thermodynamic equilibrium constant, whereas the Langmuir equilibrium constant has units of liters per mole. The relationship of ΔG° to enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption is expressed as[56]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \dots\dots\dots (1.2)$$

In surface processes, the Gibbs free energy depends on different parameters e.g., temperature, pressure, and system composition. The Gibbs free energy(ΔG_{ads}) reflects the spontaneity of adsorption; the higher the negative value of (ΔG),the more energetically favourable the adsorption. the ΔG_{ads} is calculated as follows:

$$\Delta G = -RT\ln K_a \dots\dots\dots (1.3)$$

where T is the absolute temperature in kelvins, R the gas constant (8.314 J/mol·K), and K_a the thermodynamic equilibrium constant without units [57].

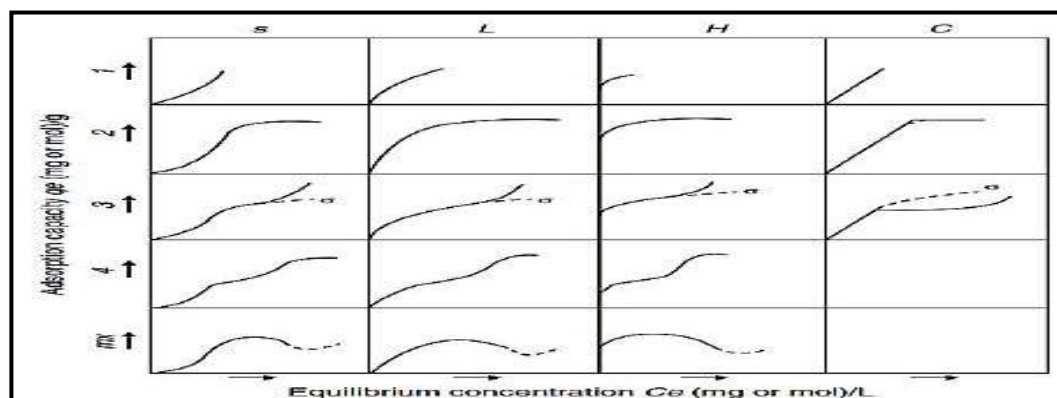
1.5 Adsorption Isotherms

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 contacted with the adsorbent surface for enough time, and its adsorbate concentration in the bulk solution remaining in a stable balance with the interface concentration[58]. 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 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 [33].

1.6 Classification and Modelling of the Isotherms

The adsorption isotherm is associated with the amount of adsorption uptake at 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. Bruner 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 Bruner, the stepped isotherm. Type I (Langmuir isotherm) is model of microporous adsorbents and is characterized by monolayer adsorption. Type II isotherm has multilayer adsorption and the two types (III and IV)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 [59][60][61]. Figure (1.1) illustrates these shapes.



Figure(1.1) Classification of GILES Types of Adsorption Isotherms[62]

Giles classify all the isotherms into four major groups S-curve, L (Langmuir type), H (high affinity), and C (constant partition) [63]. The (C) isotherm has a stationary 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 (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 [64].

The distribution of adsorbate between the liquid phase and the solid phase, when the uptake reached equilibrium, was assessed by different adsorption isotherms [65]. 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 and Freundlich, isothermal equations, also used to evaluate the best-fitting isotherm, and the applicability of isotherm equations is matched by evaluating the correlation coefficients [66].

Table (1-3)Types of adsorption isotherms [67]

Isotherm	Application
Langmuir	Physical and chemical adsorption
Freundlich	Physical and chemical adsorption

1.6.1 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 [68]. The linear form of the isotherm may be expressed as follows [69]:

$$\text{Log } q_e = \log K_f + 1/n \log C_e \dots\dots\dots (1.4)$$

Where; q_e : The quantity of adsorbate (mg/g) at equilibrium time.

C_e : The equilibrium concentration of dyes in solution phase (mg L⁻¹) at equilibrium.

K_f & n : The adsorption constants for Freundlich equation. Where their values depend on the nature of the adsorbate and the adsorbent. The plot of $\log q_e$ versus $\log C_e$:is employed to determine the K_f and n .

1.6.2 The 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 [70]. The Langmuir isotherm is represented as the following form [71]:

$$\frac{C_e}{q_e}=1\backslash q_m * b + C_e \backslash q_m \quad \dots\dots\dots (1.5)$$

Where: q_e : Is equilibriumm 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).

1.7 The Adsorbent

Adsorbents may divided according to the nature of surfaces, pore size and nature of structures [72]. As a result, developing new adsorbent materials with a variety of functions, characteristics, and compositions has been extremely beneficial [73]. Many researchers have lately produced modern materials by using natural origin materials [74]. Clay, chitosan, wood, rice husks, tea waste, palm kernel fibers, rice bran, banana and pineapple peels, and seed shells are examples of low-cost adsorbents used in adsorption processes [75].

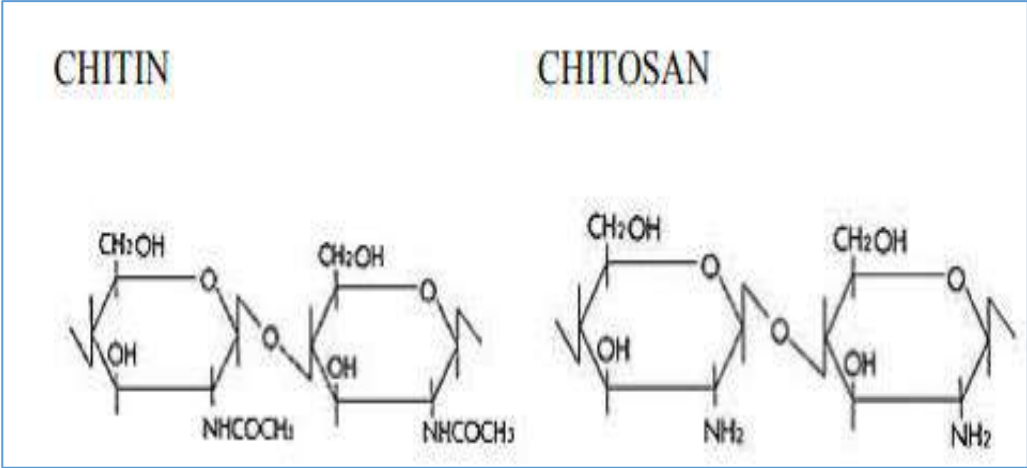
1.7.1 Soot

Soot, sometimes called lampblack or carbon black, is a fine black or brown powder that can be slightly sticky. It consists of the element carbon and a variety of organic compounds and is one of the products generated by the incomplete combustion of fuel. In this regard, transportation is believed to be responsible for approximately 25% of the total anthropogenic emissions of these carbon aerosols. Soot particles in the atmosphere are widely acknowledged to contribute to global warming and have a significant impact on the radiative balance, either directly absorbing solar energy or indirectly serving as cloud condensation

nuclei. Furthermore, soot has health consequences such as respiratory, cardiovascular, and allergy illnesses [76]. Smoke emissions are undesirable for all devices, both in terms of pollution and because smoke represents unburned carbon and hydrogen, resulting in worse combustion efficiency. The creation of soot is beneficial in some devices, such as candles and furnaces, since hot soot particles are effective radiators; in the case of the candle, visual radiation is used, but in furnaces, enhanced thermal radiation allows efficient heat transfer to the walls. However, soot generation is undesirable in gas turbine and diesel engines, with the main problems being radiative heating of the combustor walls and soot deposition. Aside from the aforementioned equipment where soot emission is undesirable, the abundant carbon black industry is concerned with the production of soot that is then used in, for example, the fabrication of automobile tyres [77], and soot from wood fires is ideal to utilize because it is the most valuable fertilizer for a variety of plants. When sprayed to the soil in the spring, microbes convert it to nitrates, which can be used as a plant food. It can also be recycled as waste and used to filter water using adsorption.

1.7.2 Chitosan

Chitosan is a carbohydrate biopolymer made from the deacetylation (DA) of chitin, a significant component of crustacean shells like crab, shrimp, and crawfish. Chitin is the second most prevalent natural biopolymer in nature, after cellulose [78].



Scheme (1.1) Structure of Chitin and Chitosan

Chitosan has many attractive properties such as hydrophobicity, biocompatibility, biodegradability, non-toxicity and the presence of very reactive amino (–NH₂) and hydroxyl (–OH) groups in its backbone, which makes chitosan to be used as an effective adsorbent material for the removal of wastewater pollutants.

Chitosan is a soluble polymer that can be used in dilute acid solutions. Chitosan is a poly cation in solution, unlike other polysaccharides that are either neutral or anionic. It exhibits ion adsorption and complicated connotation characteristics. In terms of chemical, physical, and biological properties, chitosan is a very versatile substance. It is non-toxic, mucoadhesive, biodegradable, and biocompatible polymer that is utilized in food and nutrition, textile and paper industries, cosmetics, photography, and water engineering, among other things [79].

1.8 The Organic Dyes

Dyes are made of natural sources and synthetic sources, Natural dyes have a long history of being used to color textiles. Since prehistoric times, these dyes

have been used to color food, leather, and textile products. Natural colors can be made from plant or animal waste with no or minimal chemical processing. However, after the advent of synthetic dyes in 1856, natural dyes were no longer in demand for dyeing textiles and it was then declined [80]. Furthermore, at the turn of the twentieth century, the cost of producing synthetic dyes fell dramatically, and natural dyes were mostly ignored [81]. As a result, using natural dyes instead of synthetic dyes offers a big chance of collecting carbon credits. Natural dyes have a disposal difficulty because they are completely biodegradable and can even be utilized as bio fertilizers in some situations, such as indigo dyeing [82]. 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 [83]. Dye molecules consist of two key components: chromophores, responsible for color production, and auxochromes, which make the molecule soluble in water [84].

1.8.1 Classification Systems for Dye

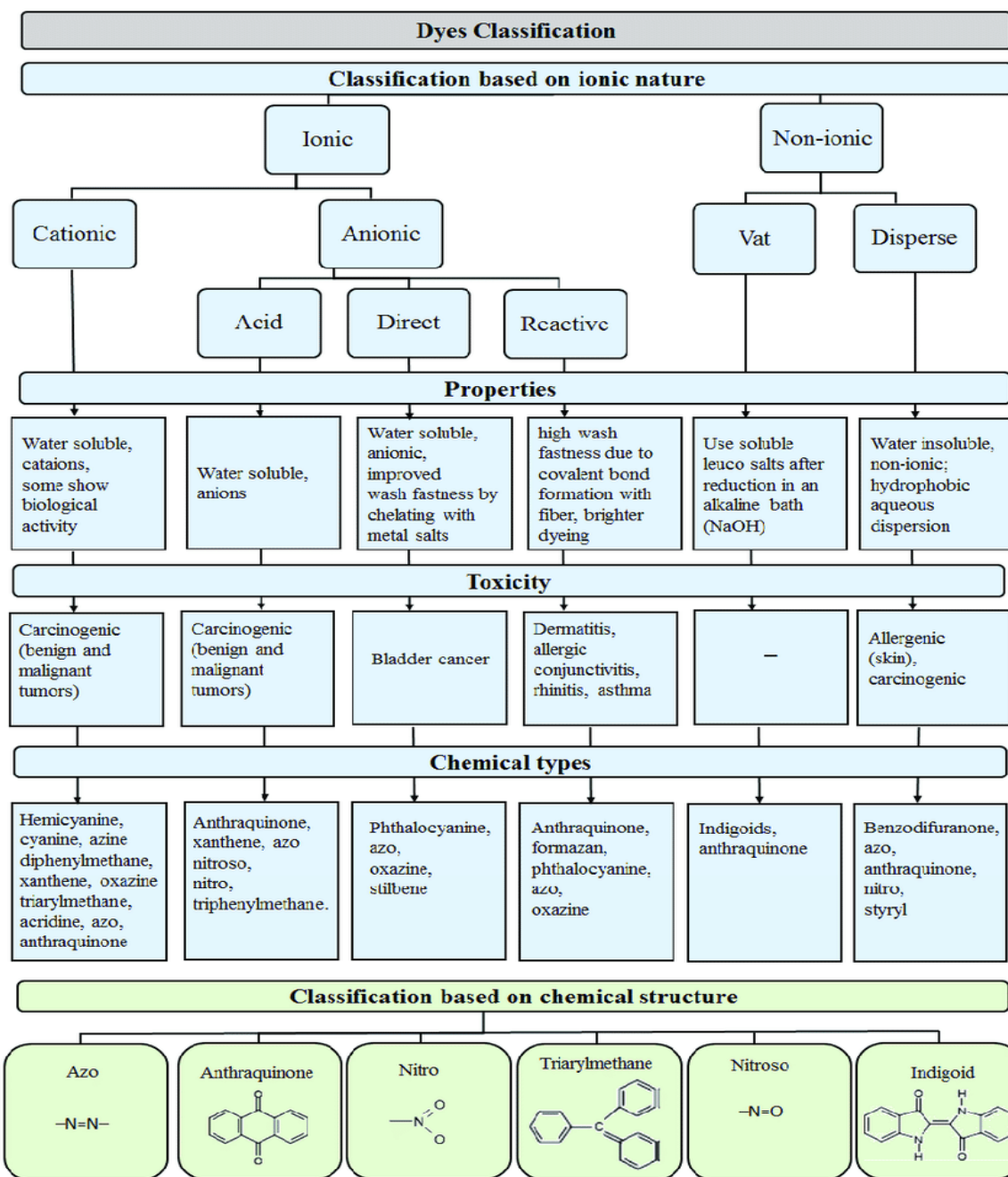


Figure (1.2) Classification of dyes based on ionic charge with corresponding characteristics, chemical kinds, and some of the observed toxicity affects (in blue) , and based on chemical structure with corresponding chromospheres (in green) [57].

1.8.2 Toxicity effects of Dyes

Complex dyes are often chromium-based, which is carcinogenic. Basic dyes have strong color intensity and are highly visible even at extremely low concentrations. Dyes may reduce photosynthetic activity in aquatic life due to reduced light penetration, and they may also be hazardous to some aquatic species due to metals, aromatics, and other contaminants. Dyes have also been found to be carcinogenic, mutagenic, or teratogenic in a variety of marine fish species. Furthermore, it has the potential to cause significant harm to humans, including kidney, liver, brain, and central nervous system malfunction [85]. Because poisonous amines are present in the effluent, azo dyes are toxic; similarly, anthraquinonoid-based dyes are the most resistant to degradation and retain their color for a long period in effluents [86]. Reactive dyes are soluble in water and produce 5-10% of dyes in the dye bath, resulting in a highly colored effluent that causes significant environmental problems [87]. Furthermore, because the reacting dyes are chemically stable and biodegradable, they are likely to pass out of standard treatment plants untreated, so their elimination is of great importance. Because of the dyes toxic effects, they have generated much concern regarding its use. Mutagenesis, chromosomal fractures, carcinogenesis, and pulmonary toxicity have all been reported. As a result, it is desirable to concentrate on specific methods and technologies to remove dyes from various types of wastewater currents [85].

1.8.3 Present Treatment Methods for Dye Removal

Dye-bearing effluents can be treated in a variety of ways. Despite the availability of numerous strategies for removing dye pollutants from

wastewaters, such as coagulation, chemical oxidation, membrane separation, electrochemistry, and aerobic and anaerobic microbial degradation, each of these processes has inherent limitations. The technologies can be classified into three types: physical, chemical and biological [41]. Each of these methods has their own advantages and disadvantages.

Table(1-4) Advantages and disadvantages of the dye removal methods [46]

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 ARo-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.
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
Electrokinetic coagulation	Economically feasible	High sludge production
Biological Treatments		
Decolourization by white-rot ARngi	White-rot ARngi 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

1.9 Previous Studies

Activated carbon is a type of carbon that has been processed to make it extremely porous for adsorption. It is also known as activated charcoal or activated coal. A number of batch experiments have been reported for the removal of various pollutants using various low-cost adsorbents, including activated carbon. Additionally, activated carbon has large inside superficies area and porosity[88]. In general, activated carbon generated from agrarian waste has been extensively used to remove pollutants from aqueous solutions [89].

(M.S. Chiou *et.al*, 2002) also asserts that Cross-linked chitosan beads were used to study the adsorption of the reactive dye (reactive red 189) from aqueous solutions. The Langmuir model was found to be accurate. The adsorption capacity of dye RR 189 is significantly increased when the pH of the solution is reduced. Except for the dried beads, which fit better with the first-order model, the results fit with the second-order kinetic model [90].

(Kadirvelu, *et al.*, 2005) depict that Chemical activation of sago waste with sulfuric acid and ammonium produced activated carbon. The efficacy of activated carbon for removing Rhodamine-B from aqueous media was then examined as a function of agitation time, adsorbent dosage, starting dye concentration, pH, and desorption. Adsorption equilibrium investigations were also carried out in order to optimize the experimental conditions. At an initial pH of 5.7, the adsorption of Rhodamine-B onto carbon followed a second-order kinetic model, with an adsorption capacity Q_0 of 16.12 mg^{-1} . Furthermore, the equilibrium period was determined to be 150 minutes for dye concentrations of

10, 20 mg L⁻¹ and 210 minutes for dye concentrations of 30, 40 mg L⁻¹. All of these research show that a waste can be used to treat another waste [91].

(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 Cr⁶⁺, Cu²⁺ and Pb²⁺ from aqueous solutions, has been studied. The affinity for the three ions was different as in the following order Cu²⁺ > Cr⁶⁺ > Pb²⁺. The process is governed by the monolayer adsorption fitting with the Langmuir model [92].

(V. P. Singh & Vaish, 2018) a batch study of adsorption experiments on candle soot was conducted and successfully applied as an adsorbent for the removal of two basic dyes (methylene blue and rhodamine B). The effect of variables such as contact time, adsorbent and adsorbate dosage, solution temperature, and pH explore the amount of soot required to remove two dyes was found to be 0.2 g. It took 150 minutes to achieve the quasi-equilibrium. Methylene blue dye effectively removed at pH 12 and rhodamine B dye at pH 6. According to a thermodynamic analysis, the adsorption process for dyes is spontaneous. According to a kinetic research, both pseudo first- and second-order equations suit adsorption kinetic data best, whereas the Langmuir isotherm fits equilibrium data best. For the desorption of rhodamine B from candle soot, ethanol was

utilized as the desorption medium. Up to a certain cycle, the adsorbent was also proven to be recyclable [93].

(R. Bagheri, *et al.*, 2019) presented an intriguing study on physical activation. Waste *Amygdalus scoparia* is used as a precursor in the synthesis of activated carbon. The material was treated to heat treatment under argon-atmosphere with temperature rate of 5 °C/min after being impregnated with *A. scoparia* in deionized water, until the ultimate temperature reached 600 °C, and the heating remained continuous at this temperature for 1.5 hours. Fourier transform infrared spectroscopy, Brunauer–Emmett–Teller and scanning electron microscope techniques were used to characterize the activated carbon generated. Also, the various influences on malachite green dye [94].

(Jabr., 2021) asserts that to make soot (AS₂), which is commonly used in adsorption procedures, this study used locally available and inexpensive ingredients. The AS₂ was made by thermally treating the AS₁ for 2 hours at 40 °C. FTIR, SEM, BET, and XRD techniques were used to identify the characteristics of AS₂. The AS₂ was utilized to adsorb the DR and CV dyes from aqueous solutions, and the results suggest that the AS₂ made from AS₁ is an excellent adsorbent. The effects of pH, temperature, equilibrium period, and the adsorbent weight of adsorption dyes were investigated, it was shown that the efficiency of adsorption decreased at pH = 10 and increased at pH = 4. The results also revealed that when the temperature rises, the efficacy of the adsorption dye on AS₂ reduces, with the optimum contact time of adsorption being 15 minutes and the optimum adsorbent weight being 0.08gm [95].

The Aim of the Study

The main aims that were reported in this thesis are :

1. Preparation of ACS₁ from soot and chitosan that are available and cheap, and evaluate the efficiency of ACS₁ to adsorb dyes from an aqueous solution.
2. Increase the efficacy of the adsorbent material from industrial waste of powder the soot and chitosan(ACS₂) by activated using nitric acid solution.
3. Characterization of the activated carbon (ACS₁, ACS₂) by different analytical techniques such as: N₂ adsorption-desorption, FT-IR, XRD, SEM.
4. To utilize prepared adsorbents in removing AR, CV and DR dyes from their aqueous solution at various conditions (contact time, adsorbents dose, different pH of the solution, and temperature) to obtain optimum condition of adsorption.
5. To study the adsorption modelling of ACS₁ and ACS₂ by using isotherm (Langmuir and Freundlich) models.

Chapter Two

Experimental Part

2.1 The Chemicals

The three dyes, which have been used in the experiments, include: -

2.1.1 Alizarin Red S

Alizarin Red S (ARS) has been extensively used in the textile industry. Unfortunately, a remarkable fact is that ARS is extremely resistant to degradation owing to its fused aromatic structure, which may cause a serious threat to the water ecosystem and human health [96].

Table (2-1): The physical and chemical properties of Alizarin Red dye.

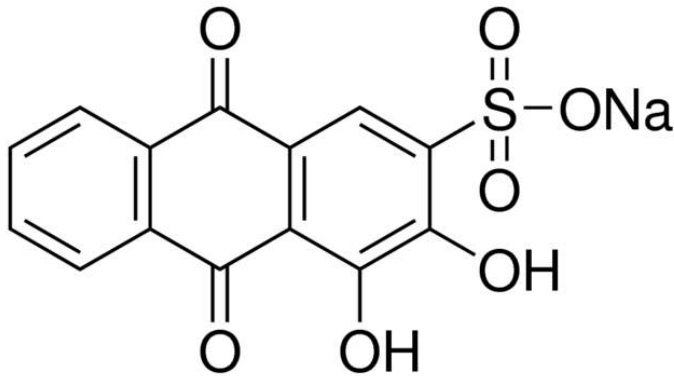
characteristics		structure of dye
MF	C ₁₄ H ₇ NaO ₇ S	
MW	342.26	
Class	Acidic dye	
Colour	Orange	
Solubility	Water	
Company	Sigma-Aldrich	
λ max (nm)	516	Sodium 1,2-Dihydroxy-3-sulfonyl-9,10-anthraquinone



Figure (2.1) :The solid and aqueous solution of the alizarin red dye.

2.1.2 Crystal Violet

Other names for it include Basic Violet 3, Methyl violet 10B, gentian violet, hexamethylpararosaniline chloride, and aniline violet [97], is a cationic dye.

Table(2-2): The physical and chemical properties of crystal violet dye.

characteristic		Structure of dye
MF	C ₂₅ N ₃ H ₃₀ Cl	
MW	407.979	
Class	Basic dye	
colour	Dark green crystal	
Solubility	Water	
company	Sigma Aldrich	Bis[3,5-N,N-dimethyl aminobenzene]-4-N,N dimethyl amin methyl chloride
λ max (nm)	580	



Figure(2.2): The solid and aqueous solution of the Crystal Violet dye.

2.1.3 Disperse Red

Disperse Red 65 and C.I. 11228 are non-ionic dyes that are widely used in textiles. [98]. Table (2-3) shows the description of Disperse red used in the work.

Table(2-3): The physical and chemical properties of disperse Red dye

characteristic		Structure of dye
MF	C18H18ClN5O2	
MW	371.82	
Class	Azo	
Colour	Dark red	
Solubility	Water	
Company	Ciba	
λ max (nm)	537	1-Amino-9-hydroxy-2-phenoxy-9,10-anthraquinone



Figure(2.3): The solid and aqueous solution of the disperse Red dye.

2.2 Chemical and Solvent

There are other materials used in the experiments. The purity percentage and the companies are listed in Table (2-4).

Table(2-4): Identifies the Materials and the manufacture companies and the purity percentage.

Materials	Structure	companies	Purity%
Acetic acid	CH_3COOH	ALPHA	99
chitosan	$\text{C}_{56}\text{H}_{103}\text{N}_9\text{O}_{39}$	HIMEDIA	75
Hydrochloric acid	HCl	ROMIL	36
Nitric acid	HNO_3	CDH	69
Sodium hydroxide	NaOH	SIGMA	98

2.3 Instruments

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

It 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) was 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 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.

2.3.6 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.

2.3.7 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 Procedures

2.4.1 Determination of Maximum Wavelength ($\lambda_{\max}$) and Calibration Curve

A stock solution was prepared for the three dyes (AR, CV, and DR) at a concentration (100 ppm) by dissolving a certain weight of the solid dyes in an amount of distilled water under constant 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 figures (2.4, 2.5, and 2.6) for the three dyes.

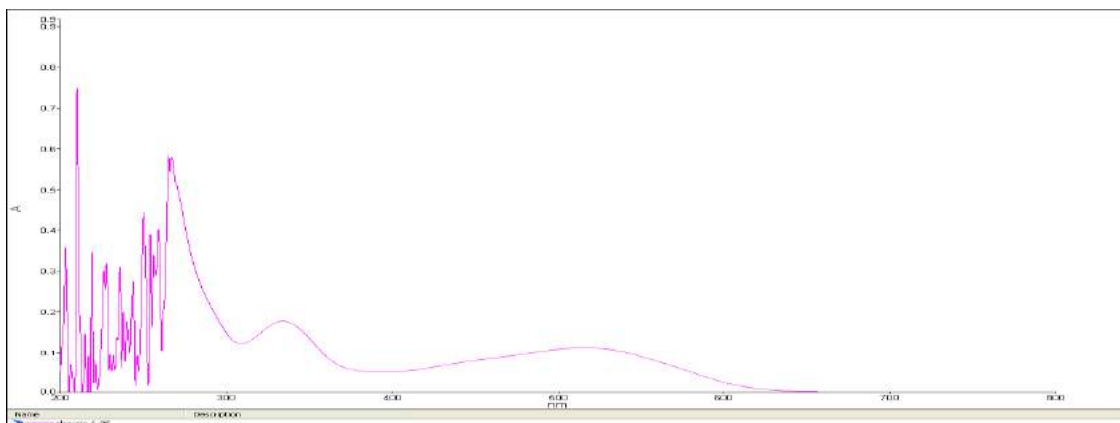


Figure (2.4): The spectrum curve of AR dye.

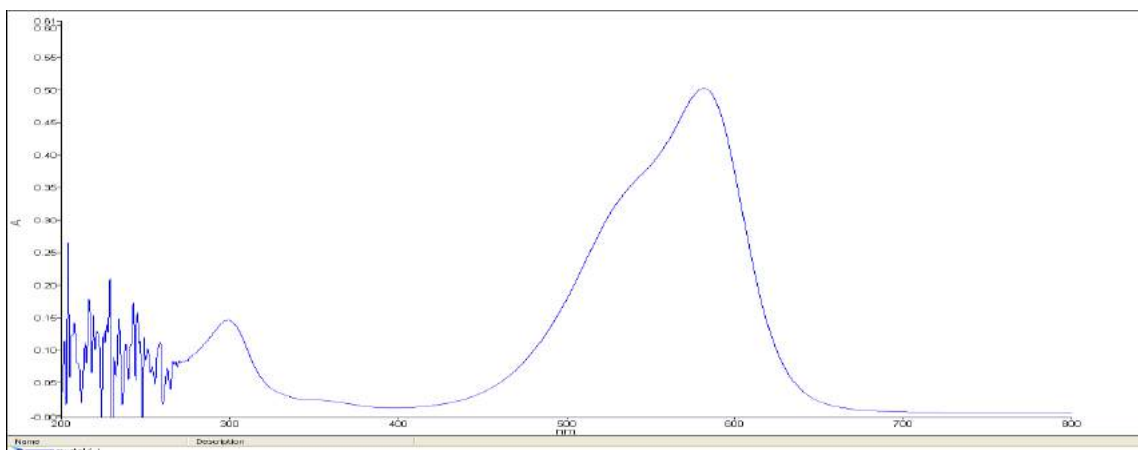


Figure (2.5): The spectrum curve of CV dye.

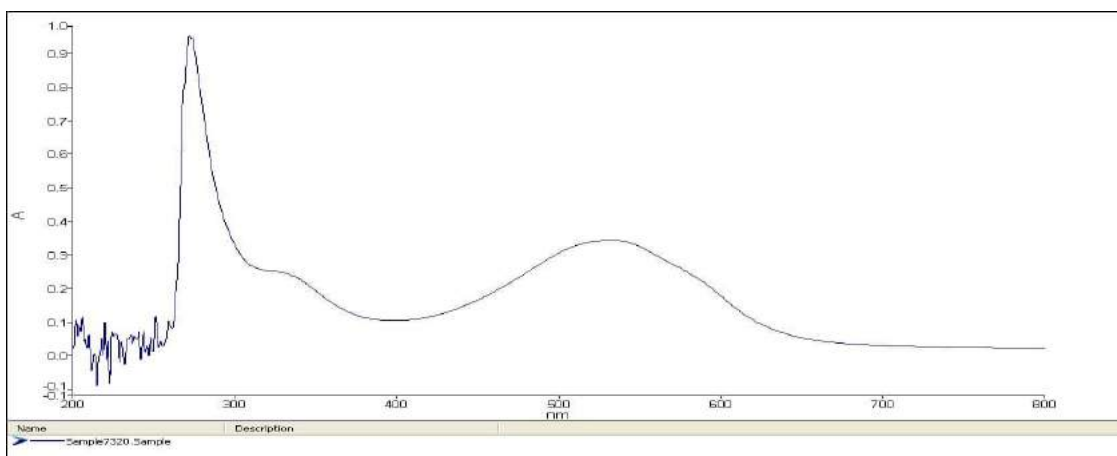


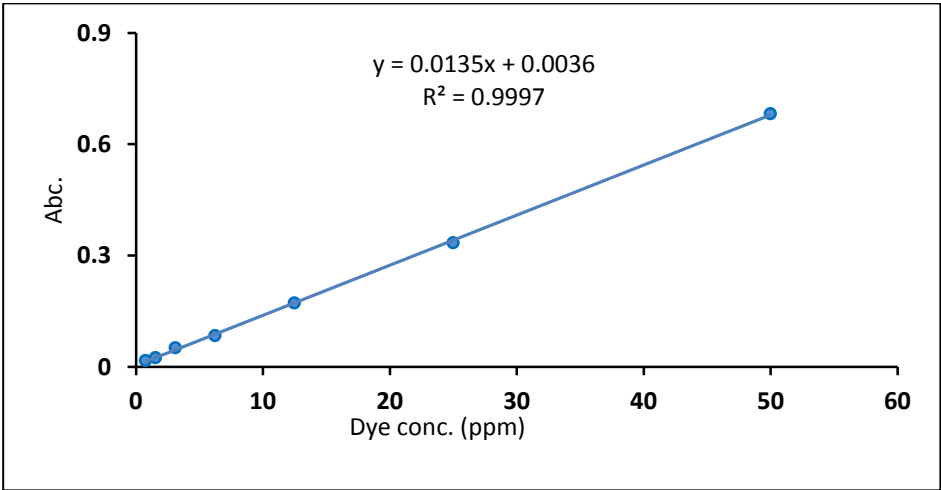
Figure (2.6): The spectrum curve of DR dye.

The maximum wavelength (λ_{max}) obtained for the three dyes (DR, CV, and AR) were listed in Table (2-5)

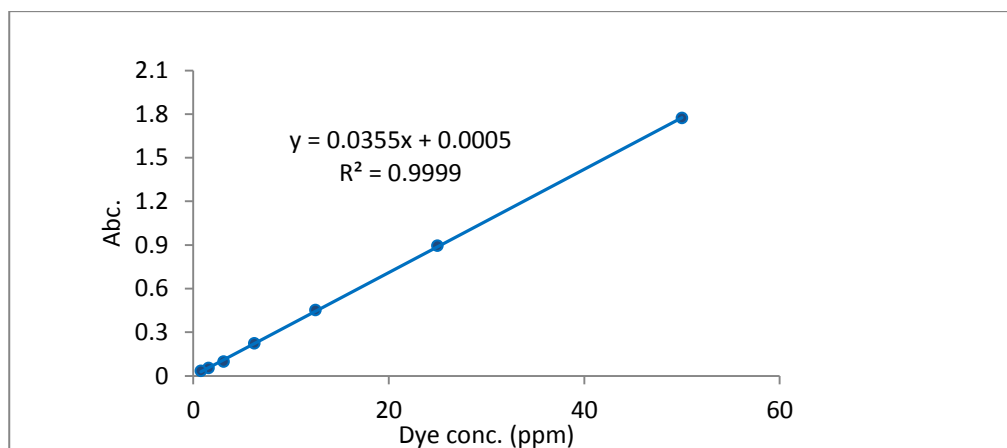
Table(2-5): The (λ_{max}) for AR, CV and DR dyes.

The Dyes	$\lambda \text{ max}(\text{nm})$
Alizarin Red	516
Cristal Violet	580
Disperse Red	537

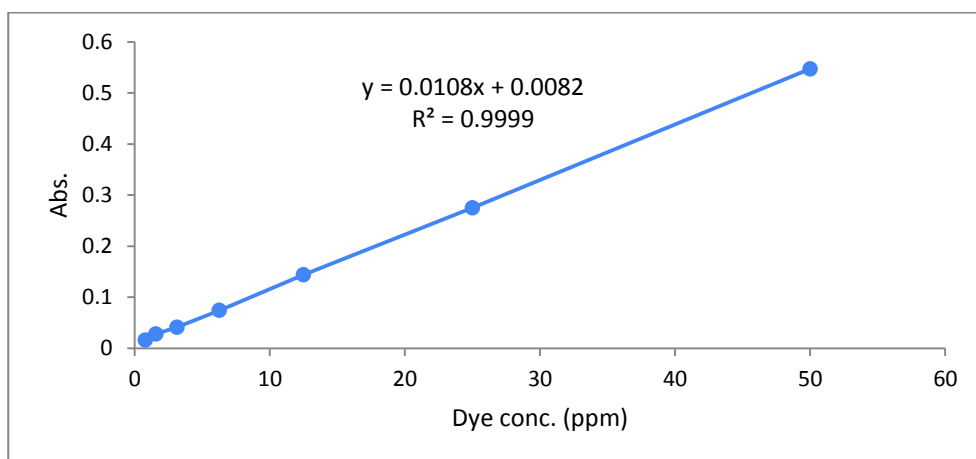
To determine (λ_{max}) for each dye to establish the calibration curves. Series of solutions with concentrations ranging from (10-50) ppm were made by dilutions of the standard dye solution. The calibration curve between concentration and absorption was established by recording absorption. The calibration curves for AR, CV, and DR are shown in figures(2.7 , 2.8 and 2.9) respectively.



Figure(2.7): The calibration curve of AR.



Figure(2.8):The calibration curve of CV.



Figure(2.9):The calibration curve of DR.

2.4.2 Preparation of Soot and Chitosan (ACS₁)

The surface of ACS₁ has been prepared from soot and chitosan in a 1:2 ratio. The utilized soot was collected from paraffin wax with weight of 2gm and treated with 1% acetic acid in an ultrasonic water bath for 15 min; later, 4gm of chitosan was added and placed in an ultrasonic water bath for 15 minutes as well. Then, an 80°C was applied to the prepared surface (composite) by placing it in a hot plate accompanied by a stirring for 5 hours until the mixture turns into a gel. The pH of the resulted gel surface modified to be equal to 10 by treating it with 1M NaOH in the form of drops in the burette. The surface is then washed by a distilled water and

separated by centrifuge to get rid of the base and change the pH level to be equal to 7. finally, the surface was placed inside an oven at 60°C for a period of 24 hours to dry out the surface and obtain the ACS₁ [99].The ACS₁ preparation steps are shown in figure (2.10).

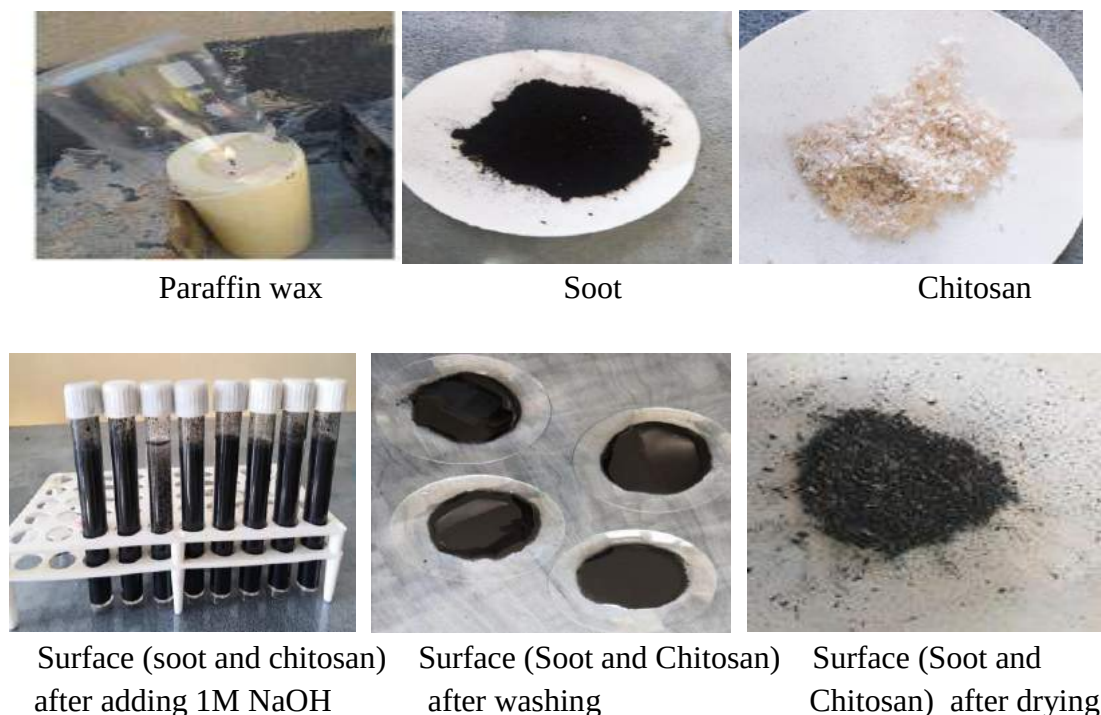


Figure (2.10):Shows the preparation steps of adsorbent surface.

2.4.3 Treatment ACS₁ with Nitric acid

Nitric acid solution was prepared by 10% (HNO₃) was added into the surface 12gm ACS₁ with stirring using the magnetic bar with vigorous stirring motion to avoid agglomeration for 2 hours at 40°C. The mixture was filtered and then washed with distilled water for three times. Finally, the product was dried in the oven at 105°C for 1hour and kept in a box for use in this form with the symbol ACS₂ [100].

2.4.4 Preparation of Stock Solutions

Dyes stock solutions were prepared by dissolving dyes in deionized water by using volumetric flasks, which were also minutely weighted at a concentration of 0.1gm in 1000 mL of water 100 ppm for AR, CV and DR dyes. Afterward, from these concentrated solutions for dyes. Series of diluted solutions were prepared with different concentrations of dyes ranging from (10-50 ppm) and the solutions were stored.

2.5 The Study Factors that 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 concentration of dyes, the weight, the pH, and temperature are constant only time the was changed. Different times (10, 20, 30, 40, 50 ,60 ,90) min were taken with (15 mL, 25 ppm) and the weight of the adsorbents surface was (0.01gm). The pH of the dyes (AR, CV, and DR) solutions was not changed. Tubes were placed in water-bath shaker at 25°C and 180 rpm. After the time is up the sample was drawn from the water bath. Then filtered, after separation the solutions were measured through UV-Visible spectrophotometer. By following the change in the percentage removal with time, the equilibrium time was determined, as the optimum time was 20 minutes, according to the following formula [101].

Removal (%) = $\frac{C_o - C_e}{C_o} * 100$ (2.1)

Where: C_o and C_e are the initial and final concentration (mg/L) of dye in solution, respectively. The adsorbed amount (mg/g) was calculated using the formulae [101].

$$q_e = \frac{V(C_o - C_e)}{m} \dots\dots\dots (2.2)$$

Where: q_e : The amount of equilibrium adsorption

(C_o 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 weight of adsorbent

To study the effect of the adsorbent weight on the adsorption process, different weights have been taken (0.01, 0.02, 0.05, 0.1 and 0.2)gm at 25°C, volume and concentration (10ml, 25ppm) for the three dyes were constant. The equilibrium time (20min) and each dye was studied as accordance to its pH value. The tubes were placed in the water-bath shaker at 180 rpm and then filtered through a micro filter paper, after that the solutions were measured through UV-Visible spectrophotometer [102].

2.5.3 Effect of pH

To estimate the effect of pH on the adsorption process, adsorption procedures were done at pH(3, 7 and 10). Take a constant volume (25mL) of the three dye solutions with (10, 20, 30 and 40) ppm 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 (0.01g), the temperature (25°C) and contact time (20min) remains constant. Afterward, the conical flasks were placed in the water-bath shaker at 180rpm. Then, the solutions were measured with the UV-Visible spectrophotometer [103].

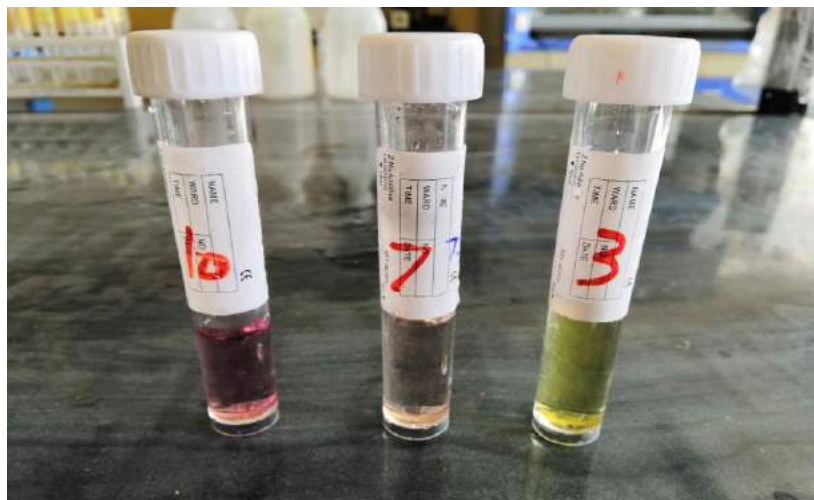


Figure (2.11): Show test tube through determination of change pH.

2.5.4 Effect of Temperature

To determine the effect of temperature, adsorption of three dyes on (ACS_1 & ACS_2) were conducted an adsorbent amount of 0.01 g with 10 ml of 25 ppm concentration for three dyes in conical flasks, at different three temperatures (25,35 and 45)°C .The pH of the dyes solutions were not changed and the contact time for three dyes was 20 min. Then, the conical flasks were placed in the water bath shaker at a 180 rpm, the temperature was controlled by the regulator of the water bath shaker. After that, the samples were placed in the centrifuge for 15 min at 6000 rpm. The solutions were measured using UV-Visible spectrophotometer.

2.6 Adsorption Isotherms

Five solutions of each dye were prepared in volumetric flask 250 ml capacity with concentrations ranging from(10, 20, 30, 40 and 50) ppm. Which were taken 25 ml of each concentration and put in contact with 0.01 g of (ACS_1 & ACS_2) in conical flasks then placed in the water bath shaker at a 180 rpm at 25°C for 20 min. The pH of the three dyes solutions was not changed. The adsorbate solutions were placed in the

centrifuge for 15 min at 6000 rpm. After separation, residual the solutions were measured through UV-Visible spectrophotometer. After that, the amount of equilibrium adsorption, q_e (mg /g), was calculated using following equation [104].

$$q_e = \frac{v(C_o - C_e)}{m} \dots\dots\dots (2.3)$$

Where;

q_e : The amount of equilibrium adsorption (mg/gm)

C_o : 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 (gm).

Chapter Three

Results & Discussion

3.1 Characterization of the Prepared Activated Soot and Chitosan

3.1.1 Fourier Transform Infrared Spectroscopy (FT-IR)

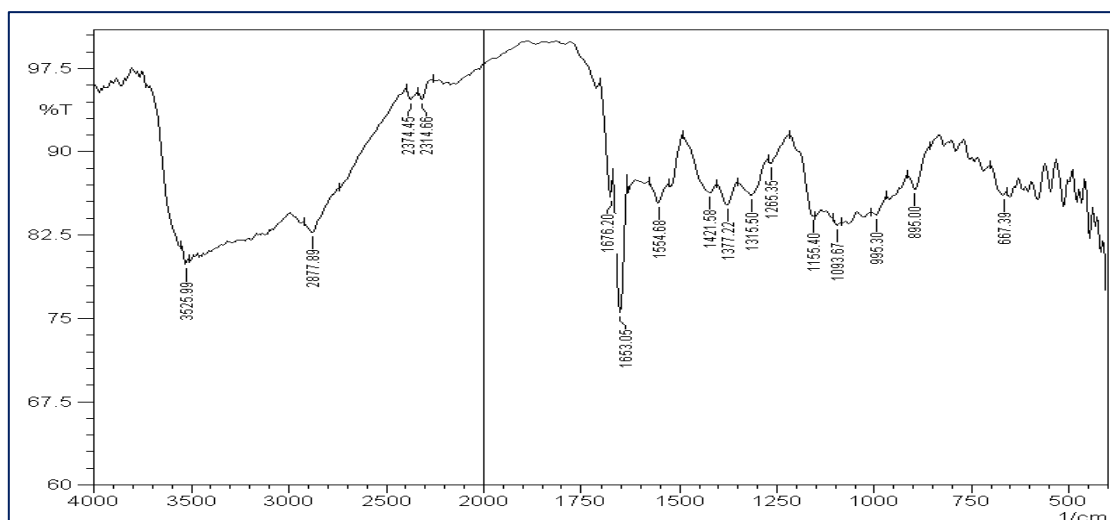
The functional groups present in the chitosan were assessed using the FTIR assay. The infrared spectra of chitosan was shown in Figure(3.1). The hydrogen bonds are represented by a strong band in the region 3525 cm^{-1} , and the N-H stretch is represented by a strong band in the region 3065 cm^{-1} . C-H is responsible for the absorption bands at 2877 cm^{-1} . The bands at around 1676 cm^{-1} (C=O stretching of amide I) and 1265 cm^{-1} (C-N stretching of amide III), and it was most likely overlapping with others. The N-H bending of the main amine is shown by a band at 1554 cm^{-1} [107]. The appearance of bands at around 1421 cm^{-1} and 1377 cm^{-1} corroborated the CH_2 bending and CH_3 symmetrical deformations, respectively. The asymmetric stretching of the C-O-C bridge is responsible for the absorption band at 1155 cm^{-1} . C-O stretching is shown by the band at 1093 cm^{-1} . C-C is responsible for the absorption band at 995 cm^{-1} . All bands are found in the spectra of samples of chitosan reported by others [108][109].

The functional groups and bonding among atoms in ACS_1 and ACS_2 were assessed using the Fourier transform infrared spectroscopy assay. Despite multiple FTIR spectroscopy experiments on various types of soot, a single wave number cannot be ascribed to a particular functional group. This is because different functional groups shifted depending on surroundings and molecular structures. The functional group could help or prevent the adsorption process [110]. Initially, the FT-IR spectra of the ACS_1 & ACS_2 are depicted in Figure (3.2). It is clear from the figures that there is a perceptible change in spectra and that many peaks emerged and shifted after chemical treatment, such as NH_2 transformed into NH_3 after the added of Nitric acid. Indicating that the oxidizing agents successfully revised the spectra, where this figure the FT-IR (KBr disc,

cm⁻¹) spectra of ACS₂ showed the presence of absorption bands is (O-H) at 3402 cm⁻¹, FT-IR spectra also showed the presence of strong bands at 2847 (-CH stretching). A strong band in the region stretch 3213 cm⁻¹ corresponds to N-H stretch, and 895 cm⁻¹ corresponds to C-C stretching. Moreover, 1558 cm⁻¹ is imputed for C=O group. Lastly, the bands at 1427.37 cm⁻¹ and 1377.22 cm⁻¹ are caused by the bending of C-H group [111][112].

Table (3-1):Wave numbers and ascription of the principal bands in FTIR spectra of ACS₁ and ACS₂.

Assignment group	Wave numbers (cm ⁻¹)	
	ACS ₁	ACS ₂
-NH- ben	1566	1558
-NH- str.	3213	-
O-H str.	3402	3300
-C-N str.	1246	-
C-C ben.	895	900
C-H str.	2847	2870
C-O str.	1722	1720
NH ₂	1500	-
NH ₃ ⁺	-	965



Figure(3.1): The FT-IR Spectrum of chitosan

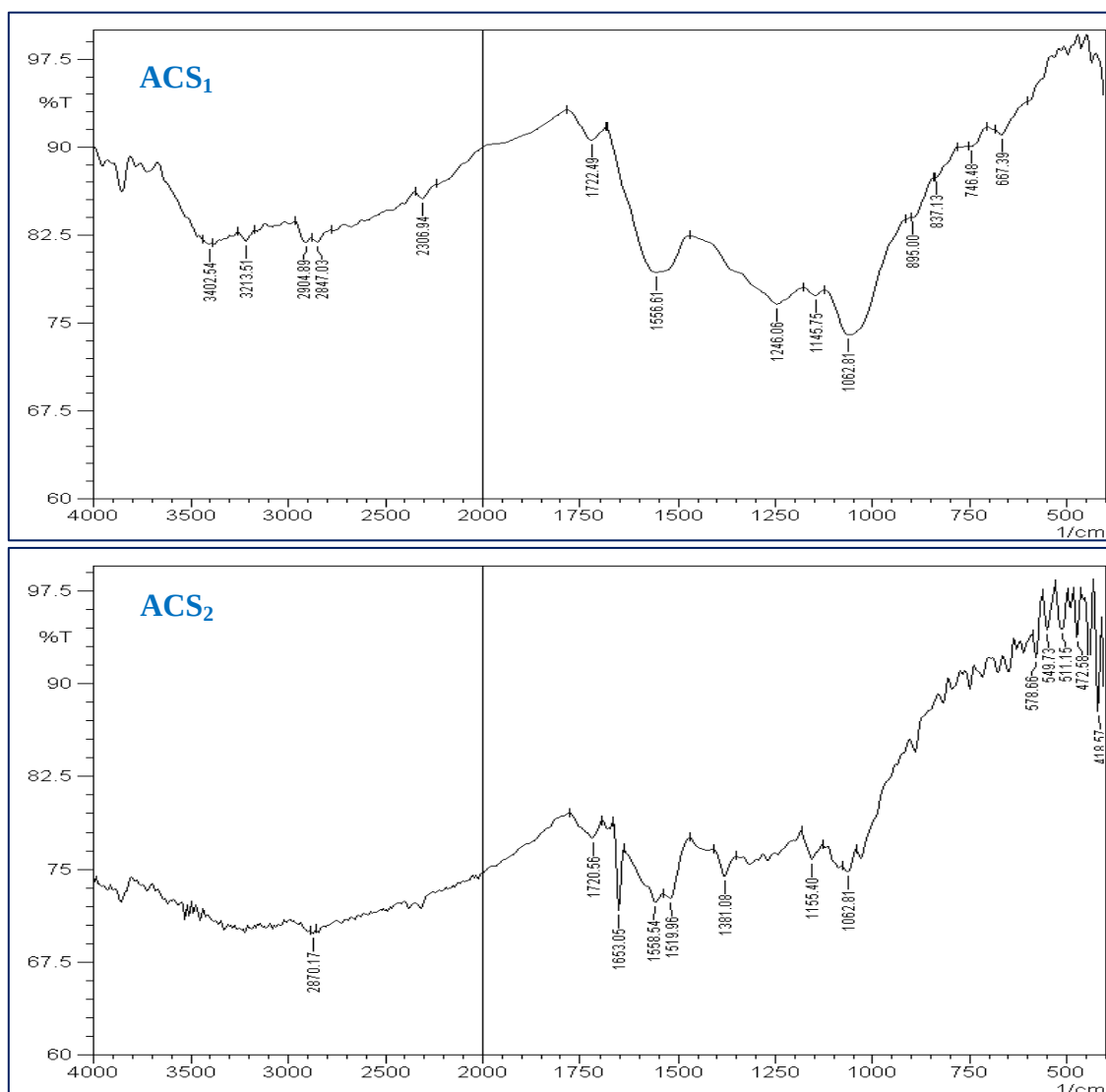


Figure (3.2):The FT-IR Spectrum of ACS₁ and ACS₂

3.1.2 X-Ray Diffraction (XRD)

The XRD diffraction is used to study the crystal structure, degree of crystallinity, phase purity, and quantitative material by directing a x-rays on the crystalline matter according to Bragg equation [113]:
$$n\lambda = 2d \sin\theta \dots\dots\dots(3.1)$$

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

The XRD diffraction patterns of chitosan is recorded in Figure(3.3). The diffraction pattern of chitosan shows two pattern's at $2\theta=10^\circ$ and 20° indicating the ordered crystalline structure of chitosan. [114].

XRD diffraction was used to examine the crystalline composition of activated surface ACS₁ and ACS₂ pattern show in Figure(3.4). The (XRD) study of the ACS₁ sample reveals the presence of two crystalline phases in this range at $2\theta=12^\circ$ and 25° . On the other hand, the XRD diffraction spectrum for ACS₂ revealed that the angle at $2\theta=12^\circ$ is the same as the angle at $2\theta=25^\circ$ indicate the presence of the second crystalline phase. Due the influence of nitric acid, which induces a breakdown of the crystalline form, caused the crystalline state to change and become broad. According to the literature, the crystalline size decreases when increasing the width of these pattern. The two peaks are depicted in the diagram, the First, at $2\theta= 12^\circ$, has a much higher intensity but a smaller width than the second, at $2\theta= 25^\circ$. The length and width of the peaks were once widely employed to determine crystal size. In general, the first band at $2\theta= 25^\circ$ return to the non-crystalline structure of ACS₂ consequently, the breadth grows as the intensity or length decreases, indicating that the sample (activated soot and chitosan) is in amorphous form [115].

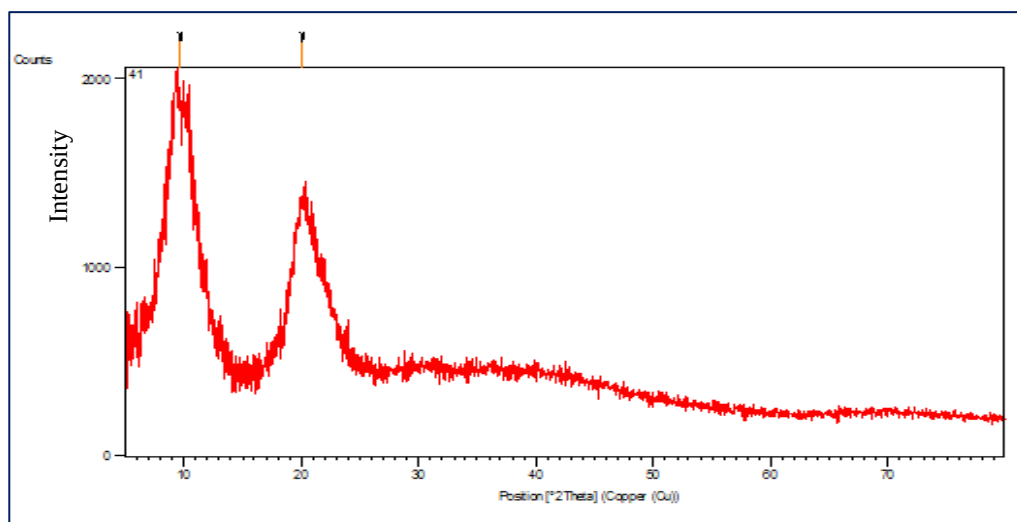


Figure (3.3): XRD spectrum of chitosan

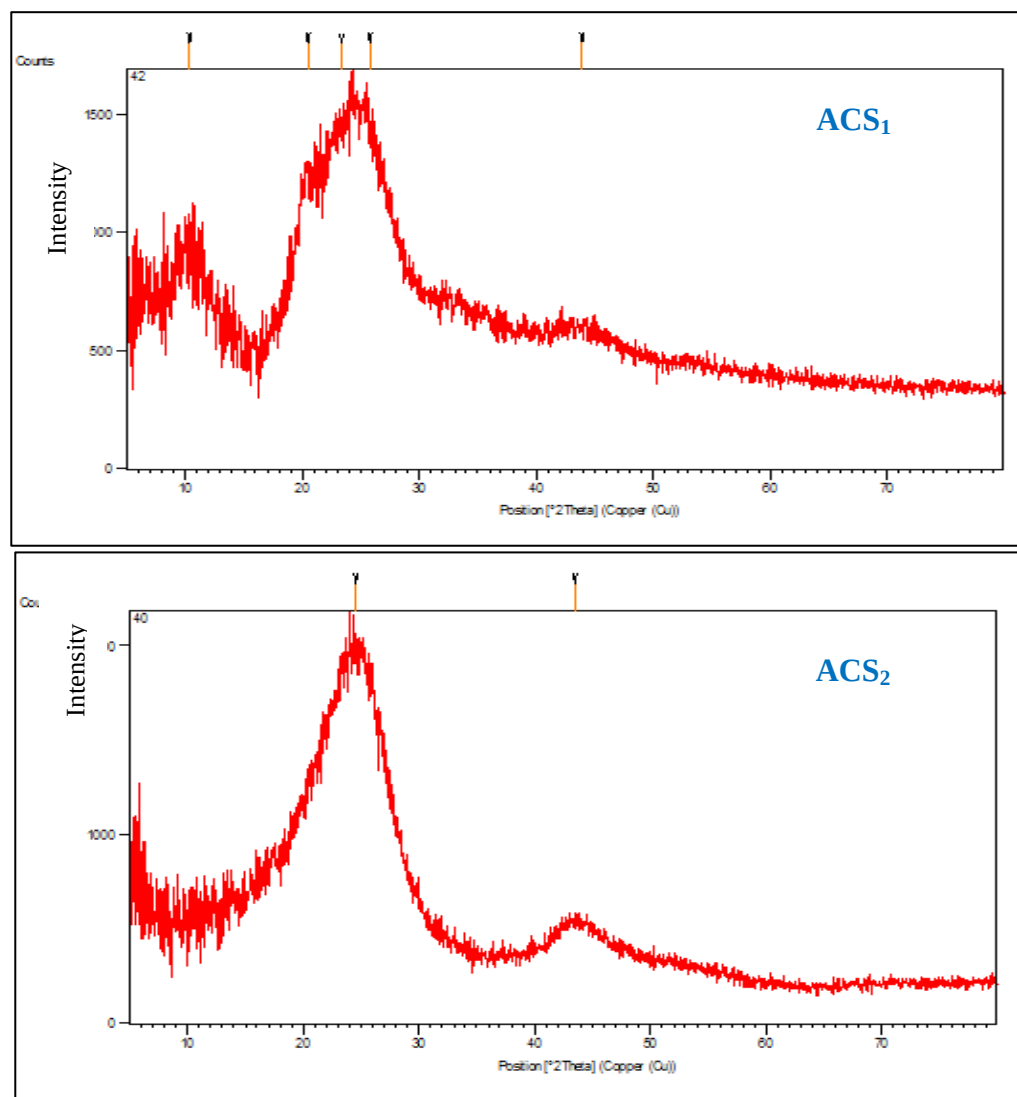
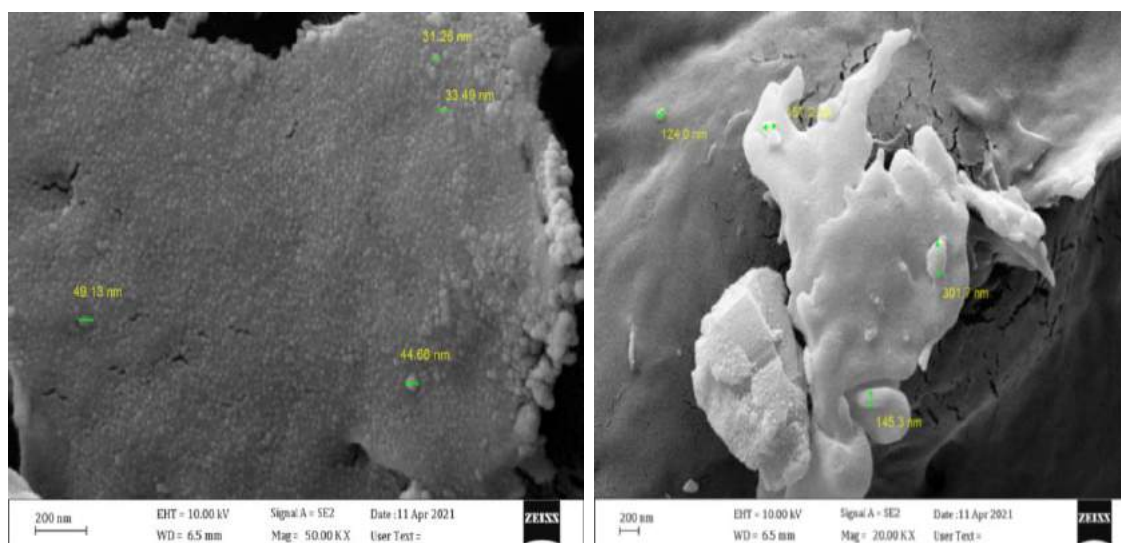


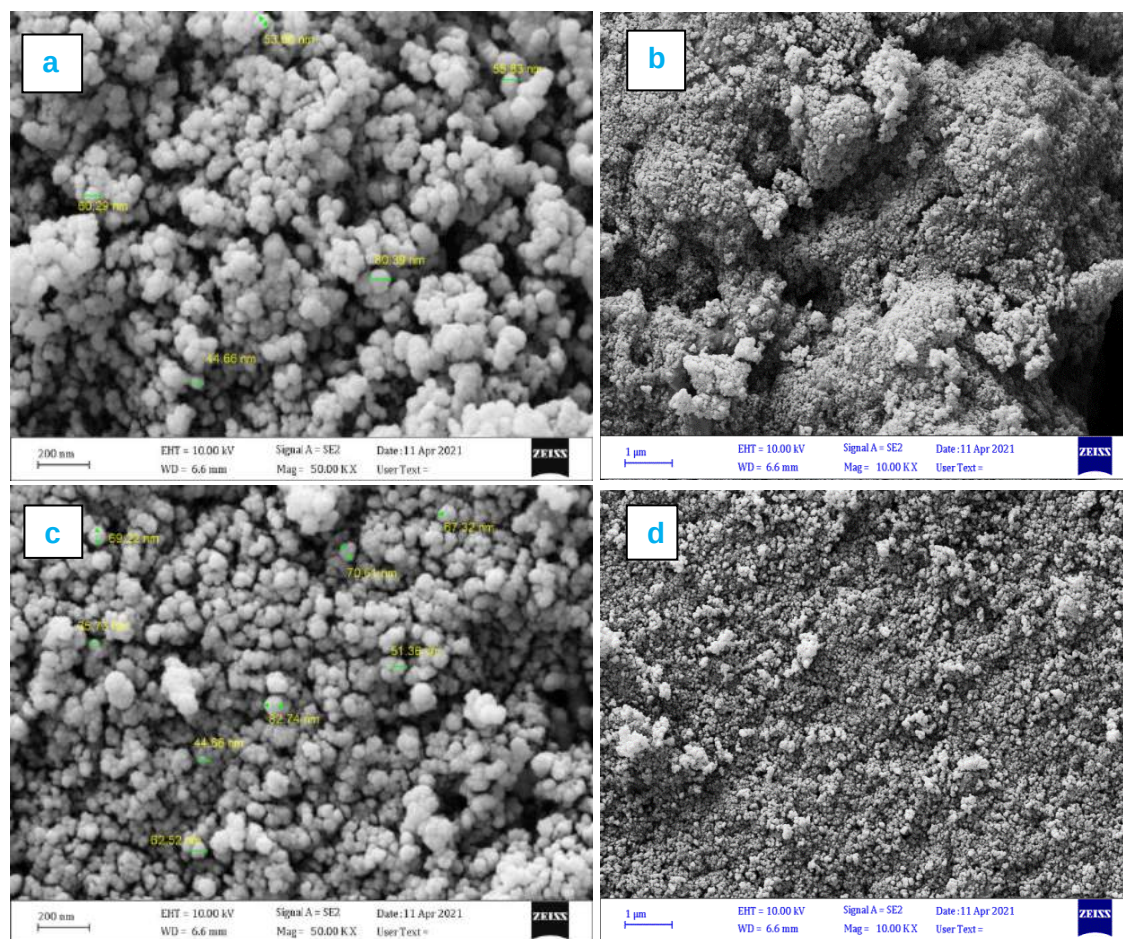
Figure (3.4):XRD spectrum of ACS₁and ACS₂

3.1.3 Scanning Electron Microscopy (SEM)

The Scanning electron micrographs image of chitosan nanoparticles in Figure(3.5). The formed chitosan appears slightly aggregated due to the absence of strong surface protecting ligands and found to be irregular in shape [116]. The SEM of chitosan revealed that it has a rough surface and it showed prominent sheath-like layers[117]. Scanning electron microscopy is used to analyze the important properties of surfaces ACS₁& ACS₂ such as the shape, size particle and nature of the surface. Figure(3.6) shows the SEM images of surface before and after activation were examined by scanning electron microscopy nanostructure. Figure 3.6 (a, b) for ACS₁ shows regular particle shapes nm with large scale of pores the particles are spherical and surface were smooth the presence of some cavities and particles. While Figure 3.6 (c, d) indicated that after treatment, the surface shape changed and the shape were more uniform because added nitric acid, revealing smooth and large-pore nanoparticles as well as regular spherical particles. Higher porosity increased ACS₂ surface area, which is compatible with BET analyses; no geometries were found[118].



Figure(3.5): SEM micrographs of chitosan



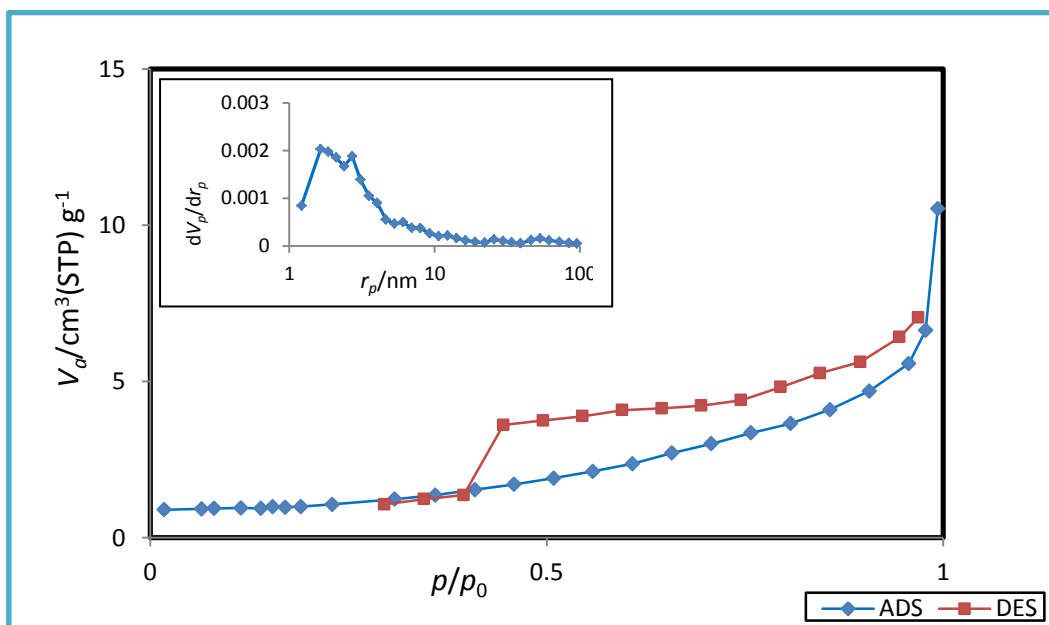
Figure(3.6):The SEM images (a, b) for ACS₁, (c, d) for ACS₂ at different magnifications

3.1.4 Surface Area Analysis (BET, BJH)

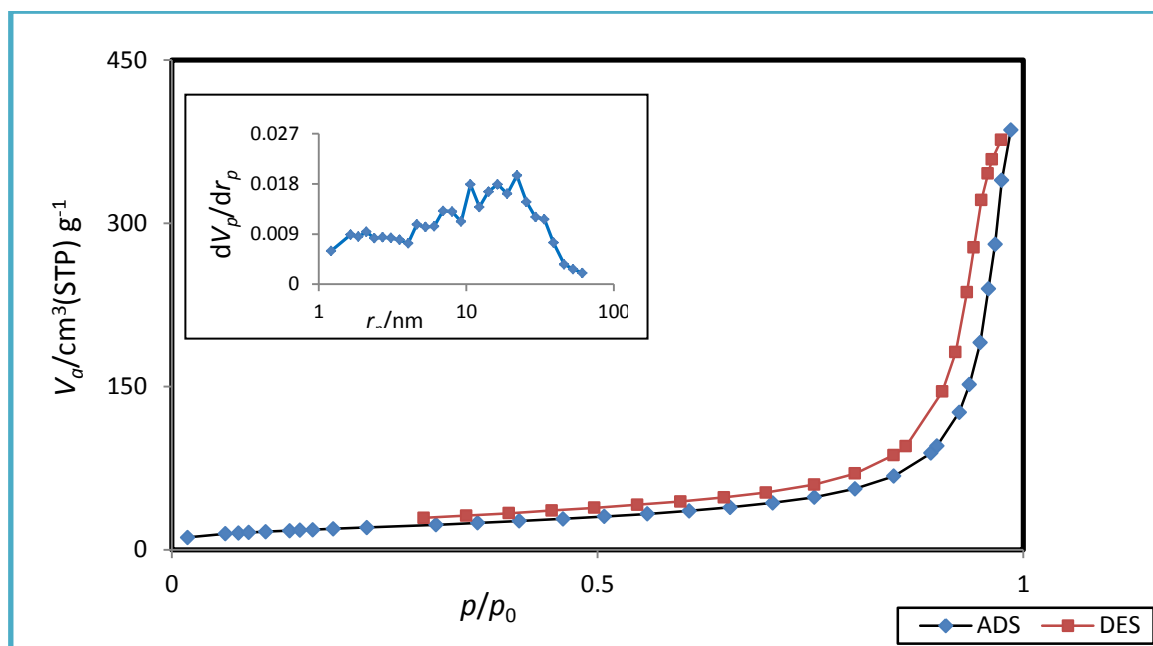
In BET, nitrogen (N₂) is usually used due to its availability in high purity and its strong interaction with most solids. The interaction between gaseous and solid phases is commonly weak, therefore the surface is cooled by liquid nitrogen (N₂) to obtain a detectable amount of adsorption [119]. The surface area of ACS₁ and ACS₂ were studied where the results showed that the surface area of ACS₁ was 68.845 m² gm⁻¹. Either the ACS₂ activated surface treated with nitric acid showed a change in the surface area which is increased to 78.159 m² gm⁻¹ Table (3-2) compared to ACS₁. It could be due to the dispersion of the soot and chitosan grains due to the positive and negative charged formation of the active atoms on the surface and the attraction between charged and this caused an expansion in the surface particles and this led to increase in the surface area

and may be due to the presence of nitrate ions[120]. This is consistent with SEM analysis. The pore size distribution by (BJH) method for ACS₁ & ACS₂, the form of the isotherm is reversible and convex and the relative pressure axis corresponding to (type IV) isotherm according to the nomenclature of (IUPAC). This type is often encountered with microporous materials, and refers to a multilayer adsorption [120].

The results of Figure (3.7) and (3.8) indicate The figures belonging to the pore size indicate that there are many types of pores, some of which are within the mesoporous region and the others are within the macropores for chitosan and ACS₁. As for the Figure (3.9) of the ACS₂ pore size, it indicates that the pores exist in one type, which is the Mesoporous region. The hysteresis loop of ACS₁& ACS₂ range from $0.3 < P/P_0 < 0.11$ and is related to capillary condensation. According to (IUPAC) classification, this isotherm of type III and hysteresis loop have been associated with H₃.



Figure(3.7):The N₂ adsorption/desorption isotherms of the chitosan with their corresponding pore size distribution (inset)



Figure(3.8):The N_2 adsorption/desorption isotherms of the ACS₁ with their corresponding pore size distribution (inset).

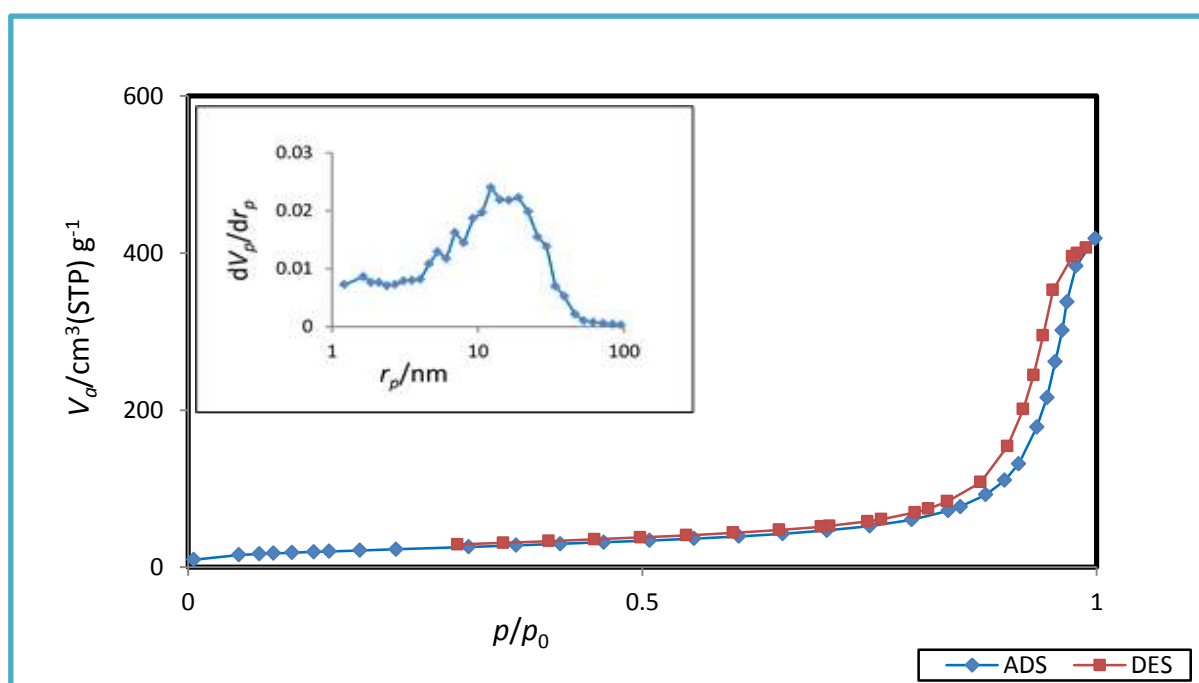


Figure (3.9):The N_2 adsorption/desorption isotherms of the ACS₂ with their corresponding pore size distribution (inset).

Table (3-2):Surface area, volume and diameter of pore in ACS₁& ACS₂

sample	BET surface area (m ² /g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore dimeter(nm)
ACS ₁	68.8	0.59	34.6
ACS ₂	78.1	0.62	32.0

3.2 Parameters effect on adsorption of ACS₁ and ACS₂

3.2.1 The Influence of Contact Time

Batch experiment to evaluate the relationship between contact time and adsorption of three dyes (AR-CV-DR) on the surfaces of ACS₁ & ACS₂, were studying. The contact time required to achieve equilibrium time for the solution of dyes on the two surfaces of ACS₁& ACS₂ at periods of time (10, 20, 30, 40, 50, 60, and 90 minutes) with constant concentration (25ppm), temperature (25°C), and pH nature of dyes solution were evaluated. The time required to reach the equilibrium of the three dyes is 20 minutes, as shown in Tables (3-3) and (3-4), and the percentage of removal rate (R %) were given in table(3-3, 3-4). Figure(3.10, 3.11) illustrates how the proportion of removed dyes increases as the time of both ACS₁ and ACS₂ increases at varied rates in the first 10 min. After 20 min of stabilization, the dyes' chemical and physical characteristics, as well as the saturation of active sites on the surface, remained consistent. Because empty active sites are available more for the adsorption of the dyes at first, the percentage removal of the dyes increases with time, and as time passes, the active sites are used up, resulting in a stable state, an equilibrium state. Where the sites are reached fully saturate [121], the

shaking time of 20 min was used to ensure full equilibration. The percentages of removal (R%) dyes calculated as follow:

$$\%R = \frac{C_o - C_e}{C_o} * 100 \dots\dots (3.2)$$

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

Table (3-3): Show the R% the dyes (AR-CV-DR) by ACS₁ at different times

Dyes	Time (min)							R%
	10	20	30	40	50	60	90	
AR	68.5	72.7	72.8	73.1	73.5	73.4	73.7	
CV	85.2	87.5	87.7	87.8	87.6	88.1	88.8	
DR	37.6	48.6	48.7	48.8	48.1	49.3	49.7	

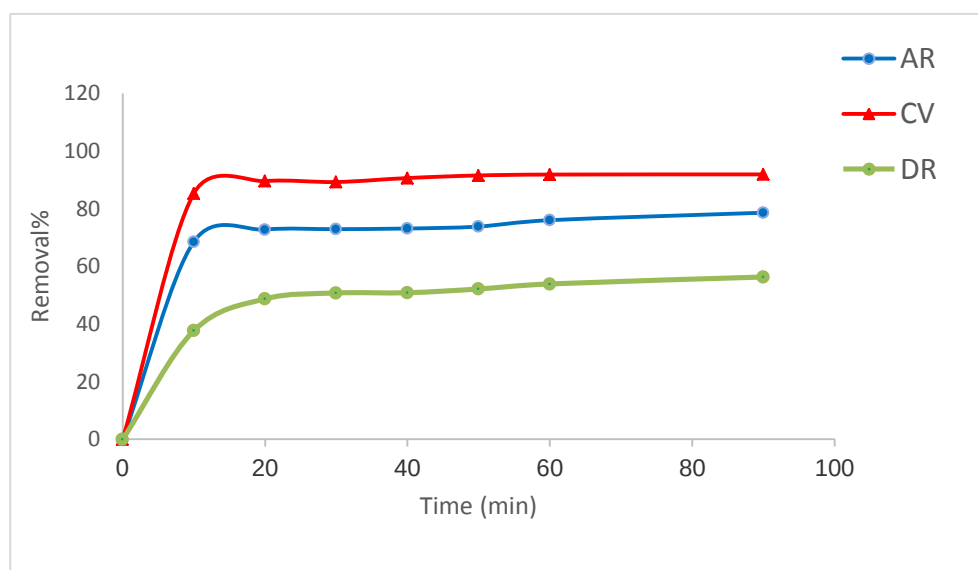
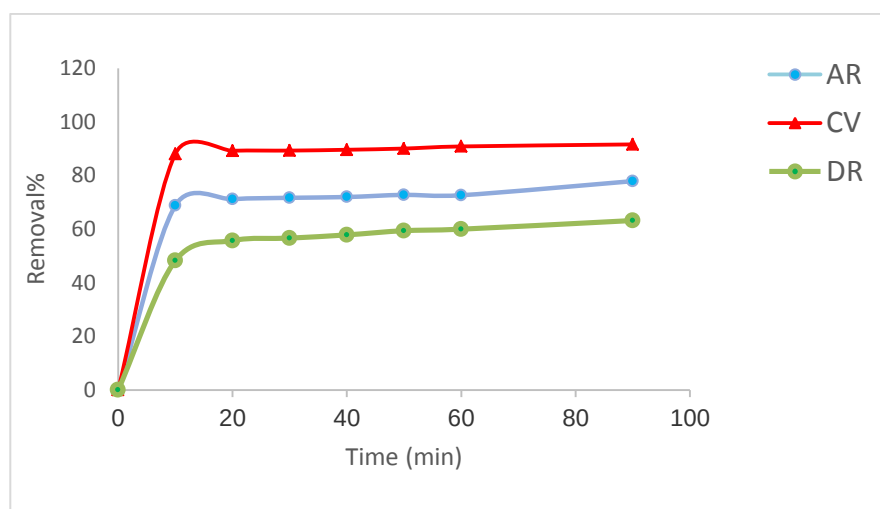


Figure (3.10): The effect of contact time on the adsorption of three dyes for ACS₁

Table (3.4):Show the percentage of removal the dyes (AR-CV-DR) by ACS₂ at different times

Dyes	Time (min)							R%
	10	20	30	40	50	60	90	
AR	68.8	71.1	71.7	72.0	72.6	73.4	73.9	
CV	85.1	89.2	89.5	89.9	90.4	90.5	90.5	
DR	48.2	55.6	55.7	56.8	56.4	57.0	57.2	



Figure(3.11):The effect of contact time on the adsorption of three dyes for ACS₂

3.2.2 Effect of Adsorbent Dosage on Adsorption

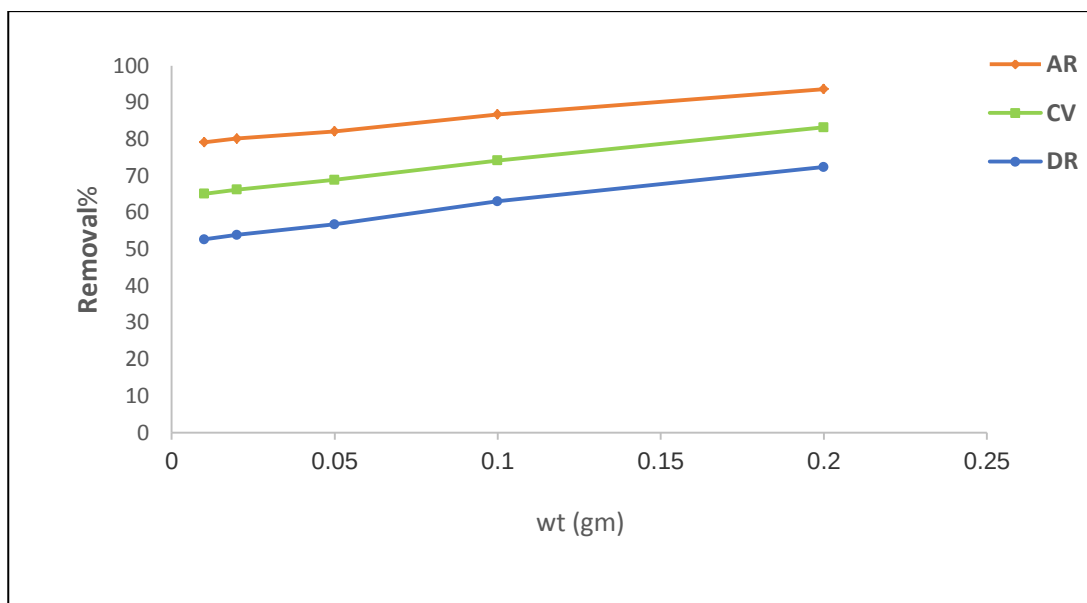
The goal of this experiment was to see how different adsorbent weights affected the adsorption of dye solutions while keeping the contact time (20 minutes) and initial dye concentration (25 ppm) constant. Adsorption was done with different adsorbent weights (0.01, 0.02, 0.05, and 0.1) gm per (25 mL) at 25°C. Table (3-5) &(3-6) shows the results where the percentage of removal for three dyes increases with the increase of adsorbent

weights of both ACS₁ & ACS₂. This could be due to higher availability of sorption sites and a larger surface area where adsorption took place. The results show that increasing the weight of the adsorbent under the same experimental conditions can enhance the percentage of dye removal for the three dyes on both ACS₁ & ACS₂ surfaces and reach a high percentage. 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 both ACS₁ & ACS₂ surface that are available to adsorb the dyes, so the efficiency of the dye removal will increase with the increase in surface mass [122]. In this study, the suitable weight of, ACS₁ & ACS₂ is 0.01 g for the dyes adsorption.

It is obvious from the Tables (3-5) & (3-6) that the lower surface mass show 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.

Table (3-5):The Values of R% and Quantity of Adsorbent for ACS₁

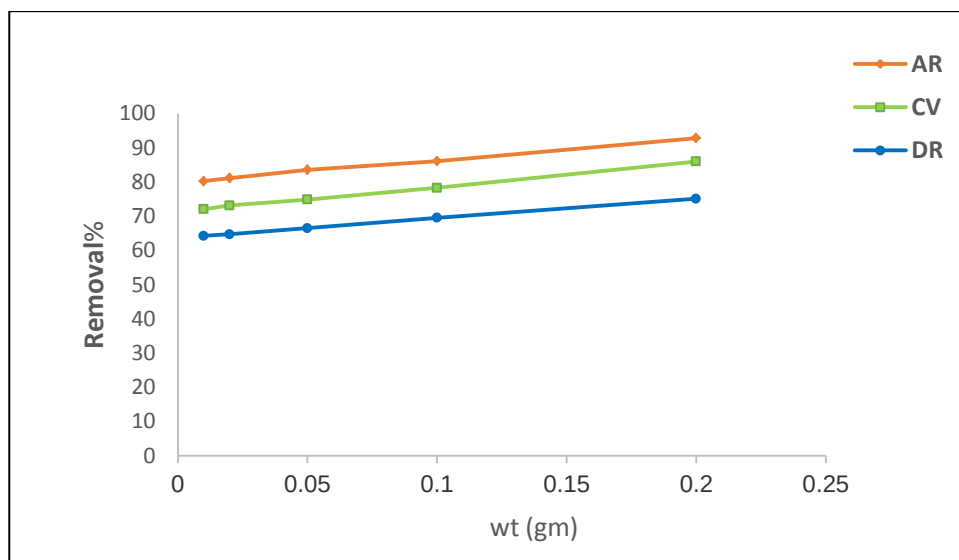
Quantity of adsorbent (g)	AR			CV			DR		
	C _e mg/l	q _e mg/g	R%	C _e mg/l	q _e mg/g	R%	C _e mg/l	q _e mg/g	R%
0.01	20.8	197.6	79.1	34.8	162.8	65.1	47.3	131.7	52.6
0.02	19.8	100.2	80.2	33.7	82.8	66.2	46.1	67.3	53.8
0.05	17.6	41.1	82.1	31.1	34.4	68.9	43.2	28.3	56.7
0.1	13.2	21.6	86.7	25.8	18.5	74.1	36.9	15.7	63.1
0.2	11.7	6.3	93.6	16.7	10.4	83.2	27.5	10.1	72.4



Figure(3.12):Effect of adsorbent dosage on removal of the three dyes onto ACS₁

Table (3-6): The values of R% and Quantity of adsorbent for ACS₂

Quantity of Adsorbent (g)	AR			CV			DR		
	C _e mg/L	q _e mg/g	R%	C _e mg/L	q _e mg/g	R%	C _e mg/L	q _e mg/g	R%
0.01	19.7	200.5	80.2	27.9	180.1	72.1	36.8	157.8	63.1
0.02	18.8	101.3	81.1	26.8	91.4	73.1	35.2	80.9	64.7
0.05	16.4	41.7	83.5	25.1	37.4	74.8	33.5	33.2	66.4
0.1	13.9	21.5	86.1	22.1	19.4	77.9	29.5	71.6	70.4
0.2	7.1	11.6	92.8	14.1	10.7	85.9	24.9	9.3	75.1



Figure(3.13):Effect of adsorbent dosage on removal of three dyes for ACS₂

3.2.3 The pH effect

The values of the solution pH are affected both by the binding sites of the adsorbents surface and the aqueous chemistry of the dye [122]. Many studies have proved that the pH of an aqueous solution is an important parameter in the whole adsorption process [123]. 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 [124]. To investigate the effect of pH on (AR, CV, and DR) dyes adsorption onto the surfaces of ACS₁ & ACS₂ were studied under the pH (4, 7 and 10) at 25°C with keeping contact time (20min) and the weight of adsorbent (0.01g) are constant. The results showed that the pH affects the absorption efficiency of the three dyes. The effect of pH for AR onto the ACS₁ & ACS₂ surfaces, the adsorption of AR dye is a phenomenon which is strongly affected by the pH of the solution. The obtained results indicate that the maximum percentage of removal for AR 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 Figures (3.14, 3.15) and Table (3.7). In aqueous solution, the AR dye is

dissolved and sulfonate groups of the AR dye are dissociated and converted into anionic ions, at lower pH solution values, and due to the presence of H^+ ions, the dye ions will be attracted to the positive charge of the ACS_1 & ACS_2 surfaces due to increasing the electrostatic attraction forces. While lower adsorption of the anionic dye (AR dye) at basic pH could be attributed to the abundance of OH^- ions which will compete with the AR dye anions for the same sorption sites, causing a decrease in the adsorbed amount of the dye[125]. Either that the percentage of removal for CV on the surfaces of ACS_1 & ACS_2 was following the order: $10 > 7 > 4$. Figures (3.16 , 3.17) and Table (3.8) show the effect of pH for CV onto the surfaces. The adsorption of CV dye is a phenomenon where is strongly affected via the pH of the solution. Adsorption of CV dye at acidic solution [126]. 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 favors the adsorption of CV dye due to the electrostatic attraction [127]. The results in Figures (3.18, 3.19) and Table (3-9) show 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 ACS_1 & ACS_2 surfaces (adsorbent), and then an electrostatic attraction exists between the positively charged surface of the adsorbent and the DR dye. In this case, slight interaction dipole charge like can be suggested, taking into consideration both the negatively delocalized charge presents on anthraquinonoid residue and also, the dipole of ketone. 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 DR 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 [122].

Table (3-7): The effect of the pH on the adsorption of AR dye to the ACS₁ & ACS₂

	C ₀	pH = 4			pH = 7			pH = 10		
		C _e mg/L	q _e mg/g	%R	C _e mg/L	q _e mg/g	%R	C _e mg/L	q _e mg/g	%R
ACS ₁	10	1.9	20.1	80.4	6.1	9.5	38.2	8.6	3.2	13.0
	20	6.1	34.5	69.1	10.6	23.2	46.5	13.6	15.8	31.7
	30	7.2	56.7	75.7	12.6	43.2	57.6	16.1	34.7	46.3
	40	13.7	65.6	65.6	20.8	47.8	47.8	23.3	41.5	41.5
	C ₀	pH = 4			pH = 7			pH = 10		
		C _e mg/L	q _e mg/g	%R	C _e mg/L	q _e mg/g	%R	C _e mg/L	q _e mg/g	%R
ACS ₂	10	1.2	21.9	87.8	4.6	13.2	53.0	6.4	8.8	35.2
	20	5.5	36.2	72.4	8.3	29.2	58.3	12.1	19.5	39.1
	30	6.5	58.6	78.1	8.9	52.5	70.0	13.8	40.2	53.7
	40	11.6	71.2	71.2	15.6	60.8	60.8	22.6	43.4	43.4

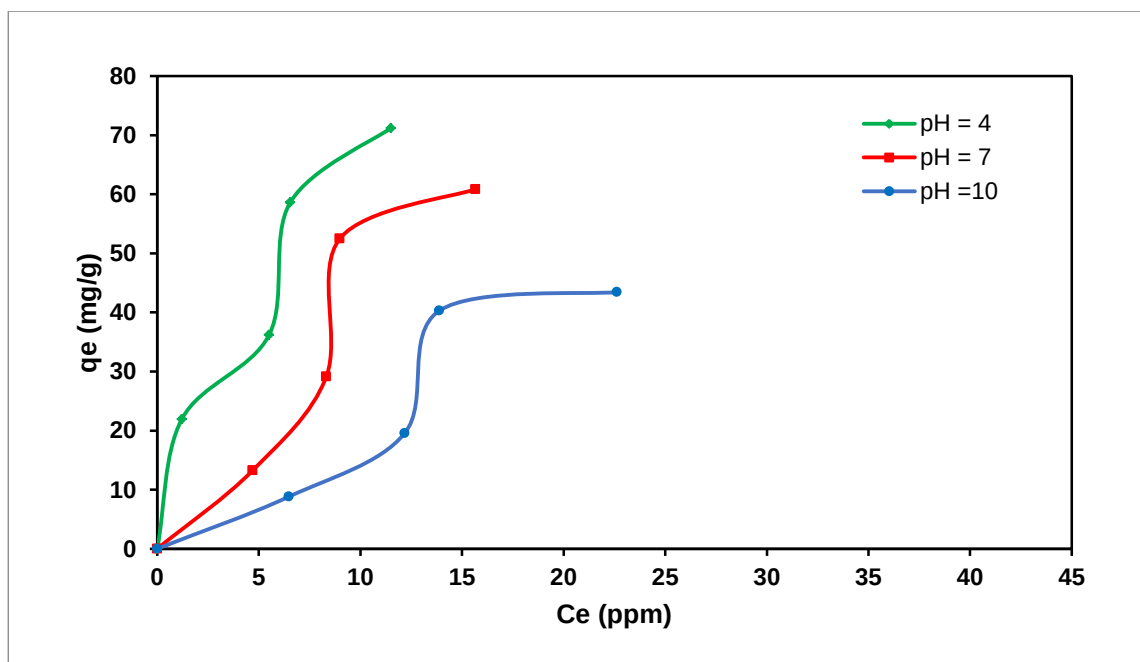


Figure (3.14): Effect of pH on the adsorption of AR into ACS₁.

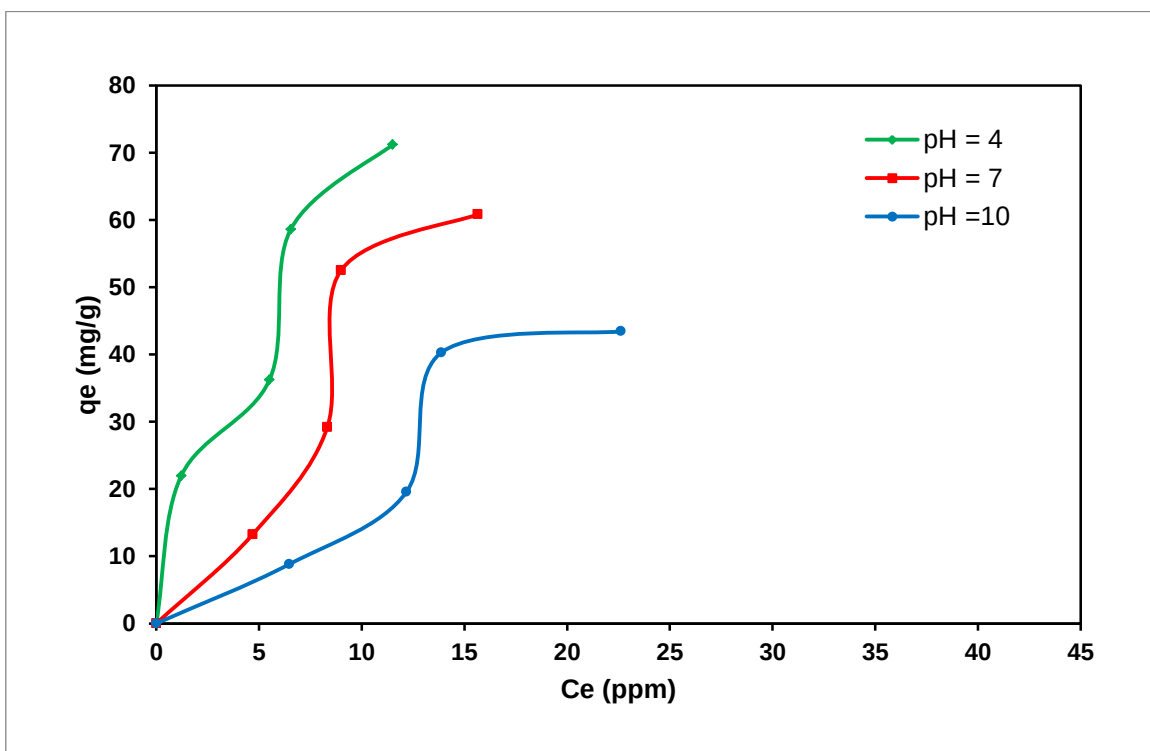


Figure (3.15): Effect of pH on the adsorption of AR into ACS₂

Table(3-8):The effect of the pH on the adsorption of CV dye to the ACS₁ & ACS₂

	C ₀	pH = 4			pH = 7			pH = 10		
		C _e mg/l	q _e mg/g	%R	C _e mg/l	q _e mg/g	%R	C _e mg/l	q _e mg/g	%R
ACS ₁	10	8.4	3.7	15.1	6.1	9.7	39.0	3.10	17.2	68.8
	20	10.8	22.7	45.5	8.3	29.0	58.1	4.7	38.2	76.4
	30	11.1	47.4	63.2	8.2	54.2	72.3	5.5	61.0	81.4
	40	16.8	57.8	57.8	14.1	64.8	64.8	9.10	77.0	77.0
	C ₀	pH = 4			pH = 7			pH = 10		
		C _e mg/l	q _e mg/g	%R	C _e mg/l	q _e mg/g	%R	C _e mg/l	q _e mg/g	%R
ACS ₂	10	7.1	7.2	29.1	5.8	10.4	41.8	2.8	17.9	71.6
	20	10.6	23.4	46.8	8.1	29.8	59.7	4.4	38.9	77.8
	30	10.8	48.1	64.1	8.4	54.9	73.2	5.3	61.7	82.2
	40	16.5	58.5	58.5	13.6	65.8	65.8	8.9	77.5	77.5

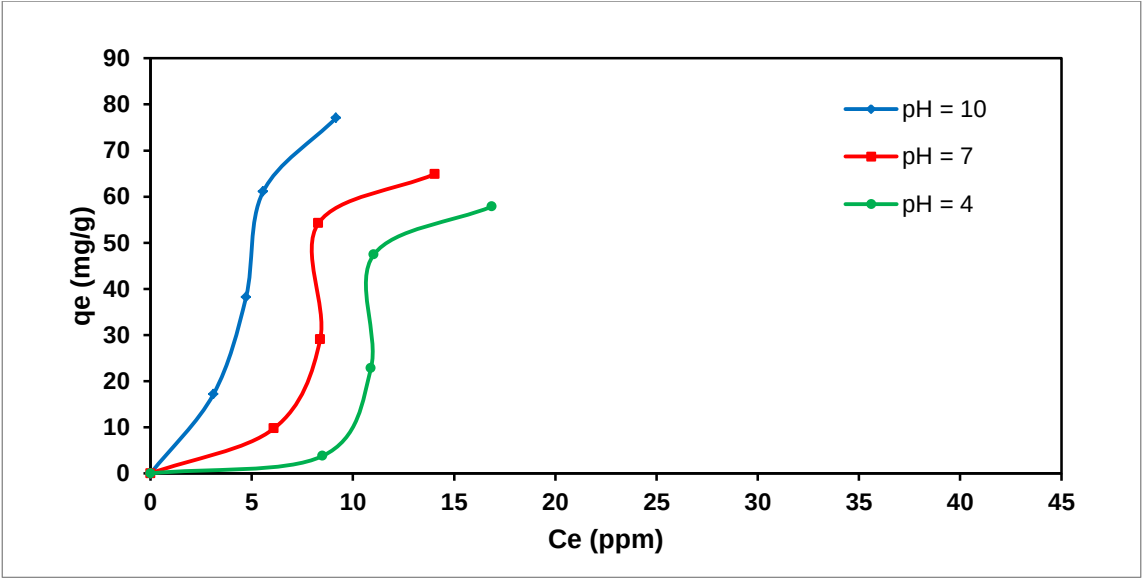
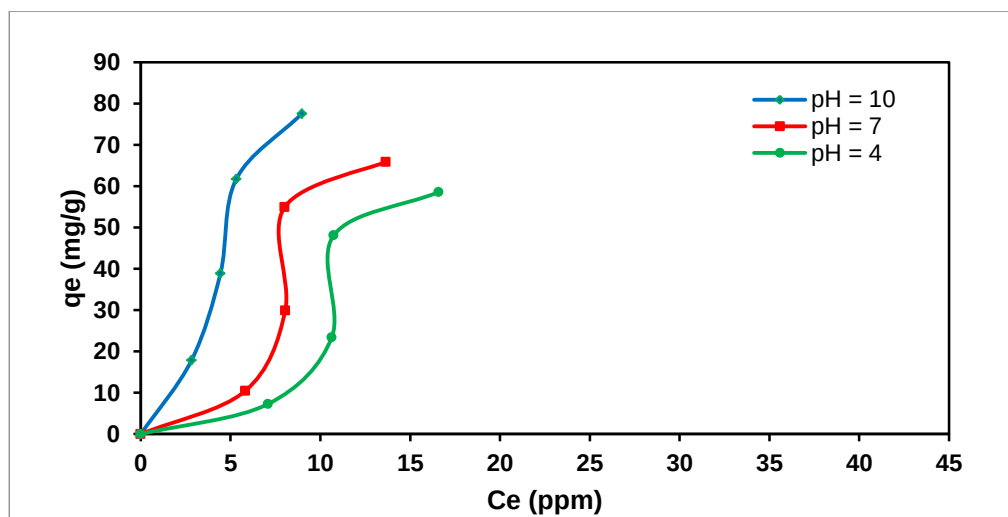


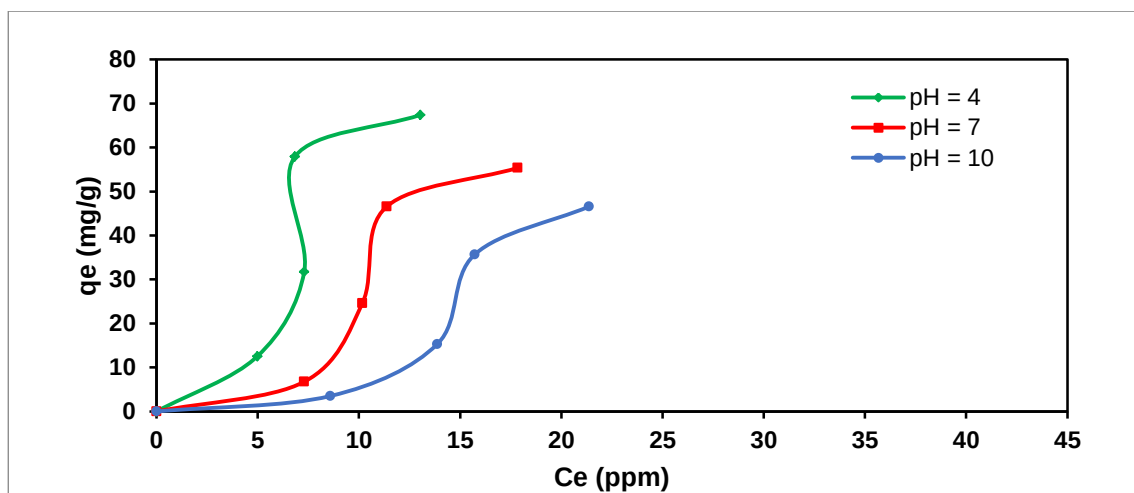
Figure (3.16): Effect of pH on the adsorption of CV into ACS₁



Figure(3.17): Effect of pH on the adsorption of CV into ACS₂

Table (3-9):The effect of the pH on the adsorption of DR dye to the ACS₁ & ACS₂

	C ₀	pH = 4			pH = 7			pH = 10		
		C _e mg/L	q _e mg/g	%R	C _e	q _e mg/g	%R	C _e mg/L	q _e mg/g	%R
ACS ₁	10	4.9	12.5	50.1	7.2	6.7	27.1	8.5	3.5	14.1
	20	7.2	31.7	63.5	10.1	24.5	49.2	13.8	15.3	30.6
	30	6.8	57.9	77.2	11.3	46.5	62.1	15.7	35.6	47.5
	40	13.1	67.4	67.4	17.8	55.3	55.3	21.3	46.5	45.4
	C ₀	pH = 4			pH = 7			pH = 10		
		C _e mg/L	q _e mg/g	%R	C _e mg/L	q _e mg/g	%R	C _e mg/L	q _e mg/g	%R
ACS ₂	10	4.1	14.8	59.4	6.2	9.3	37.2	7.8	5.3	21.4
	20	6.2	34.3	68.6	9.6	25.9	51.9	12.4	18.7	37.5
	30	6.1	59.5	79.3	11.7	45.6	60.8	15.1	37.1	49.4
	40	12.2	69.2	69.2	18.2	54.4	54.4	21.1	47.1	47.2



Figure(3.18): Effect of pH on the adsorption of DR into ACS₁

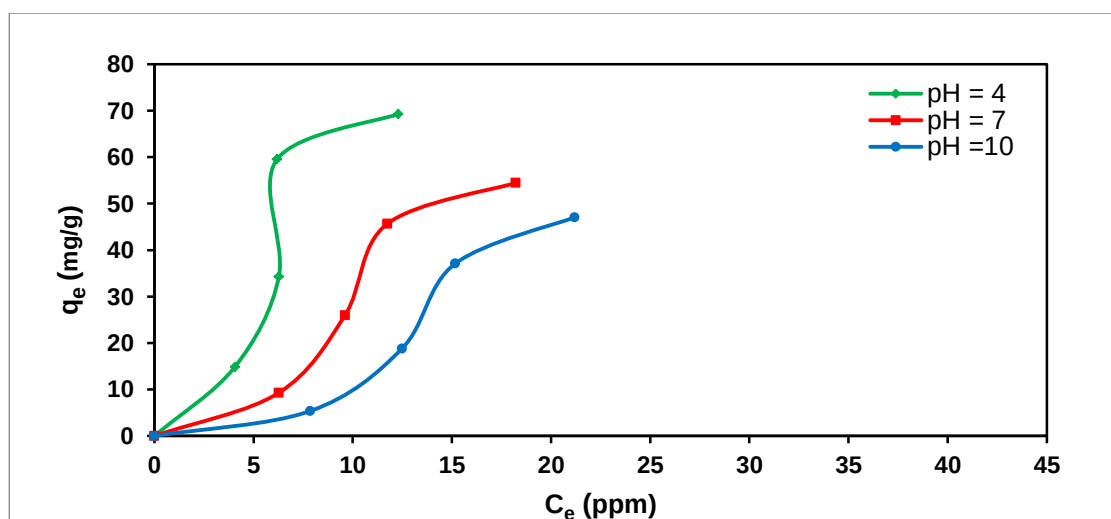


Figure (3.19): Effect of pH on the adsorption of DR into ACS₂

3.2.4 The Influence of Temperature

The effect of temperature on the adsorption of (AR, CV, and DR) dyes on ACS₁& ACS₂ was investigated at three different temperatures (25, 35, and 45)°C while keeping the contact time (20 minutes), pH, and adsorbent weight (0.01g) constant. The quantity of AR, CV and DR adsorbed dyes (q_e) was estimated using the equation:

$$q_e = \frac{(c_o - c_e)v}{m} \dots\dots\dots (3.3)$$

From Tables (3-10, 3-11, and 3-12) note the impact of temperature on the adsorption, was decreased in the adsorbed amount of AR, CV, and DR dyes with increasing the temperature. This reveals that the interactions between the adsorbent (ACS₁ & ACS₂) and the adsorbate (AR, CV, and DR) is exothermic process in nature. Figure (3.20, 3.21, and 3.22) show the decrease in the (q_e) of the three dyes with increasing temperature. This is because 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 [128]

Table (3-10):The effect of temperature on (q_e) AR dye for ACS₁ and ACS₂ surface.

	C_0	25 °C			35 °C			45 °C		
		C_e mg/g	q_e mg/L	R%	C_e mg/g	q_e mg/L	R%	C_e mg/g	q_e mg/L	R%
ACS ₁	10	5.8	10.4	41.9	6.7	8.1	32.2	8.2	4.3	41.9
	20	14.1	14.7	29.4	15.8	10.4	20.9	17.6	5.8	29.4
	30	17.8	30.4	40.6	21.1	22.3	29.7	23.7	15.6	40.6
	40	25.1	37.1	37.1	28.5	28.6	28.6	31.8	20.4	37.1
	C_0	25°C			35°C			45°C		
		C_e mg/g	q_e mg/L	R%	C_e mg/g	q_e mg/L	R%	C_e mg/g	q_e mg/L	R%
ACS ₂	10	5.1	12.3	49.3	6.0	9.9	39.7	7.5	6.2	24.8
	20	13.3	16.5	33.1	14.9	12.5	25.0	16.9	7.6	15.4
	30	16.3	34.1	45.5	19.6	25.8	34.4	22.2	19.3	25.8
	40	23.6	40.8	40.8	27.7	30.6	30.6	30.4	24.1	24.1

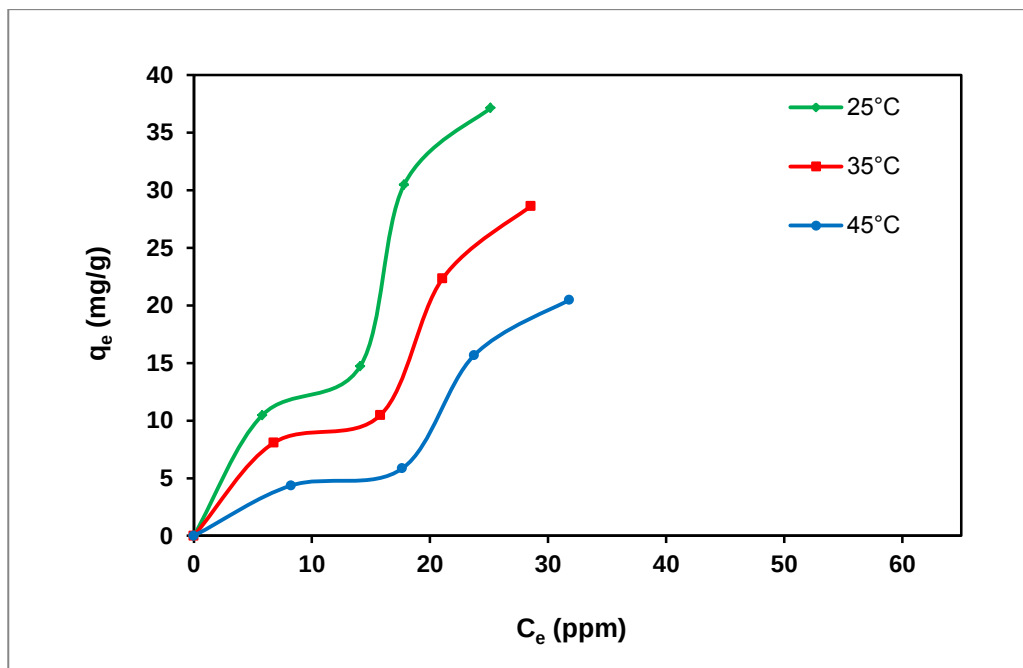


Figure (3.20): Effect of temperature on the adsorption capacity of AR dye for ACS₁.

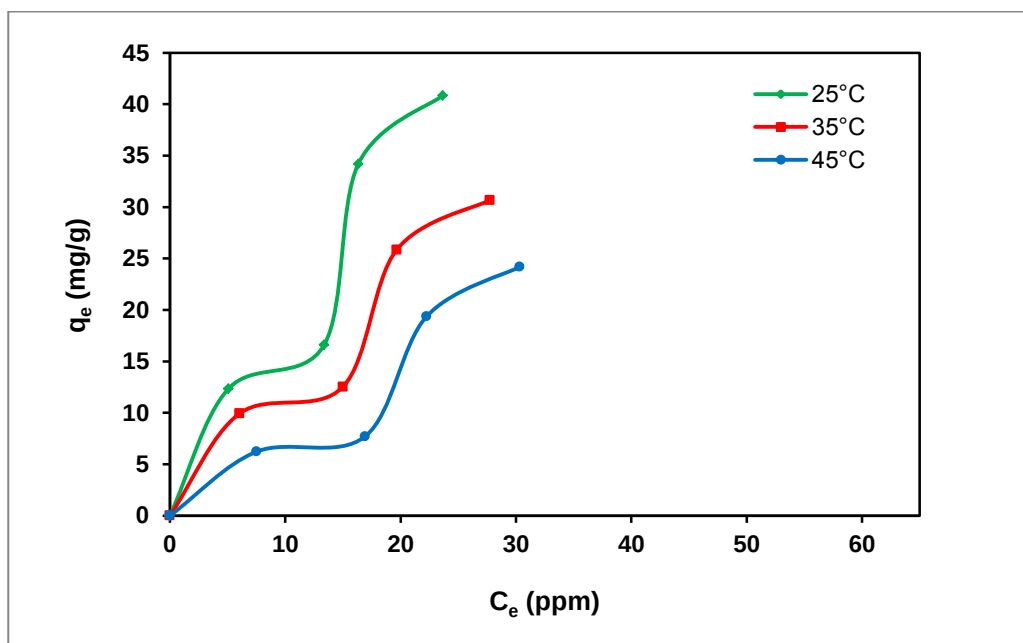


Figure (3.21):Effect of temperature on the adsorption capacity of AR dye for ACS₂.

Table (3-11): The effect of temperature on (q_e) CV dye for ACS₁ and ACS₂ Surface.

	C_0	25 °C			35 °C			45 °C		
		C_e mg/g	q_e mg/L	R%	C_e mg/g	q_e mg/L	R%	C_e mg/g	q_e mg/L	R%
ACS ₁	10	1.7	20.6	82.6	2.6	18.4	73.6	5.1	12.0	48.0
	20	6.8	32.8	65.7	10.3	24.1	48.3	11.8	20.3	40.6
	30	7.9	55.1	73.3	10.9	47.7	63.6	15.8	35.3	47.0
	40	16.6	58.2	58.2	18.5	53.6	53.6	22.4	43.7	43.7
ACS ₂	C_0	25°C			35°C			45°C		
		C_e mg/g	q_e mg/L	R%	C_e mg/g	q_e mg/L	R%	C_e mg/g	q_e mg/L	R%
	10	1.5	21.3	84.9	2.4	18.9	75.9	4.9	12.7	50.8
	20	6.6	33.2	66.5	10.0	24.8	49.9	13.8	15.3	30.7
	30	7.8	55.7	74.3	10.6	48.3	64.4	15.7	35.5	47.3
	40	16.4	58.6	58.	18.3	54.1	54.1	22.1	44.6	44.6

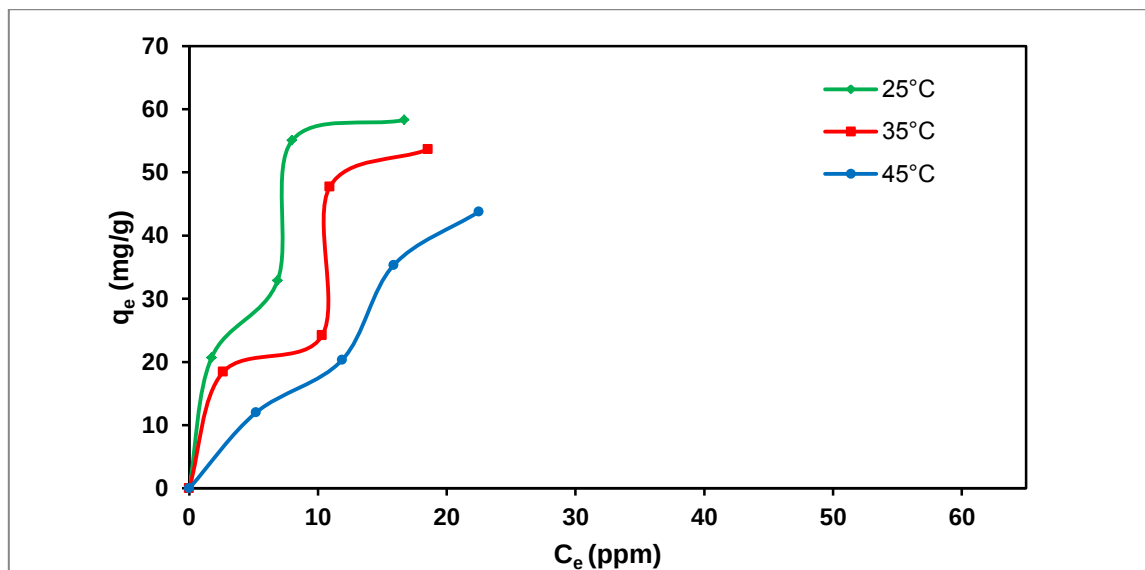
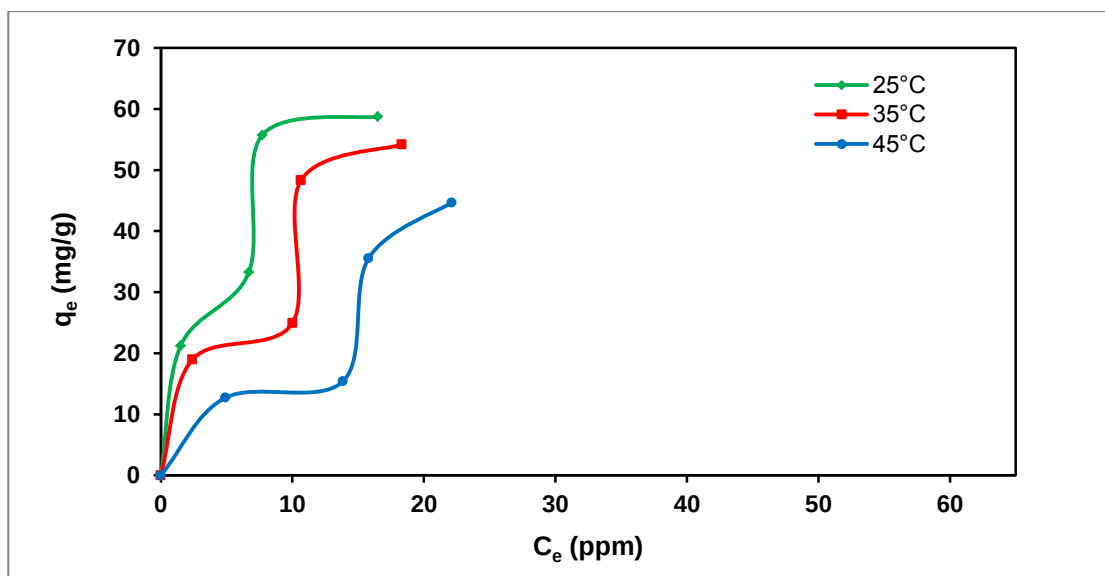


Figure (3.22): Effect of temperature on the adsorption capacity of CV dye for ACS₁.



Figure(3.23): Effect of temperature on the adsorption capacity of CV dye for ACS₂.

Table (3-12): The effect of temperature on (q_e) DR dye for ACS₁ and ACS₂ Surface.

	C_0	25 °C			35 °C			45 °C		
		C_e	q_e	R%	C_e	q_e	R%	C_e	q_e	R%
		mg/g	mg/L		mg/g	mg/L		mg/g	mg/L	
ACS ₁	10	5.1	12.0	41.8	7.6	5.8	23.3	8.5	3.5	41.8
	20	16.2	9.3	18.6	17.3	6.5	13.0	18.9	2.9	18.6
	30	22.7	18.1	24.1	25.2	11.8	18.8	26.8	7.8	24.1
	40	31.8	20.1	20.1	34.5	14.8	14.8	37.2	6.9	20.1
ACS ₂	C_0	25°C			35°C			45°C		
		C_e	q_e	R%	C_e	q_e	R%	C_e	q_e	R%
		mg/g	mg/L		mg/g	mg/L		mg/g	mg/L	
	10	4.7	13.2	52.9	6.8	7.9	31.6	8.3	4.2	16.8
	20	15.3	11.6	23.2	16.4	8.8	17.6	18.2	4.4	8.8
	30	19.8	25.0	33.3	24.4	13.9	18.5	26.4	8.9	11.7
	40	31.0	22.2	22.2	34.2	14.3	14.3	36.1	9.7	9.7

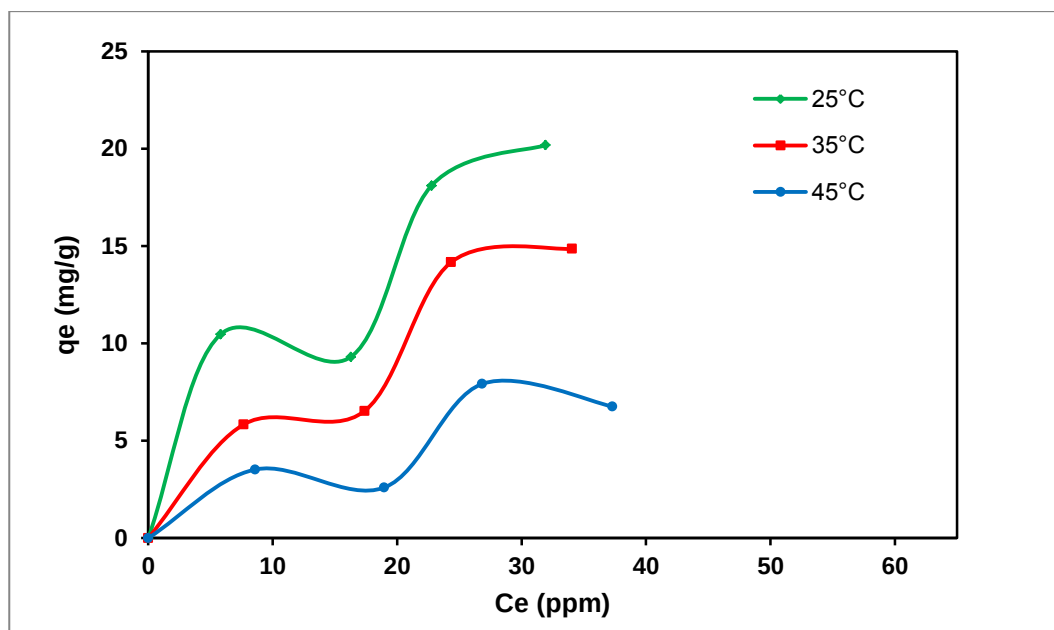


Figure (3.24): Effect of temperature on the adsorption capacity of DR dye for ACS₁.

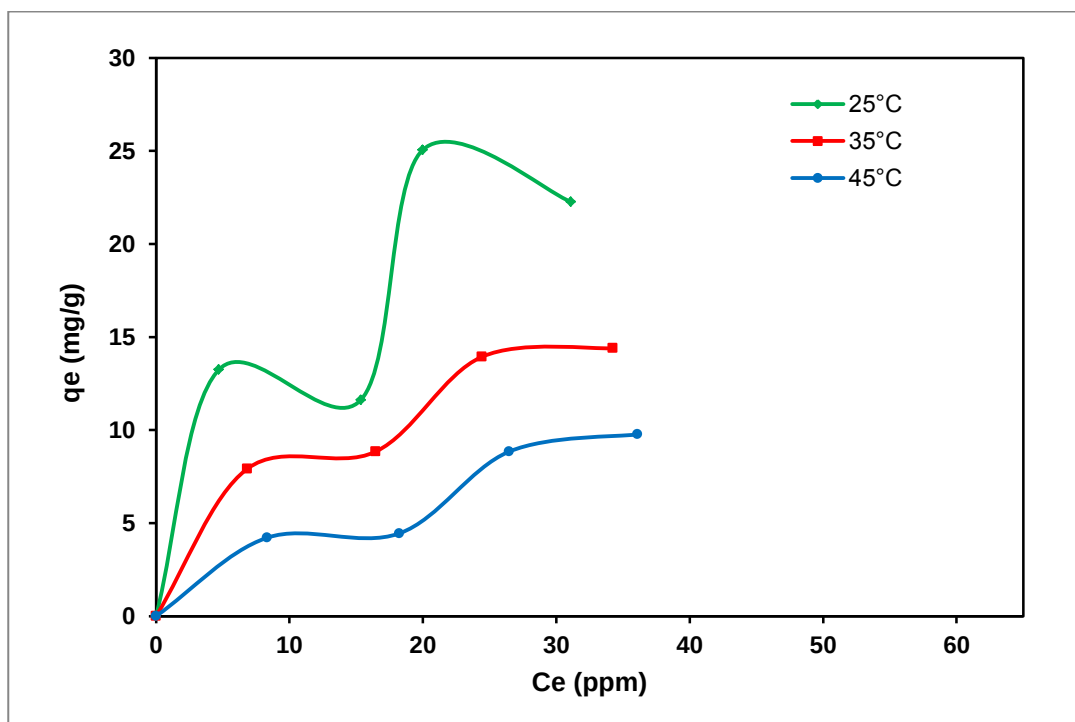


Figure (3.25) :Effect of temperature on the adsorption capacity of DR dye for ACS₂.

3.2.5 Adsorption Isotherm

The adsorption isotherm is studied because it gives important information in describing the adsorption process conditions and the adsorption capacity of the adsorbent when the adsorption process reaches the equilibrium state where the adsorption isotherm suggests how the adsorption particles distribute between liquid phase and solid phase. The isotherm data are analyzed 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 [129]. The adsorption is carried out at concentrations (10,20,30,40 and 50 ppm) and at (25)°C for (20 min). This study employed two isotherm models: the Langmuir and Freundlich isotherm models. The general form of adsorption for (AR,CV and DR) dyes on the surface (ACS₁ & ACS₂) gives the general form of adsorption isotherms as shown in Figure(3.26 & 3.27) all the Figures were S-type as stated by the Giles classification of adsorption isotherms [130]. Also, these isotherms indicate to overlap between the adsorbate and the adsorbent which occurs through types of forces depending on the nature of adsorbate and the adsorbent. 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[131] . The S-type isotherm indicates that the adsorbent tends to stack vertically in regular arranging on the surface [132].

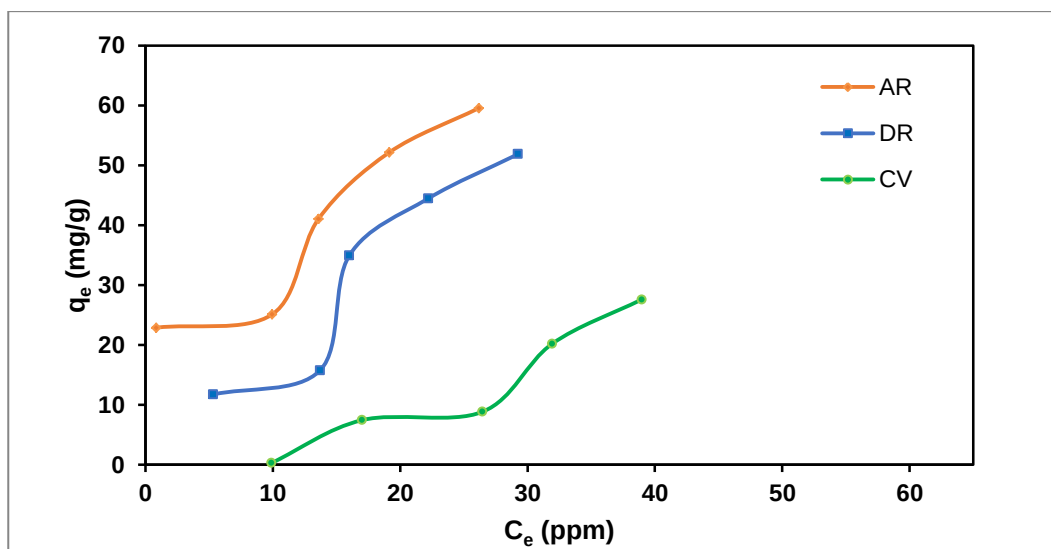


Figure (3.26): Adsorption isotherms of three dyes on ACS₁

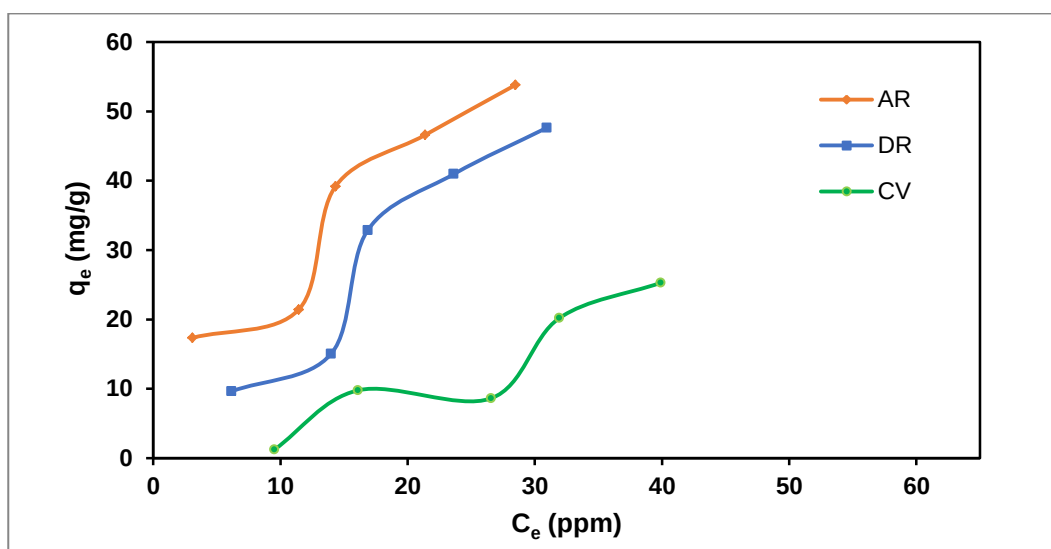


Figure (3.27): Adsorption isotherms of three dyes on ACS₂

The data gained are used to study the adsorption nature of the three dyes (AR, CV, DR) on the surfaces (ACS₁ & ACS₂) and are analyzed as stated by isotherm Langmuir equation (1-5). Values C_e/q_e and C_e are listed in the Tables (3-13), (3-14), and figure (3.28 & 3.29) show the linear plots of Langmuir equation of the adsorption for the three dyes on the surfaces ACS₁ & ACS₂. The values of Langmuir constant (b), coefficient of

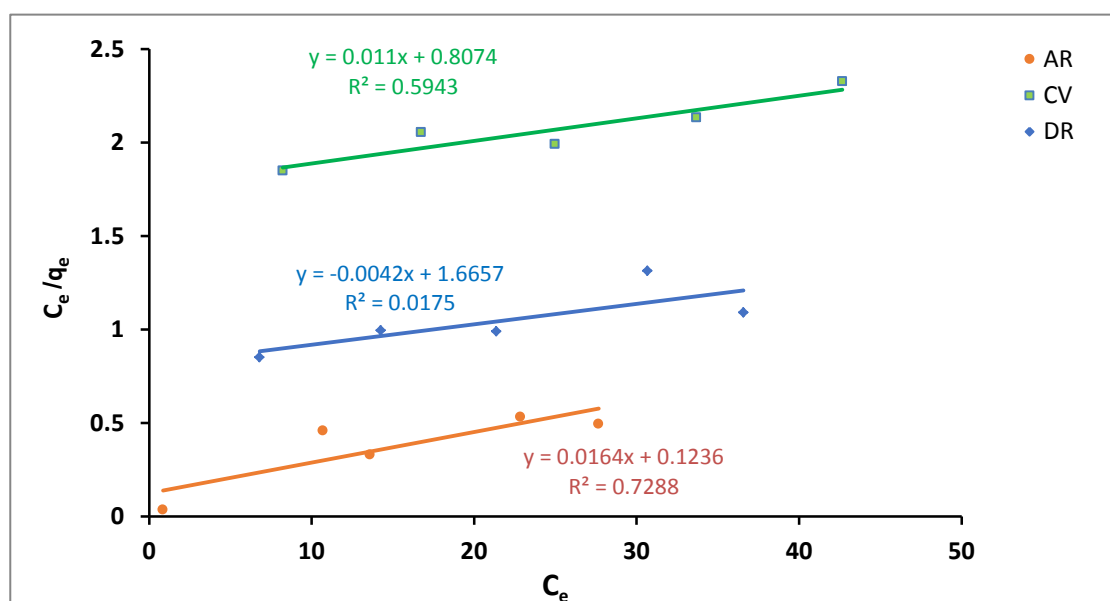
correlation (R^2) and maximum adsorption capacity (q_m) have been studied as shown in Tables (3-13) & (3-14). Additionally, The data obtained in the Tables (3-15) & (3-16) are analyzed according to the isotherm Freundlich equation (1-5), and Figures (3.30 & 3.31) show the linear plots of the Freundlich equation for surfaces ACS₁ & ACS₂ 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 either (n) to define the adsorbent surface is homogeneous or heterogeneous. Moreover, if n is greater than one so the surface is homogeneous and if n is smaller than one then the surface is heterogeneous [133]. Therefore, n values indicate that the surfaces (ACS₁, ACS₂) are heterogeneous as presented in Tables (3-15) & (3-16).

Table (3-13): Values of parameters of Langmuir equation for ACS₁

	C_e mg/l	q_e mg/g	C_e/q_e	q_{max} (mg/g)	b_e (L.mg ⁻¹)	R^2
AR	0.8	22.8	0.03	60.97	0.132	0.728
	10.6	23.2	0.4			
	13.5	41.0	0.3			
	22.8	42.8	0.5			
	27.6	55.6	0.4			
CV	8.2	4.4	1.8	90.91	0.0136	0.594
	16.7	8.1	2.0			
	24.9	21.5	3.3			
	33.6	15.7	2.1			
	42.6	18.3	2.3			
DR	6.8	7.9	0.8	238.09	0.0025	0.0175
	14.2	14.3	0.9			
	21.3	21.5	0.9			
	30.6	23.3	1.3			
	36.5	33.5	1.09			

Table (3-14):Values of parameters of Langmuir equation for ACS₂

	C_e mg/L	q_e mg/g	C_e/q_e	q_{max} (mg/g)	b_e (L.mg ⁻¹)	R^2
AR	3.1	17.3	0.17	87.71	0.048	0.551
	11.4	21.4	0.53			
	14.3	39.1	0.36			
	21.4	46.5	0.45			
	28.4	53.8	0.52			
CV	8.5	3.5	2.4	6.24	0.022	0.508
	17.4	6.2	2.7			
	25.6	10.9	2.3			
	34.6	13.4	2.5			
	43.5	16.0	2.8			
DR	6.9	7.5	0.9	83.33	0.013	0.400
	15.1	12.2	1.2			
	21.6	20.8	1.3			
	28.1	29.6	1.4			
	39.3	26.5	1.5			



Figure(3.28):The linear of Langmuir equation of three dyes for ACS₁.

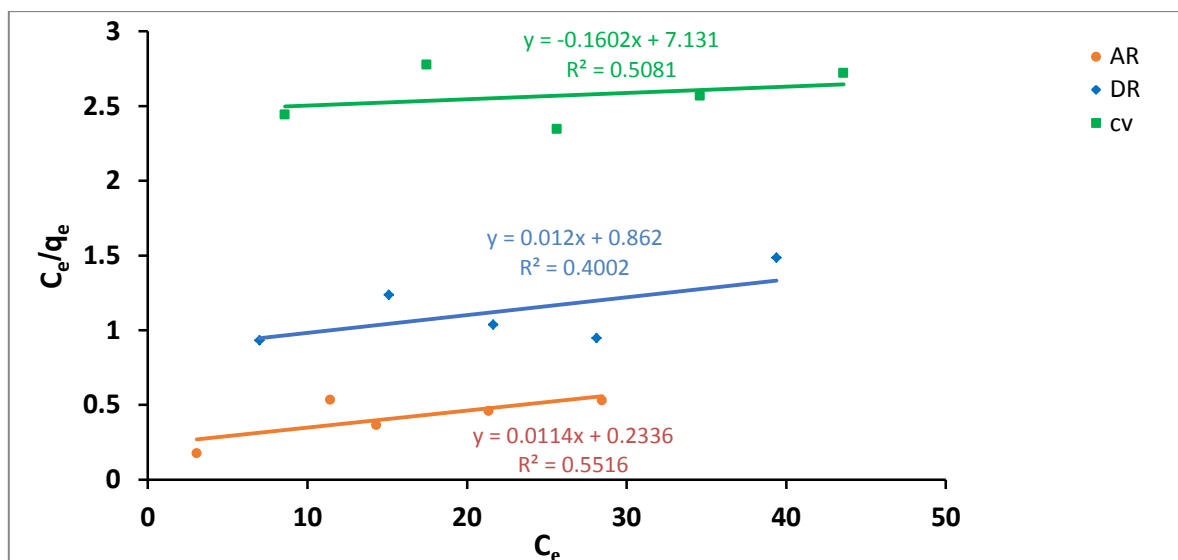


Figure (3.29): The linear of Langmuir equation of three dyes for ACS₂

Table(3-15): Values of parameters of Freundlich equation for ACS₁

	Log C_e	Log q_e	C_e/q_e	n	K_f (mg/g)	R^2
AR	-0.07	1.35	0.03	0.44	23.76	0.971
	1.02	1.36	0.45			
	1.13	1.61	0.33			
	1.35	1.63	0.53			
	1.44	1.74	0.49			
CV	0.91	0.64	1.85	0.35	0.69	0.995
	1.22	0.91	2.05			
	1.39	1.09	1.99			
	1.52	1.19	2.13			
	1.63	1.26	2.32			
DR	0.83	0.90	0.85	0.24	1.71	0.973
	1.15	1.15	0.99			
	1.32	1.33	0.98			
	1.48	1.36	1.31			
	1.56	1.52	1.09			

Table (3-16):Values of parameters of Freundlich equation for ACS₂

	Log C _e	Log q _e	Ce/qe	n	K _f (mg/g)	R ²
AR	0.48	1.23	0.17	0.40	8.64	0.823
	1.05	1.33	0.53			
	1.15	1.59	0.36			
	1.32	1.66	0.45			
	1.45	1.73	0.52			
CV	0.93	0.64	2.44	0.31	2.30	0.988
	1.24	0.79	2.77			
	1.40	1.03	2.34			
	1.53	1.12	2.56			
	1.63	1.20	2.72			
DR	0.84	0.87	0.93	0.19	1.46	0.918
	1.17	1.08	1.23			
	1.33	1.31	1.03			
	1.44	1.47	0.94			
	1.59	1.42	1.48			

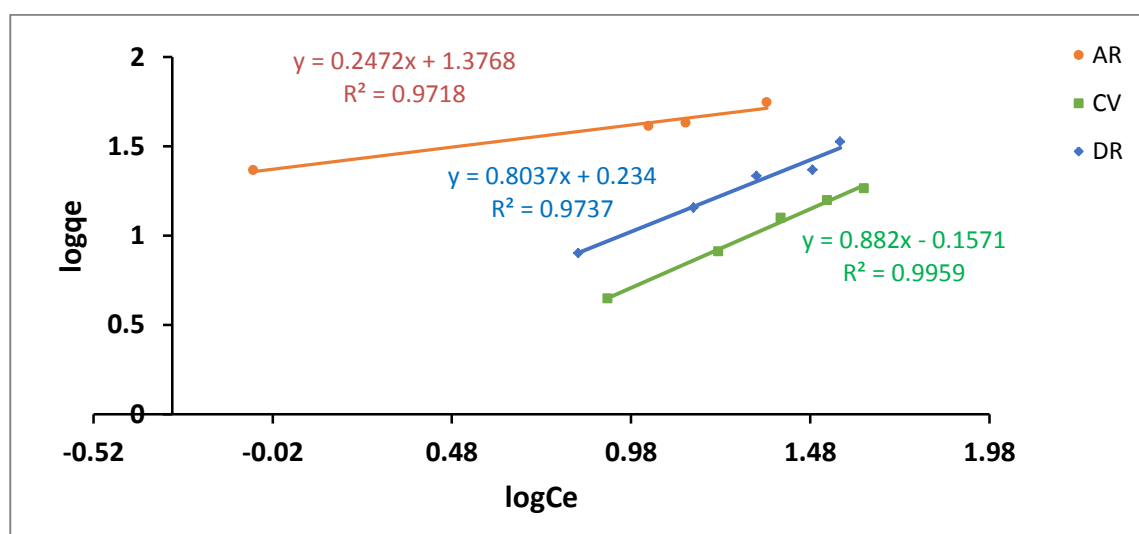


Figure (3.30):The linear of Freundlich equation of three dyes for ACS₁

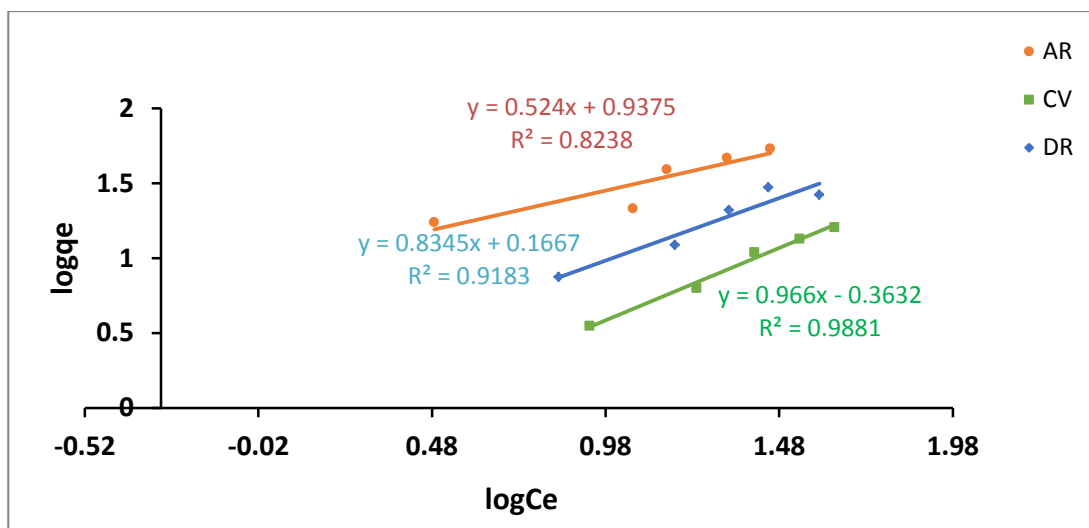


Figure (3.31):The linear of Freundlich equation of three dyes for ACS₂

When compared the coefficient of correlation (R^2) values from Freundlich isotherm with Langmuir's R^2 , the Freundlich's R^2 greater than Langmuir's R^2 . Therefore, the Freundlich equation is more suitable for the adsorption processes for three dyes in aqueous solutions onto the surfaces. Therefore, the adsorption is more than one layer (multilayer) [92].

3.3 Thermodynamic of Adsorption Process

Thermodynamics studies were applied to the adsorption of AR, CV and DR dyes by the ACS₁& ACS₂ surface for estimating the nature of the adsorption reaction. Thermodynamics parameters at 298 to 318 K of the adsorption involve entropy (ΔS°), Gibbs free energy (ΔG°) and change in standard enthalpy (ΔH°). Gibbs free energy change can be calculated from the following equation [21]:

$$\Delta G^\circ = -RT \ln K \quad \dots\dots (3.4)$$

ΔG° 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

$$K = (q_e m) / (C_e v) \dots\dots\dots (3.5)$$

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

$$\ln k = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots\dots\dots (3.6)$$

The values of ($\Delta S/R$) and ($-\Delta H/R$) have been calculated from the intercept and slope of the linear plots [118]. The data obtained from the intercept and slope are listed in the Tables (3.17), (3.18) and are plotted in the Figures (3.31 & 3.32).

Table (3-17): Values of the equilibrium constant (K) and thermodynamic parameters of adsorption the three dyes onto ACS₁

The dyes	T (C°)	T (K)	1/T (K ⁻¹)	K	Lnk	-ΔG° (J.mol ⁻¹)	-ΔH° (J.mol ⁻¹)	-ΔS° (J.mol ⁻¹ .K ⁻¹)
AR	25	298	0.0033	3.42	1.23	3151.34	37525.2	115.656
	35	308	0.0032	2.12	0.75	1924.47		
	45	318	0.0031	1.32	0.27	711.371		
CV	25	298	0.0033	13.78	2.62	6717.88	44427.5	126.93
	35	308	0.0032	8.72	2.16	5551.96		
	45	318	0.0031	4.43	1.49	3822.82		
DR	25	298	0.0033	1.59	0.46	1188.66	16922.3	53.1722
	35	308	0.0032	1.16	0.15	389.72		
	45	318	0.0031	1.03	0.03	93.6948		

Table (3-18): Values of the equilibrium constant (K) and thermodynamic parameters of adsorption the three dyes onto ACS₂

The dyes	T (C°)	T (K)	1/T (K ⁻¹)	K	Lnk	-ΔG° (J.mol ⁻¹)	-ΔH° (J.mol ⁻¹)	-ΔS° (J.mol ⁻¹ .K ⁻¹)
AR	25	298	0.0033	0.82	0.196	503.1435	42375.6	140.29
	35	308	0.0032	1.29	0.258	661.819		
	45	318	0.0031	2.41	0.881	2257.03		
CV	25	298	0.0033	0.61	0.479	1228.514	47155.3	154.374
	35	308	0.0032	0.18	0.184	473.165		
	45	318	0.0031	0.71	0.716	1834.16		
DR	25	298	0.0033	0.47	0.735	1882.505	33997.6	108.789
	35	308	0.0032	1.01	0.011	30.5482		
	45	318	0.0031	1.12	0.121	310.545		

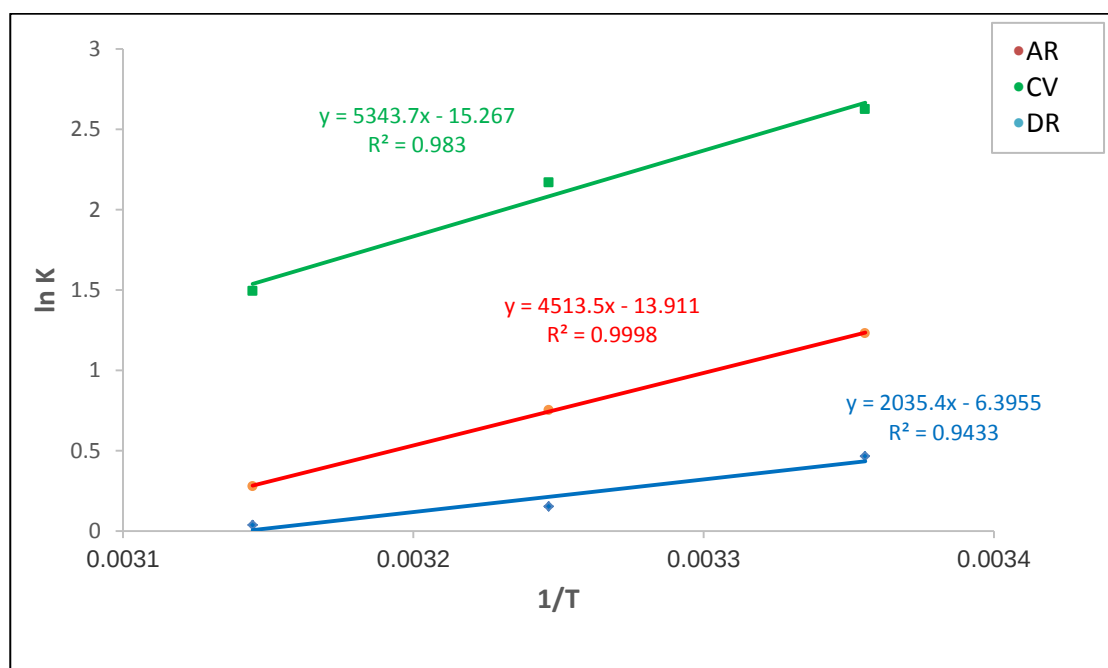


Figure (3.32): Values of $\ln K$ versus $1/T$ of adsorption for the three dyes onto ACS₁

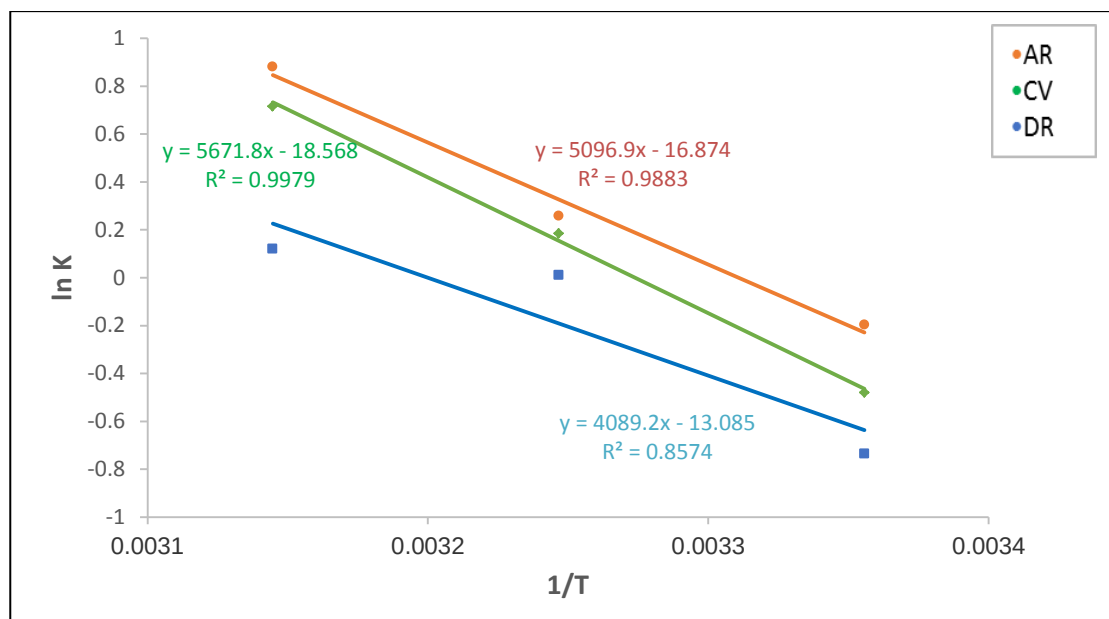


Figure (3.33): Values of $\ln K$ versus $1/T$ of adsorption for the three dyes onto ACS₂

The results obtained in the Tables (3-17)& (3-18) show that:-

1. The negative values of enthalpy (ΔH°), which indicate the adsorption of dyes (AR, CV and DR) onto ACS₁ & ACS₂ were an exothermic process. Furthermore, the values indicate that the process was adsorption only and the energy stability of CV, CR and DR onto ACS₁ & ACS₂. The thermodynamic values of ΔH° suggest that the adsorption of CV, CR and DR onto ACS₁& ACS₂ were solely physisorptions. When the temperature increases, it leads to an increase in the kinetic energy of the adsorbed molecules which leads to the possibility of separation from the surface of the adsorbent and return to the inside of the solution that leads to a decrease in the residual forces with increasing temperature onto the surface activated. Therefore, the adsorption of the three dyes onto the surfaces activated decreases with increasing temperature as presented in Tables (3-17) & (3-18).
2. The negative values of ΔG° indicated that the adsorption of dyes onto ACS₁& ACS₂ was a spontaneous process.

3. The negative values of ΔS° that point to decreased randomness and disorder at the solid-solution interface of CV, AR and DR with ACS₁, ACS₂. Therefore, the adsorbed particles are more organized onto the adsorbent more than inside the liquid phase.

3.4 Adsorption Kinetics

Kinetic modeling is important for the study to understand the mechanism of adsorption and to estimate the rate of sorption, by applying two kinetic models involving 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 PFO equation is based on the amounts of AR, CV and DR dyes removed at time (t), (q_t) and a weight capacity of the adsorbent at equilibrium (q_e). The PFO kinetic equation can be expressed as follow:[135]

$$\text{PFO: } \ln(q_e - q_t) = \ln q_e - K_1 * t \dots\dots\dots (3.7)$$

Where (q_e) and (q_t) are the amounts of the three dyes adsorbed per gram of surface (mg/g of ACS) 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:

$$q_t = \frac{V(C_0 - C_e)}{m} \dots\dots\dots (3.8)$$

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 Figures(3.33) and (3.34)

3.4.2 Pseudo-Second Order Kinetic Model

The PSO equation 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 :[136]

$$\text{PSO: } \frac{t}{qt} = \frac{1}{k_2 * q_e^2} + \frac{1}{q_e} * t \quad \dots\dots\dots (3.9)$$

The values of k_2 (rate constant of PSO) and q_e have been calculated by plotting t/qt against time (min) and determined R^2 from the linear plots which should match with the experimental values as Figure (3.21). The results obtained from 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) show that the calculated adsorption capacity $q_e(\text{cal})$ is 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 AR, CV and DR dyes onto AS surface follows PSO kinetics. These results are identical with some studies [137].

Table (3-19). Values of kinetic parameters for the three dyes onto ACS1 obtained from PFO equation

The dyes	Time (min)	q_t (mg/g)	$q_e(\text{exp})$ (mg/g)	$\text{Ln}(q_e - q_t)$	q_e (cal) (mg/g)	K_1	R^2
AR	5	171.2	182.7	2.44	12.85	0.065	0.3199
	10	181.8		0.07			
	15	182.2		0.58			
	20	182.7		0			
	25	184.4		-1.66			

CV	5	205.0	226.5	3.07	13.12	0.015	0.068
	10	223.8		0.98			
	15	223.0		1.23			
	20	226.5		0			
	25	228.8		-2.25			
DR	5	94.2	127.0	3.49	17.74	0.030	0.182
	10	121.7		1.67			
	15	122.2		1.58			
	20	127.0		0			
	25	128.1		-0.92			

Table (3-20) .Values of kinetic parameters for the three dyes onto ACS₂ obtained from PFO equation

The dyes	Time (min)	q _t (mg/g)	q _e (exp) (mg/g)	Ln(q _e -q _t)	q _e (cal) (mg/g)	K ₁	R ²
AR	5	172.0	180.0	2.07	79.43	0.097	0.644
	10	177.9		0.71			
	15	179.2		0.30			
	20	180.0		0			
	25	182.1		-2.03			
CV	5	172.0	180.0		19.40	0.051	0.401
	10	177.9		0.98			
	15	179.2		1.23			
	20	180.0		0			
	25	182.1		-2.25			
DR	5	94.2	127.0	3.49	30.74	0.16	0.917
	10	121.7		1.67			
	15	122.2		1.58			
	20	127.0		0			
	25	128.1		-0.92			

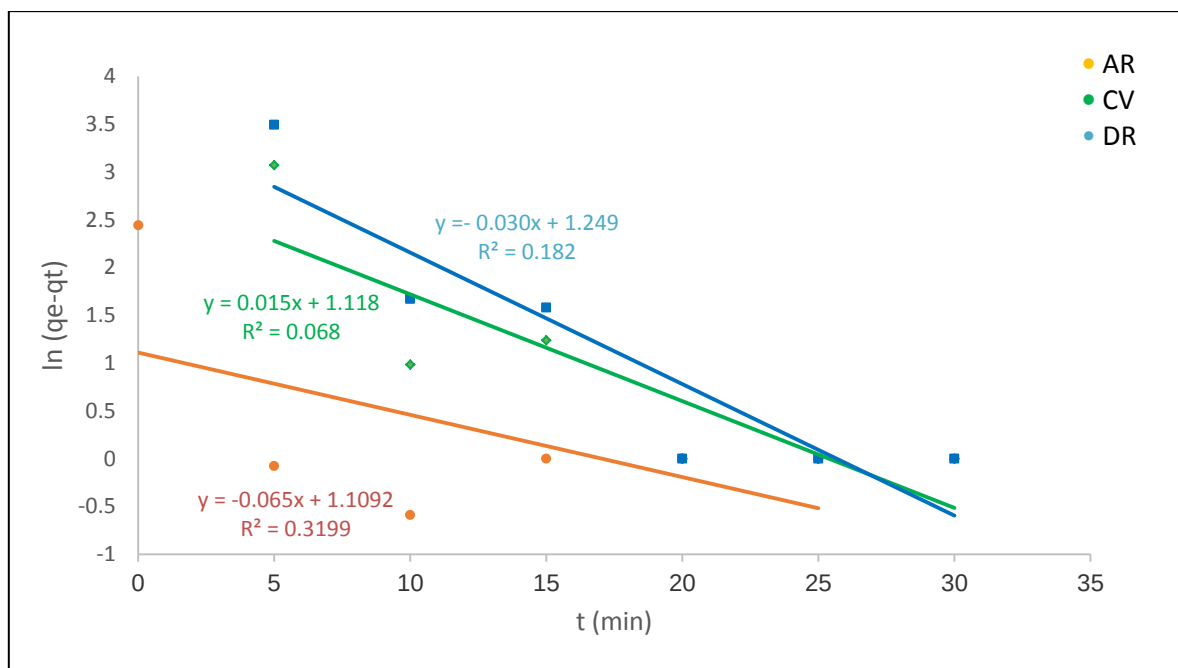


Figure (3.34): The PFO kinetics of the three dyes onto ACS₁

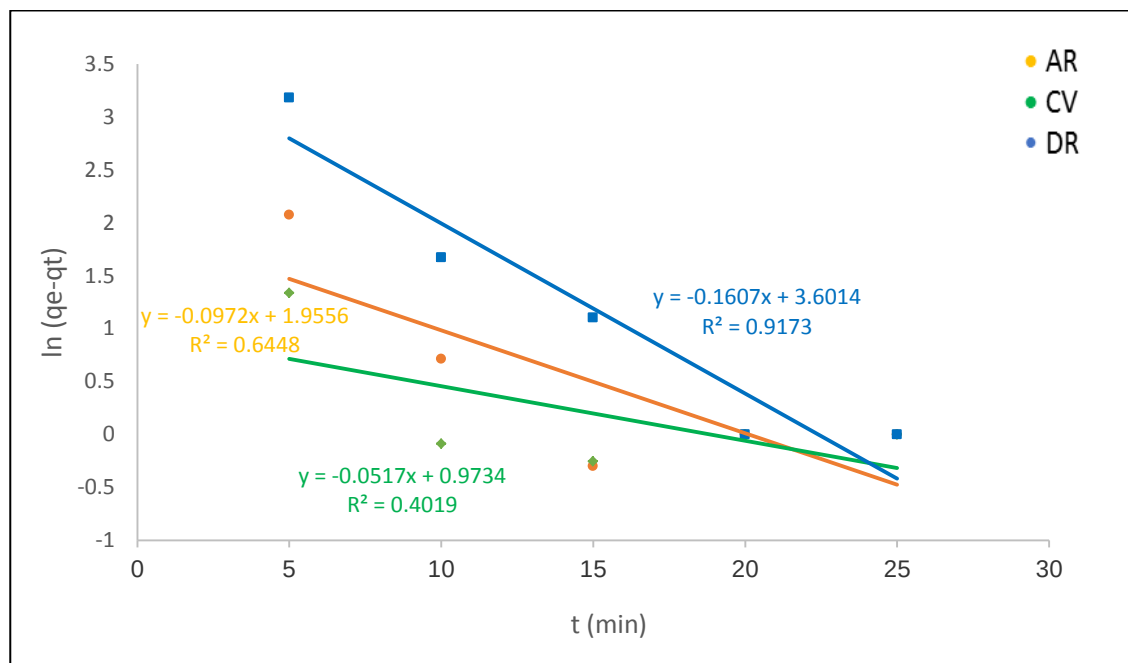


Figure (3.35): The PFO kinetics of the three dyes onto ACS₂

Table (3-21): Values of kinetic parameters for the three dyes onto ACS₁ obtained from PSO equation

The dyes	Time (min)	q _t (mg/g)	q _e (exp) (mg/g)	t/q _t	q _e (cal) (mg/g)	K ₂ (1/min)	R ²
AR	5	171.2	182.7	0.029	200.0	0.0039	0.998
	10	181.8		0.054			
	15	182.2		0.082			
	20	182.7		0.109			
	25	184.4		0.135			
CV	5	205.0	226.5	0.03	232.5	0.0073	0.999
	10	223.8		0.04			
	15	223.0		0.06			
	20	226.5		0.08			
	25	228.8		0.10			
DR	5	94.2	127.0	0.05	149.2	0.0022	0.997
	10	121.7		0.08			
	15	122.2		0.12			
	20	127.0		0.15			
	25	128.1		0.10			

Table (3-22): Values of kinetic parameters for the three dyes onto ACS₂ obtained from PSO equation

The dyes	Time (min)	qt (mg/g)	qe(exp) (mg/g)	t/qt	qe (cal) (mg/g)	K ₂ (1/min)	R ²
AR	5	172.0	180.0	0.029	196.07	0.004	0.996
	10	177.9		0.056			
	15	179.2		0.083			
	20	180.0		0.111			
	25	182.1		0.137			
CV	5	172.0	180.0	0.022	232.55	0.009	0.999
	10	177.9		0.044			
	15	179.2		0.067			

	20	180.0		0.089			
	25	182.1		0.111			
DR	5	94.2	127.0	0.041	163.93	0.002	0.998
	10	121.7		0.071			
	15	122.2		0.105			
	20	127.0		0.138			
	25	128.1		0.168			

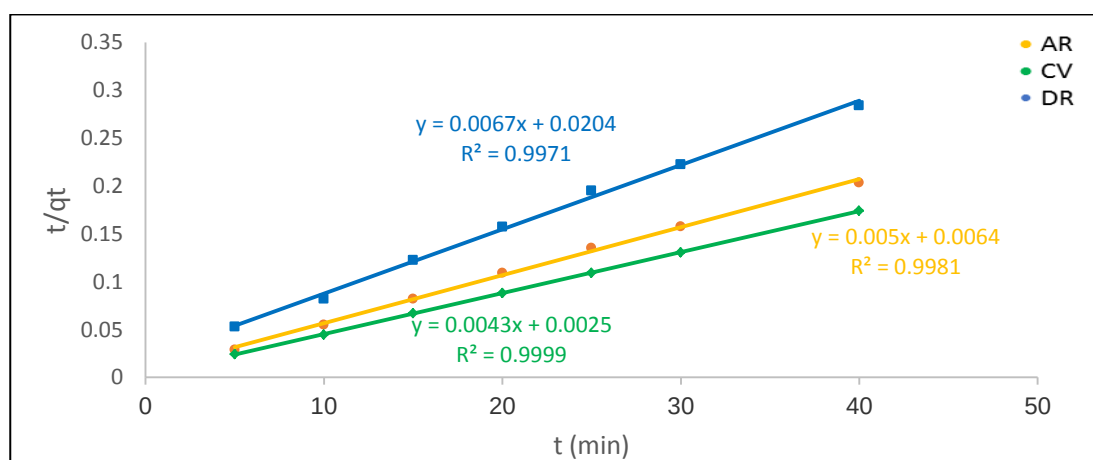


Figure (3.36) :The PSO kinetics of the three dyes onto ACS₁

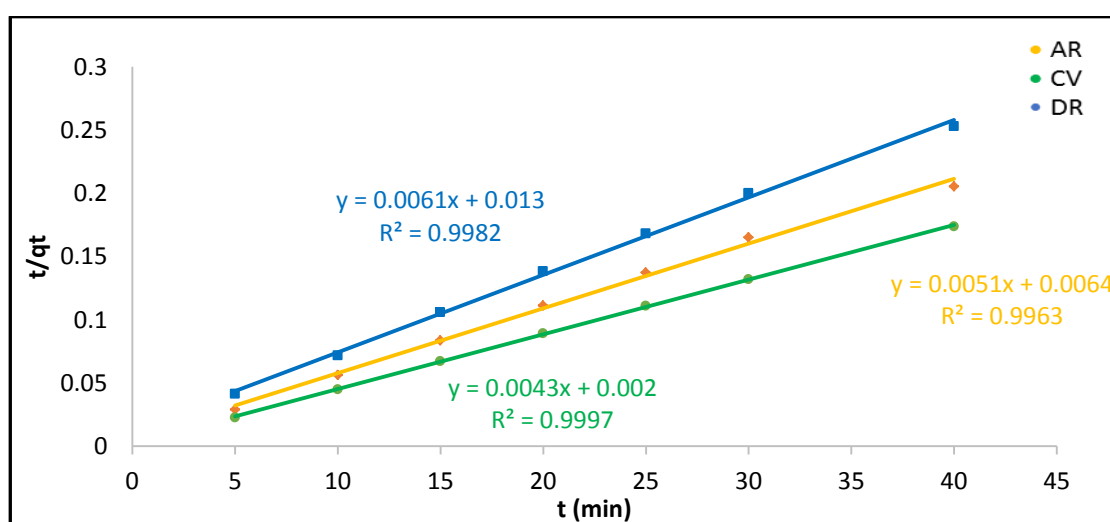


Figure (3.37):The PSO kinetics of the three dyes onto ACS₂

3.5 Conclusions

This chapter presents the main conclusions that can be obtained from the foregoing results as in follows paragraphs: -

- 1- The possibility of using locally available materials, such as the soot and chitosan to produce a good adsorbent activated surface under modification by chemical activation with nitric acid at a low cost and with high efficiency.
- 2 - The ratio of the components of the nanocomposite (soot - chitosan) plays an important role in the nature of the surface properties of the nanocomposites. The ratio of 2:1 between soot and chitosan particles is the best ratio compared to the rest of the ratios, because with this ratio some distinct properties have been obtained from granular size, surface area and the size of the pores.
- 3- The optimum pH for the adsorption were 4 for AR and 10 for CV and DR dyes onto surface ACS₁ and activated surface ACS₂.
- 4- Through the results obtained, it was found that the percentage of removal of the three dyes increases with the increase in the weight of the adsorbents for the surface (soot - chitosan) and the activated surface (soot - chitosan).
- 5- The adsorption data showed that activation of the surface has an effect on the percentage of removal for three dyes and they are as follows ACS₂ > ACS₁.
- 6- Thermodynamically, the adsorption of the three dyes AR, CV and DR on the surface of the composite (soot-chitosan) and the activated surface (soot-chitosan) was spontaneous and exothermic (physical adsorption), which was obtained from the values of ΔG and ΔH .

7- The adsorption kinetics of the three dyes on the surface(ACS_1) and the activated surface (ACS_2) fit well with a pseudo-second-order equation.

8- The adsorption isotherms of the three dyes (AR, CV, DR) on the surface (ACS_1) and activated surface (ACS_2) are of the (S-type) according to the Giles classification, and the adsorption was consistent with Freundlich's model.

9- The dyes that were removed by ACS_1 and ACS_2 indicating these surfaces can be used in the construction of plants for the treatment of wastewater

3.6 Recommendations

1- Study of adsorption of nanocomposite (soot - chitosan) to remove toxic metals from wastewater and using nanocomposite (soot - chitosan) to remove various chemical pollutants.

2- Synthesis of nanocomposites from chitosan molecules or other types of polymers with soot and natural materials such as cellulose and other type.

3-Several modification methods could be used to produce the activated compound prepared from paraffin candle and chitosan (extracted from oyster shells) and improve the adsorption capacity.

4-Another test to showA the performance of activated soot by removing other dyes such as rhodamine, dispersed blue, direct red dyes and other water pollutants.

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الخلاصة

تهتم هذه الرسالة بتحضير سطح مترابك نانوي (س خام - كايوسان) ACS_1 وتشخيص المركب المحضر باستخدام تقنيات مختلفة. تم تحضير السطح ACS_1 بعدة خطوات . تم استخلاص الس خام من شمع البرافين عن طريق جمعه في ورق نظيف وجاف ، وإضافة بوليمر الكايوسان إليه بنسبة 2:1 ، ثم معالجته بحامض الخليك 1% والتجفيف عند $60^{\circ}C$. بعد ذلك معالجة ACS_1 بحامض النيتريك بنسبة 10% للحصول على سطح منشط ACS_2 (س خام- كايوسان). ثم تم تشخيص ودراسة الخصائص التركيبية والكيميائية والسطحية للجسيمات النانوية للأسطح (ACS_1 & ACS_2) باستخدام تقنيات (XRD, SEM, BET, FT-IR) و دراسة كفاءة وفعالية الامتزاز للمركبات النانوية المحضرة ACS_1 و ACS_2 من خلال امتزاز الأصباغ الثلاثة (Disperse red ,Crystal violet ,Alizarin red) من محاليلها المائية بعدة طرق ، ثم دراسة العوامل المؤثرة على الامتزاز ، مثل زمن الاتزان، وزن المادة المازة للأصباغ، الدالة الحامضية الناتجة عن عملية الامتزاز و درجة الحرارة. لقد أشارت النتائج إلى أن عملية الامتزاز كانت من النوع S وفقاً لتصنيف جيلز Giles وأن زمن الاتزان كان (20min) للأصباغ الثلاثة AR و CV و DR على السطحين ACS_1 و ACS_2 . كما أظهرت التحليلات أن قياسات امتزاز الأصباغ الثلاثة تقل مع زيادة درجة الحرارة عند الاتزان ، مما يعني أن الامتزاز باعث للحرارة. تم استخدام النتائج التي تم الحصول عليها في دراسة المعادلات الرياضية لايزوثيرمات لانكمير وفريندلش للحصول على بيانات عملية للامتزاز ، وأظهرت النتائج أن (نموذج فريندلش) هو الأنسب للبيانات التجريبية ، حيث يعطي علاقة خطية بمعاملات ارتباط (R^2) أكبر من معاملات ارتباط لانكمير. أظهر التحليل الديناميكي الحراري أن امتزاز الأصباغ الثلاثة AR و CV و DR على أسطح ACS_1 و ACS_2 كان تلقائياً من الشحنة السالبة للطاقة الحرة ΔG° والعملية باعثة للحرارة من خلال القيم السالبة للأنثالبي ΔH° ، بينما القيم السالبة من ΔS° تدل على (الانتظام) الترتيب المنتظم لجزيئات الامتزاز على السطحين. أظهرت قيم الدالة الحامضية أن pH المثلى للامتصاص هي 4 لأصباغ AR و DR و 10 لصبغة CV. في المقابل ، أظهرت معلومات الامتصاص أن النسبة المئوية لإزالة الأصباغ الثلاثة AR و CV و DR زادت مع زيادة أوزان المواد الماصة لكل من السطحين ACS_1 و ACS_2 . كما تمت دراسة حركية الامتزاز للصبغات الثلاثة AR و CV و DR من خلال تطبيق النماذج الحركية لمعادلات الدرجة الأولى الكاذبة والثانية الكاذبة. ومن ثم ، أظهرت بيانات الامتزاز التجريبية أن امتزاز الأصباغ الثلاثة على السطحين (ACS_1 ، ACS_2) يتناسب مع النموذج الحركي من الدرجة الثانية الكاذبة.



جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة المثنى / كلية العلوم

قسم الكيمياء

تحضير وتشخيص مركب نانو (سخام كايثوسان) وتطبيقاته كمادة مازة

رسالة مقدمة الى

مجلس كلية العلوم / جامعة المثنى

وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل الطالبة

رسل محمد عبد الزهرة

بكالوريوس علوم كيمياء 2014

بإشراف

أ.د. حسن صبيح جبر

2021 م

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