

**Ministry of Higher Education and
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Synthesis and Dispersing of Different Nanoparticles(Fe_2O_3 and Al_2O_3) in Paraffin and Use Them as an Enhancing Adsorption Materials

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

اقْرَأْ بِاسْمِ رَبِّكَ الَّذِي خَلَقَ (١) خَلَقَ الْإِنْسَانَ مِنْ عَلَقٍ (٢) اقْرَأْ
وَرَبُّكَ الْأَكْرَمُ (٣) الَّذِي عَلَّمَ بِالْقَلَمِ (٤) عَلَّمَ الْإِنْسَانَ مَا لَمْ يَعْلَمْ
(٥)

صدق الله العظيم

(سورة العلق: ١-٥)



Dedication

To the one who led the hearts and minds of mankind to the harbor of safety, the first teacher of mankind prophet Mohammad (Peace Be Upon Him).

To my first example and my light that illuminates my path to the one who gave me and still gives me without limits to whom I raised my head high in pride (my dear father) may Allah keep him as an asset to me

To the one whose heart I saw before her eyes and her guts embraced me before her hands To my tree that does not wither To the shadow to which I shelter at all times (my beloved mother) may Allah save her

To the candles that light the way for me, my brothers (Salam, Abbas and Mustafa) who encouraged me and continued to give without return.

To the luminous jewels, the preserved pearls, and the hidden pearls (my dear sisters).

To my supportive husband, the permanent lover (Obaida), the life partner and the firm trunk on which we lean and shelter in his shadow.

To the seed of the heart and the hope of tomorrow, my sons (Youssef and Amna) who enjoyed tearing papers and scribbling on books.

To those with whom I have been linked by the relationship of lineage, the fragrance of friendship and the roses of love.

To the brothers who brought me together in the field of work (My generous colleagues).

To every hand and heart that walked with me the path of achievement to be

To all of them, I dedicate this study

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ABSTRACT

This study includes the preparation of nanoscale aluminum oxide ($\gamma\text{-Al}_2\text{O}_3$), iron oxide nanoparticles ($\alpha\text{-Fe}_2\text{O}_3$) and their binary nanocomposites with paraffine and activated charcoal ($\alpha\text{-Fe}_2\text{O}_3/\text{paraffine}$, $\gamma\text{-Al}_2\text{O}_3/\text{paraffine}$, $\alpha\text{-Fe}_2\text{O}_3/\text{AC}$ and $\gamma\text{-Al}_2\text{O}_3/\text{AC}$) to its enhancement adsorption of methyl orange dye from their aqueous solutions.

The nano oxides were prepared in an environmentally friendly manner (by treatment with aqueous eucalyptus leaves extracts) using different sources of iron $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as the nanoscale iron oxide, and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ as the nano aluminum oxide source. The $\text{Fe}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ nanoparticles were obtained by slow addition of sodium hydroxide solution to eucalyptus extract. Then to obtain $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ nanoparticles, calcination of $\text{Fe}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ nanoparticles was carried out at 550°C . Nanoparticles were diagnosed by FTIR, XRD, FESEM and DLS techniques. Brunauer-Emmett-Teller (BET) was used to determine the surface area of the nanomaterials. X-ray diffraction (XRD) examination showed that the size of $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ nanoparticles was 48 nm and 37 nm for $\gamma\text{-Al}_2\text{O}_3$ nanoparticles. These oxides nanocomposites were used to study the adsorption of methyl orange MO from their aqueous solutions. The effect of equilibrium time, adsorbing surface weight, and temperature on the adsorption process was studied. The results showed that the best equilibrium time is (60 min), and the best equilibrium weight is (0.1 g). Experimental data were studied on the following kinetic models: pseudo first order, pseudo second order and Elovich model. It was found from the kinetic study that the Elovich model is more suitable than other kinetic models in the adsorption of methyl orange dye. The thermodynamic functions of adsorption were also studied. Calculated

values of the thermodynamic functions (ΔG , ΔH , ΔS) of the adsorption declare that it is non-spontaneous, endothermic and randomness process, that indicate the particles are not bound on samples prepared. Finally, the Langmuir isotherm and Dubinin–Radushkevich isotherm were applied to the obtained results of the study and it was found that the adsorption of methyl orange dye on all samples followed the Dubinin–Radushkevich isotherm.

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List of Symbols and Abbreviations

Symbol of Abbreviation	Definition
AC	Activated carbon
A	Langmiur Constant related with Adsorption Capacity
AAS	Atomic Absorption Spectrophotometer
Avg	Average
B	Langmuir Constant related with Energy of Adsorption
C_0	Initial Concentration of Adsorbate
C_e	Equilibrium Concentration of Adsorbate
C_t	Concentration of Adsorbate after any Time
D	Crystallite Size
E E	Eucalyptus Extract
E E	Eucalyptus Extract
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Specyroscopy
IR	Infrared Spectroscopy
IR	Infrared Spectroscopy
K	Thermodynamic Equilibrium Constant
K	Equilibrium Constant
k_1	Pseudo-First Order Constant
k_2	Pseudo-Second Order Constant
k_i	Diffusion Constant
M	Weight of adsorbent
M.O	Methyle Orange
min	Minute

pr	paraffine
q_e	Quantity of adsorbate at equilibrium
q_t	Quantity of adsorbate at any time
R	Gas constant
R%	Percentage removal of adsorbate
R^2	Correlation coefficient
T	Temperature
$t^{1/2}$	Square root of the Time
V	Volume of Solution
wt%	Weight Percentage
XRD	X-ray Diffraction
ΔG	Gibbs free Energy
ΔH	Enthalpy
ΔS	Entropy
Θ	Bragg's angle
α	Alfa
γ	Gamma

Chapter One

(Introduction)

1.1.Nanomaterials

defined as physical substances with one dimension at the smallest between (1 to 100 nm), have attracted a lot of attention due to their unique features that set them apart from their bulk counterparts [1]. The study of nanomaterials adopts a materials science-based approach to nanotechnology, making use of developments in materials synthesis and metrology that were made to assist micro-fabrication research[2]. Nanoscale structures frequently have distinctive optical, electrical, or mechanical features[3].They are gradually becoming commodities and being commercialized[4].Inorganic nonmaterials like quantum dots, nanowires, and nanorods may be used in optoelectronics because of their fascinating optical and electrical properties [5]. Metal, semiconductor, or oxide-based nanoparticles or nanocrystals [6]. Recently, a variety of nanoparticles have been applied for biomedical application like tissue manufacturing, drug delivery, and biosenser [7]. They have been employed as quantum dots and as chemical catalysts such as nonmaterial base catalysts. Size-related characteristics can be seen in nanoparticles [8].Several nanoscale materials, such as zeolite, metal oxide, carbon-based nanoparticles, nanocomposites, and nanoparticles used as absorbents to take out heavy metal ions and dyes from water or wastewater [9]. Metal oxides nano-particles are a valuable material that has a variety of applications in optical mechanical and electrical devices, gas sensors, catalysts, cosmetics and sunscreens [10]. Additional methods chemical and also physical were used to prepare the nanoparticles. However, there are a number of methods that have disadvantages including toxic solvents, the use of high energy consumption, hazardous products... etc., so elemental need to grow environmentally friendly methods for the manufacture of metallic nanoparticles. The progress of environmentally friendly technology in the production of materials is great important to develop their applications. At present, various types of nanoparticles were synthesized by green methods with chemical composition, size and morphology synthesized

by various methods and their application have been explored in many innovative technological fields [11]. The method is advantageous over other risky procedures due to the regenerative properties of the plant extracts, the ecologically friendly aqueous medium, and the moderate reaction conditions. Due to their energy efficiency, cheap cost, and benign behavior in the process of creating metallic nanoparticles, several plant extracts and products have gained interest in recent years. [12].

1.2. Classification of Nanomaterials

This classification is based on how many of the material's dimensions are larger than the nanoscale (100 nm). Nanomaterials are classified into four images according to their dimensions, which are zero -dimensional, one-dimensional, two-dimensional, and three-dimensional. and irregular as shown in (1-1) [13].

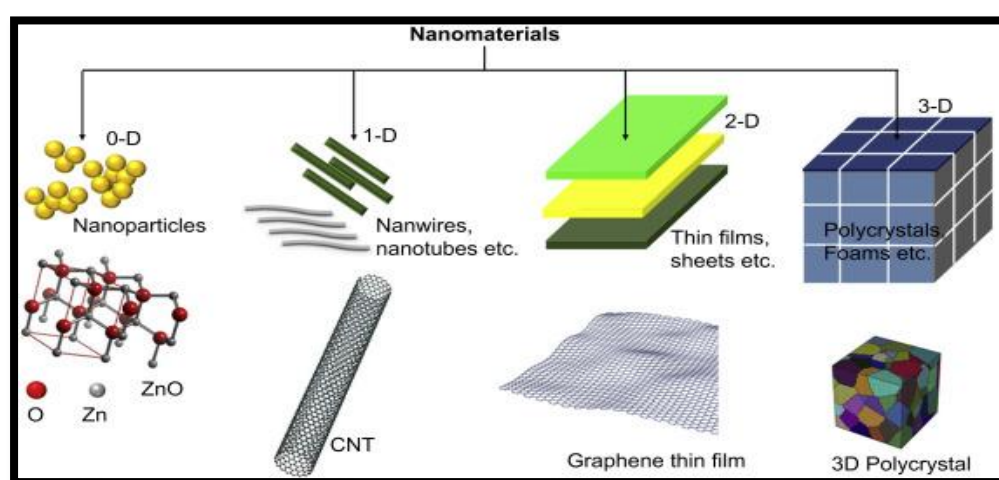


Figure (1-1) : Nanomaterials Classification

1.3. Properties of nanomaterials

The importance of nanomaterials lies in their outstanding quantitative properties; due to their small size and large surface area. Also, the ratio of the surface area of a nanomaterial to its mass is greater than the same ratio in large molecules, which lead to an raise in the rate of the chemical reaction. As opposed to that, the quantum effect plays an important role in nanomaterials, as it affects the mechanical, electrical, optical, magnetic and electrothermal properties of solid-state materials. The surface area has an effective role in affecting the behavior of nanomaterials, because in large materials there is a small percentage of atoms close to the surface. : (First) the surface area of atoms increase (Second) higher energy of surface (Third) Increasing quantum confinement (Fourth) Decreased defects compared to large particles [14,15].

1.4. Green Chemistry

1.4.1 Definition and Introduction

Since the products of environmental degradation that result from climate change, the danger of ozon hole, and the rise dangerous non-organic pollutants throughout the biosphere require environmental protection, there has been a lot of interest in what are referred to as "green and viable technologies." The goal of new legislation is to save the ecosystem. Chemicals are being developed while the chemical community works to create new substances and methods that are less harmful to both the environment and human health. A word used to describe improving chemical process and products that lessen or eliminate the usage and manufacture of toxic compounds is "green" or "sustainable chemistry.". It entails decrease dangerous compounds used in chemical processes as well as reducing harmful and toxic intermediates and products. This new discipline of chemistry takes an environmental perspective. The reagent catalyst, energy consumption and solvent must all be green for the reaction to be deemed "green." [16] . According to its definition, "green

chemistry" is the study of how to create chemical processes and products that do not affect the environment, hence preventing the development of pollution [17] .

1.4.2. Green Chemistry Principles

There are twelve principles in green chemistry that can be explained below:

1.Waste Prevention: It is superior end wasted instead of treat or clean it up after it have been formed. primary rule for green chemistry is the prevention of waste formation, which is more environmentally and humanely friendly and eventually less expensive than treatand eradicating garbage once it has appeared..

2.Atom Economy: The atom economy rule and the idea of preventing waste are logically associated since the atom economy mandates that, in order to minimize waste, all rare materials used in manufacture be utilised entirely or incorporated into the final product. This suggests that the chemical composition must be developed in a way that the end product increases the input of raw materials, or that synthetic products must be developed in a way that uses the entire starting material to build the final product.

3. Less Dangerous Chemical Syntheses: Chemical production techniques must aim to employ and produce materials with low or no toxicity to helth of human and the environment whenever possible..

4. Designing Safer Chemicals: This principle stipulates the propose of chemical prodcts to involve their desired function , reducing their toxicity to a minimum while preserving efficiency and function,The aim of synthesis safe chemicals (neurotoxic, non-carcinogenic and mutagenic) is to equilibrium the function of the chemical product and the optimum performance,in which to reduce the risk and toxicity to the lowest possible level.

5. Safer Solvents and Auxiliaries: The apply of auxiliary materials (like solvents, separating agents, etc.) should be as possible and harmless when used. Environmental contamination makes chromatographic separation operations, which demand huge quantities of solvents. The majority of traditional organic solvents are poisonous, combustible, and damaging. Because recycling them involves energy-saving distillation with significant losses, it's imperative to create ecologically friendly solvents. Green chemistry principles state that safety worker , procss safety, environmental safety, and process sustainability should all be taken into consideration when selecting an appropriate replacement for an organic solvent. Stability of Chemical and physical, low volatility, and simplicity of use are all requirements for the solvent.

6. Design for Energy Efficiency: recognizing and lowering the energy requirements of chemical processes to limit the harm they do to the environment and the economy Ideal conditions for the application of artificial methods are room temperature and pressure atmospheric.

7. Use of Renewable Feedstocks: The rare material must be renewed when it is technically and financially viable, rather than being exhausted.

8. Reduce derivatives: Avoid it completely if at all possible in order to minimize the quantity of needless derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes).

9.Catalysis: Catalytic materials, which had best quantities and quantities reaction for the stoichiometric reagents.

10- Design for degradation: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11-Real-time analysis for pollution prevention: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12-Inherently safer chemistry for accident prevention: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including explosions, and fires[18,19].

1.5 Techniques for Removing Pollutants from Water

1- Chemical precipitation is the method that is most frequently employed in industry since it is both efficient and reasonably price. Chemicals and heavy metal ions interact during precipitation processes to create an insoluble material. The formation silt can be separated from the water, and the treated water is then decanted, drained, or used as needed. Sulfide , chloride and hydroxide precipitation are two common chemical precipitation mechanisms [20].

2- Ion exchange is a technique that is frequently used to remove heavy metals from wastewater due to its many benefits, including high treatment capacity, high removal efficiency, and quick mobility. Mineral cations and anions can specifically be exchanged by an ion exchange resin, whether it is made of natural or manufactured solid resin. Synthetic resins are the chosen materials for ion exchange operations because they are efficient at removing nearly all heavy metals from solutions. pH, temperature, initial metal concentration, and contact time are some of the factors that affect exchange resins [21].

3- Membrane filtration is One sort of treatment used to remove heavy metals from various types of membranes is membrane filtration. The removal procedure might be effective, simple, and high surface area. Ultrafiltration, reverse osmosis, nanofiltration, and electrodialysis are membrane-based technologies that are used to filter out minerals from wastewater [22].

4- Electro Chemical Treatment Metal ions are laminated on the surface of the cathode during electrochemical treatment, which can return metals to their original metallic form. Technologies for electrochemical sanitation require a significant upfront investment and an expensive electrical supply, hence they have not been widely used. However, during the past 20 years, electrochemical

approaches have come back into prominence because to the severe environmental rules around wastewater disposal. Mineral recovery from wastewater is often accomplished using electrodeposition. It is a clean process for heavy metal separation that leaves no long-term leftovers[23].

5- Photodissociation :It is about breaking the bonds of a compound and converting it into lighter, non-toxic or polluting particles by means of light. This light is usually visible or ultraviolet [24].

6- Adsorption processes: When particles (ions, atoms, and molecules) from the gas phase or from a solution are present on the surface of a solid, a phenomena known as adsorption. The term "adsorbate" is a substance to be adsorbed and the term "adsorbent" is the surface on which this substance is adsorbed, for example silica gel, porous clay, resins, activated charcoal. Or adsorption can be defined as an increase in the concentration of the reactant on the surface of the catalyst, due to an increase in the concentration of the active substance [25].

1.6.Nano oxides

1.6.1. Iron Oxide Nanoparticles (Fe_3O_4 , Fe_2O_3)

Iron nanoparticles have distinguished themselves through the development of particular features, such as a high surface area-to-volume ratio and the realization and application of magnetic materials in the context of environmental cleanup [26]. In nature, iron oxide nanoparticles can take on a variety of shapes, including magnetite (Fe_3O_4), hematite (Fe_2O_3), and maghemite (Fe_3O_4). These particles are also exploited in a variety of biological and commercial processes [26,27]. The iron oxide nanoparticles have been used in a number of promising applications, including environmental remediation, biotechnology, and magnetic separation [28, 29]. Catalysis, electronics, information storage, sensors, drug delivery technology, and biology are a few examples of these uses. Numerous biological and medicinal processes where

done by material oxide including tissue engineering, magnetic fluid hyperthermia, targeted drug delivery, and magnetic fluid hyperthermia. Magnetic iron oxide nanoparticles are the preferred option for biological and biomedical applications due to their biocompatibility and chemical stability [30]. Due to their large surface area and distinct benefit of being simple to separate under external magnetic fields, magnetic nanoparticles are thought to be potential adsorbents for aqueous heavy metals [31]. Because of their proven outstanding adsorption capacities and ecologically friendly nature, iron oxide nanoparticles have recently gained a lot of attention as a result of advances in nanotechnology. It has been suggested that these reasonably priced but effective adsorbents serve as the primary raw material for treating soil contamination, sewage coagulation, radionuclide removal, and organic dye adsorption [32]. The creation of iron oxide nanoparticles has advanced significantly, and a variety of synthesis techniques have been investigated, including the heating of organic solvents, Sonochemical synthesis, co-precipitation technique, Production of sol-gels, flow injection, the polyol method, electrospray synthesis, reverse micelle and micro-emulsion technologies, and thermolysis of precursors are all examples of these techniques. Due to its simplicity and ability to produce significant quantities of nanoparticles with sizes ranging from 5 to 100 nm in a single batch, co-precipitation is the method for the synthesis of iron oxide nanoparticles that is most frequently used and most successful for producing aqueous dispersions of iron oxide nanoparticles. [33]. However, because particle growth is kinetically controlled over particle size, shape, and content. Particle growth is known to be influenced by the Fe (II)/Fe (III) ratio, pH, and ionic strength of the medium, as well as the kind of precursor salts utilized (chlorides,sulphate).

1.6.2 Nano Aluminum Oxide

Among the various forms of alumina, gamma alumina as shown in figure (1-2) is the most important because of its direct applications as a catalyst in the petroleum and other industries. This importance of gamma alumina is attributed to its distinctive structural properties such as surface area, pore size and distribution, and its acid-base properties that are due to its chemical surface composition. The main characteristics of the fine structure of γ -alumina are usually observed through the oxide produced by the calcination of aluminum hydroxide. The sequential sequence of this process has been studied for several years and also gives other forms such as alpha alumina depending on the calcification temperature [34].

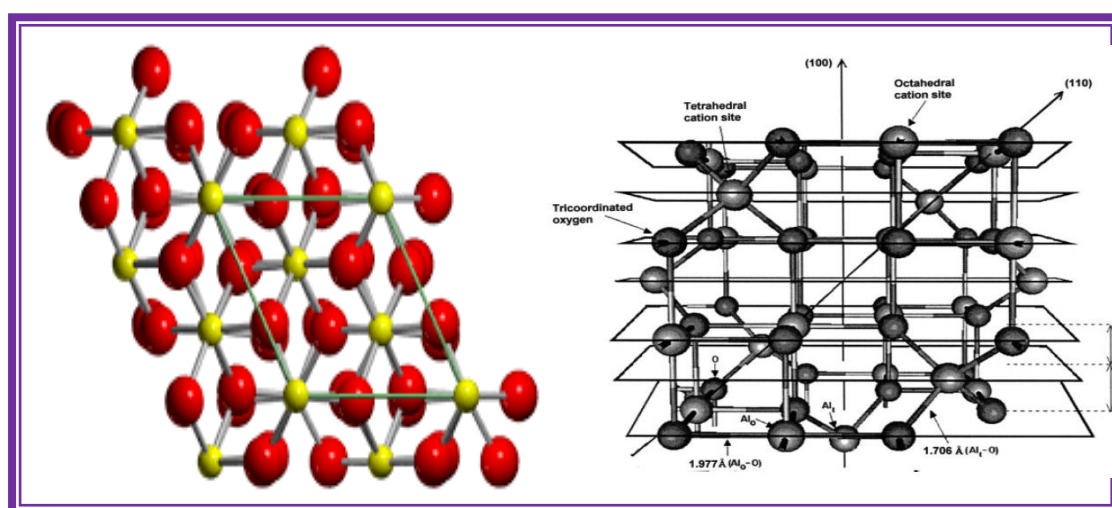


Figure (1-2) crystal structure of aluminum oxide nanoparticles

1.7 Adsorption

Adsorption is the process in which atoms, molecules or ions of another substance collect on the surface of a substance [35], and it is defined as the process in which an adsorbate moves from its solutions to the surface of an adsorbent [36]. This is the most widely used method for removing pollutants with low concentrations and which are difficult to remove by other methods [37]. The adsorbent material is the one that suffers adsorption on the adsorbent surface, and the adsorbent material is the surface on which the adsorption

process takes place. In the case that one molecular layer is formed on the adsorbing surface, it is called uni molecular adsorption, and in the case of several layers on the adsorbing surface, it is called multi molecular adsorption [38]. Among the materials used as an adsorbent material are activated charcoal and silica gel called activated alumina, molecular sieves and some types of clays. The nature and size of the adsorbent material and the surface area of the adsorbent surface are factors affecting the degree of adsorption[39].

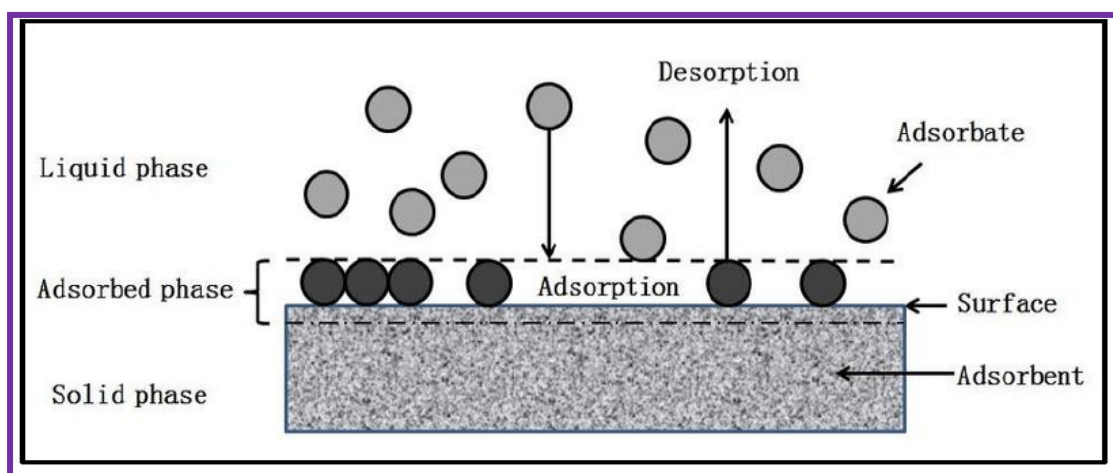


Figure (1-3): - Diagram of the adsorption process

1.8 Types of Adsorption

Adsorption can be classified based on the bonding between molecules, atoms or ions adsorbed on the surface of the adsorbent material into two types: chemical adsorption and physical adsorption. Table (1-1) shows the differences between chemical and physical adsorption [40-43].

Table (1-1) presents the most important differences between physical and chemical adsorption

Physical Adsorption	Chemical Adsorption
1- It arises when particles of the adsorbent material gather on the surface of the adsorbent due to van der Waals forces.	1- It arises when the molecules of the adsorbent material gather on the surface of the adsorbent material due to the chemical bonding (ionic or covalent bonds).
2- Low adsorption temperature (20-40 KJ/mol)	2- High adsorption temperature (40-400 KJ/mol)
3- The adsorption process requires low heat, and adsorption increases with decreasing temperature	3- The process takes place under certain conditions such as high temperature, and adsorption increases with increasing temperature.
4- The process is reversed	4- The process is not reversed
5- No activation energy required	5- You need activation energy
6- It may be single or multi-layered	6- monolayer
7- It is not accompanied by electronic transmission	7- It is accompanied by electronic transmission and the formation of a bond between the adsorbent and the surface
8- There are no interactions on the surface	8- Reactions on the surface that can occur such as: disintegration, rebuilding, cofactors

1.8.1 Factors Affecting on Adsorption Process

1- Nature of Adsorbate

The adsorption process depends on the nature of the adsorbent material, as well as on the physical properties, as the adsorption increases with the increase in the molecular weight of the adsorbent material, and the adsorption process also depends on the chemical properties, as the presence of the active and polarizing groups of the adsorbent leads to an effect on the adsorption process, as the adsorption of the most polar component in the solution is The largest such as the adsorption of the lead ion is twice the adsorption of the cadmium ion due to the large size of the lead ion .

2- Nature of Adsorbent

The nature of the adsorbent material and its properties play an important role in the adsorption process such as charge distribution, pore dimensions and chemical composition [44]. The chemical composition plays a major role with regard to the presence of polar or non-polar groups and the presence of acidic and basic groups. Also, the surface area has a major role in the adsorption process. The greater the surface area, the greater the effective sites on which adsorption occurs, and the surface area increases by decreasing the size of the adsorbent particles [45].

3- Temperature Effect

The effect of temperature on the adsorption process depends on the type of adsorption. The nature of both the adsorbent and the adsorbent material [45]. If the adsorption process is not accompanied by diffusion inside the pores of the solid phase, the change in enthalpy that accompanies the adsorption process is often exothermic [46], and in general a decrease in the amount of adsorption increases with increasing temperature according to The Lechatelier Principle [47] because the increase in the kinetic energy of the particles is related to the increase in temperature, which increases the possibilities of the separation of

the adsorbed particles from the adsorbing surface [48]. On the other hand, the possibility of penetration of the adsorbent molecules into the solid phase increases, and the adsorption increases with the increase in temperature if the process is endothermic [49].

4- pH-Effect

The acid function plays a major role in influencing the adsorption process, due to its effect on the adsorbent, adsorbent and solvent surface. Decrease or increase the acidic function of the adsorption process and varies depending on the adsorption system. The effect of the acid function on the adsorbent, adsorbent, and solvent surfaces appears through competition for (H^+) and (OH^-) ions, and as a result, it affects positively or negatively the adsorption process and also affects the behavior of adsorption isotherms and the quantity or capacity of the adsorbent on the adsorbent surface from compound to compound [50].

5- Effect of Solvent

The effect of the solvent on the behavior of the adsorption process is through the overlap of the solute in the solution together, as the less soluble substance in the solvent is more intense has strong adsorption on the surface of the adsorbent material, and the absorbing surface overlaps with the solvent depending on the chemical composition of both [51].

1.9 Types of Adsorption Isotherms

1.9.1 Langmuir Isotherm

This isotherm assumes that the adsorption sites on which the adsorption of molecules takes place are constant, and these sites are equivalent in energy, and each site can be occupied by one molecule, there is no interference with the molecules in other solutions or with each other, therefore a single layer is

Formed on the adsorbing surface [52]. And the linear relationship form of Langmuir equation is expressed by equation [53]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} k_L} + \frac{C_e}{q_{\max}} \dots \dots \dots (1-1)$$

As $q_{\max}$ is the maximum adsorption capacity, K_L , the Langmuir isotherm constant, C_e the equilibrium concentration (mg/l), and q_e the amount of adsorbent at equilibrium (mg/g), and when plotting C_e/Q_e against C_e , since $1/(q_{\max})$ represents the slope, $1/q_{\max} k_L$ represents the intersection. To diagnose the Langmuir isotherm, it is possible to use fixed separation factors or equilibrium factors given by the following relationship [54]:

$$R_L = 1/(1 + K_L C_o) \dots \dots \dots (1-2)$$

1.9.2. Dubinin Isotherm (DKR)

This equation is used to determine the range of adsorption energy, which gives us information about the adsorption mechanism, is it ion exchange, physical or chemical, and it is more comprehensive than the Langmuir model, because it is used in heterogeneous surfaces, the Dubinin isotherm is represented in the following formula [55] are: -

$$\ln Q_e = \ln q_{\max} - \beta \epsilon^2 \dots \dots \dots (1-3)$$

$q_{\max}$ = maximum adsorption capacity (mg/g)

β = a constant related to the adsorption energy (mol^2/KJ^2) and ϵ = related to the equilibrium concentration

$$\epsilon = RT \ln (1 + 1/C_e) \dots \dots \dots (1-4)$$

R = the general constant for gases (8.314 J/mol.K). The adsorption energy E can be calculated through the following equation [56]:

$$E = 1/\sqrt{2B} \dots \dots \dots (1-5)$$

To give a true picture of the adsorption mechanics, we can benefit from the energy equation. If E is less than 8KJ/mol, the forces affecting the adsorption

process are physical. But if E is greater than 16KJ/mol, this indicates that the particles have diffusion. But if E is between (8-16), this indicates a chemical ion exchange.

1.10 Apparatus Used in Characterization Nanomaterials

1-Fourier Transform Infrared Spectroscopy(FTIR)

(FTIR) is used to diagnose effective aggregates on the surface of materials using specific energy of vibration of atoms in these aggregates. The diagnosis is made within the range (4000-400cm⁻¹) and the window energy is recorded for each wave number. The particles absorb energy only at certain wavelengths and frequencies.



Figure (1-4) FTIR Infrared Spectrophotometer

2- X-ray Diffraction

This technique is used to find out how the atoms are arranged inside the crystals, and based on the intensity and angles at which the radiation deviates after the X-rays hit the crystal from several directions, it gives us a three-dimensional picture of the density of electrons inside the crystal, and based on this density we can know the average size of the crystal and its chemical bonds and information other. There are many materials that are crystallized, such as semiconductors, salts, organic and inorganic materials, so the study of X-rays has a role in the development of many scientific fields. It also helps us in studying the internal structures of many substances such as vitamins, proteins,

medicines, and nucleic acids, as well as clarifying the differences between many substances at the atomic level [57].



Figure (1-5) X-ray diffraction machine

3-Atomic Force Microscopy (AFM)

The atomic force microscope (or scanning force microscope) is a very high resolution that has an analysis capacity of parts of a nanometer. The technique of atomic force microscopy was used to diagnose samples. Prepared to see the size of the samples. This microscope has the ability to image samples in three dimensions, as it has a high analytical ability of up to parts of a nanometer. This microscope consists of a microscopic needle that is installed on a holder that is perpendicular to it, and on the surface to be examined, this needle scans the sample back and forth several times to give a clear picture of the topography of the sample. Receiver for the beam connected to the device, the terrain is drawn according to the movement of the reflected beam [58,59].

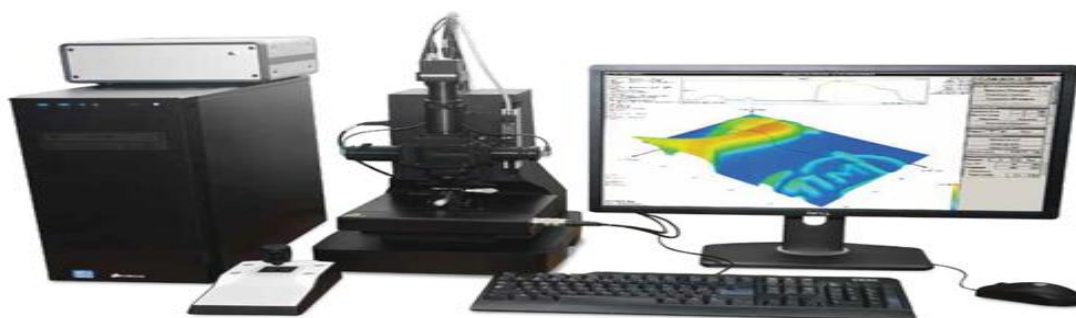


Figure (1-6) Atomic force microscope AFM

4-Scanning Electron Microscopy (SEM)

It is one of the most important types of electron microscopes in which the surface of the sample is photographed by scanning it with high-energy electron beams. Size (1-5 nm), and the magnification range of the scanning microscope is between (250000 times to 25 times). The scanning electron microscope, which is referred to by the abbreviation SEM, is considered one of the most important microscopic imaging devices, which has many major and important applications in the field of materials science, medical sciences and various natural sciences. Through these microscopes, the surface of the sample is accurately photographed using a torrent of electrons to give a very clear picture of the topography of the sample [60,61]. Through this technique, the shapes of nanomaterials can be clearly known where nanotubes can be distinguished from wires, particles, and balls. The working theory of the scanning electron microscope shown in Figure (1-7) depends on the use of a high-energy electron beam that is prepared from the electron gun that is placed at the top of the device. clear to the sample surface[62,63].



Figure (1-7) SEM . Scanning Electron Microscope

1.11 Literature Survey

(Ahmed, et. al, 2016), used Azadirachta indica aqueous plant extract to prepare Ago nanoparticles in a simple way to produce green chemicals at room temperature. It was characterized by utilizing (TEM, UV-VIS, FTIR and DLS). Alongside Gram-positive (Staphylococcus aureus) and Gram-negative (Escherichia coli) microbes, the silver nanoparticles demonstrated anti-bacterial activity. Additionally, analyses of silver particle luminescence [64].

(Nagajyothi, et. al, 2017), CuO nanoparticle synthesis was studied. Black bean extract in aqueous form was used in its green synthesis. Radian spectroscopy, FT-IR, DLS, TEM, SEM, and EDX were used to characterize the CuO powder. The nanoparticles' average size, according to the XRD explanation, was 26.6 nm. It was also investigated how well the CuO nanoparticles inhibition the cancer. [65].

(Jagpreet Singh, et. al, 2018), Highlighted the basic mechanisms and processes of green synthesis methodologies in their study, focusing in particular on metal and metal oxide nanoparticles using natural extracts, such as gold (Au), silver (Ag), copper oxide (CuO), and zinc oxide (ZnO). They also looked at the function of biological elements and crucial phytochemicals including amides, The reducing and solvent systems include alkaloids, terpenoids, and flavonoids. The stability and toxicity of nanoparticles, surface engineering techniques for achieving biocompatibility, and applications of such synthesized products to environmental remediation in terms of antimicrobial activity, catalytic activity, pollutant removal, dye removal, and heavy metal ion sensing are all covered in this article. [66].

(Karim, et. al, 2018), Report on a straightforward method for creating copper oxide nanoparticles from the appropriate salt using fig leaf extracts. The techniques of XRD, SEM, TEM, and AFM were used to characterize the

particles. The obtained particle size (7.31 nm), as shown by the XRD spectrum, was in reasonable agreement with those predicted by the SEM and TEM. [67].

(Mohammadi-Aloucheh, R., et. al, 2018), published the preparation of ZnO and ZnO /CuO nanocomposites using *Mentha longifolia* leaves extract in microwave oven (2.45 GHz and 1000 W) .They were distinguished by their size and formation using (EDX, XRD, FT-IR, SEM, TEM, TGA, UV–Vis, DRS, and BET), A results obtained from XRD, EDX showed that the impurity peaks were not detected, indicating the purity of the prepared nanoparticles. From the results obtained, the samples prepared with *M. longifolia* leaves extract have excellent ability to inhibit the growth of the studied bacteria [68].

(Abdallah, Y., et. al, 2019), Utilizing a plant extract from the fruit of the red tomato, olive leaf, and chamomile flower (*Matricaria chamomilla*), researchers explored the formation of zinc oxide nanoparticles (ZnO.NPs) (*Lycopersicon esculentum*). The created ZnO.NPs had the following properties: (UV-Vis, FTIR, XRD, TEM, and SEM). Pure crystal forms of ZnO nanoparticles are real, according to XRD research. e sample's dominating average size was shown by XRD to be 48.2 nm, which is consistent with the size distribution analysis obtained from TEM. However, SEM observation of ZnO.NPs produced by *Olea europaea* indicated the lowest size range, which ranged from 40.5 to 124 nm. [69].

(Singh, K., et. al, 2019), studied the preparation of zinc nanoparticles using *Punica granatum* leaves extract and characterized their size and shape using (UV-Vis, EDX, TEM, FESEM and XRD). The XRD pattern showed the crystalline nature of ZnO, average particle diameter was 20 nm. FESEM, TEM analysis revealed a spherical shape of 10-30 nm. Treating water from harmful dyes was a positive step during this work [70].

(Awwad, A. M., et. al, 2020), Ailanthus altissima fruit aqueous extract was used to synthesize zinc oxide nanoparticles in a straightforward and efficient manner, and their antibacterial activity was assessed. Utilizing a scanning electron microscope (SEM), UV-Vis absorption spectroscopy, and X-ray diffraction, the zinc oxide nanoparticles were studied (XRD). It was discovered that the produced nanoparticles have an average size between 5 and 18 nm. According to FT-IR research, the zinc oxide was stabilized via interactions between flavonoids and phenolic chemicals in the fruit extract. [71].

(XiaodongYi, et.al, 2017), In their research investigation, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were used as solid raw materials for the NiMo/ Al_2O_3 hydrodesulfurization (HDS), and polyethylene glycol (PEG) was used as a precursor additive. Dibenzothiophene HDS activity and catalyst characteristics for thermal decomposition were studied. The powder-prepared catalysts were characterized using N_2 adsorption-desorption measurements, X-ray diffraction, thermogravimetric analysis/differential scanning calorimetry, H_2 temperature programmed reduction (H_2 -TPR), XPS, scanning electron microscopy (SEM), and high resolution transmission electron microscopy (HRTEM). The results show that adding PEG significantly enhances the catalyst's specific surface area and pore volume. With increasing PEG addition, dibenzothiophene HDS activity rose and peaked at a weight ratio of 15% PEG to alumina. [72].

(Jbara,et.al, 2017), prepared $\gamma\text{-Al}_2\text{O}_3$ by co-precipitation under annealing temperature effect, The gamma phase of alumina has particles with a diameter ranging from 6 to 24 nm, according to structural characterisation using XRD analysis. The produced nanopowders have a surface area of between (109 and 367) m^2/g . The morphological examination shows that the grains in $\gamma\text{-Al}_2\text{O}_3$ nanopowders are virtually spherical in shape. [73].

(Tabesh, et.al,2017), modified technique sol gel, synthesis γ -Al₂O₃. The source Al⁺³, gel, chelating, and surfactant agents employed in this work were aluminum nitrate, ethylene glycol (EG), citric acid (CA), and triethanolamine (TEA), respectively. structural characterization employing thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and infrared spectroscopy (IR). The effectiveness of heavy metal ion removal in the adsorption process by produced alumina nanoparticles (lead and cadmium) has then been examined in PH (5), with contact times of 20 min and 30 min for Pb⁺² and Cd⁺² respectively [74].

(Rahmanpour, et.al, 2012), The dehydration of methanol to dimethyl ether using a precipitation method with ultrasonic vibration mixing was examined as a new approach for producing nanosize (γ -Al₂O₃). SEM, XRD, BET, and TPD techniques were used to characterize the alumina that was produced. When compared to their bulk state, the materials at the nanoscale exhibit various properties [75].

(Mukherjee,et.al,2016),A simple, single step and eco-friendly approach was taken for synthesizing iron oxide nanoparticles using *Aloe vera* leaf extract. The nanoparticles were characterized by various techniques and used for arsenic(V) remediation in synthetic system with an initial concentration range of 2–30 mg/L. The effect of pH, particle dosage and initial arsenic concentration on arsenic adsorption was investigated using response surface methodology involving five levels Central Composite Design (CCD) considering adsorption capacity as the response[76].

(Wang,et.al,2016),Fe₂O₃/ γ -Al₂O₃ sorbents that containing different quantities of iron (III) oxide were prepared by ultrasound-assisted wet impregnation method. Application of these sorbents for arsenic adsorption was tested on a fixed bed reactor and some factors, such as temperature, precursor solution concentration (PSC) and SO₂/NO concentration were discussed. The results indicated that more than 65% of gas-phase arsenic was adsorbed at 600 °C, while the efficiency decreased gradually when temperature over 600 °C. The higher precursor solution concentration could increase the amount of active substance on carrier, but also cause structure deterioration of sorbent.

SO₂ in flue gas exhibited a promotion effect on arsenic adsorption across Fe₂O₃/γ-Al₂O₃; however, the effect of NO was not as notable as SO₂[77].

(Asfaram,et.al,2016),γ-Fe₂O₃ nanoparticles were synthesized and loaded on activated carbon. The prepared nanomaterial was characterized by field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), Fourier transforms infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). The γ-Fe₂O₃ nanoparticle-loaded activated carbon (γ-Fe₂O₃-NPs-AC) was used as novel adsorbent for the ultrasonic-assisted removal of methylene blue (MB) and malachite green (MG). Response surface methodology and artificial neural network were applied to model and optimize the adsorption of the MB and MG in their individual and binary solutions followed by the investigation on adsorption isotherm and kinetics[78].

(Basavegowda,et.al,2017),A novel magnetically recoverable hematite nanoparticles (α-Fe₂O₃ NPs) was fabricated by a simple, one pot, and green method using the rhizome of *Cyperus rotundus* L., as a reducing and stabilizing agent. The prepared nanoparticles were well characterized by all parameters. TEM showed that the hematite nanoparticles had a rhombohedral shape and ranged in size from 80 to 100 nm. The phase study of the α-Fe₂O₃ nanoparticles was confirmed by Raman spectroscopy. In addition, the synthesized nanoparticles shows good photocatalytic activity in degradation of highly toxic Congo red dye within 25 min, and the same NPs exhibits higher catalytic activity for the reduction of 4-nitro-o-phenylenediamine (4-NPD) to 1,2,4-benzenetriamine in the presence of NaBH₄ within 12 min. After the reaction, the catalyst was recovered and reused three times without significant loss of catalytic activity[79].

(Ali,et.al,2017),In this study, α-Fe₂O₃ nanoparticles (NPs) have been prepared using the hot water extract of the mandarin (*Citrus reticulum*) peels as a way for recycling of domestic waste to valuable product. The prepared hematite was characterized by UV/Vis spectroscopy, thermal gravimetric analysis, XRD, FTIR, SEM, and TEM. It was found to be porous irregular sphere shaped NPs with average size of 20–63 nm, characterized by weak ferromagnetic properties and band gap (*E_g*) of 2.38 eV. The prepared α-Fe₂O₃ NPs expressed good photocatalytic degradation activity. It showed good capacity for the decontamination of polluted water from anionic and cationic dyes and dichlorophenols under visible light irradiation[80].

(Mebrahtu,et.al,2017), Nanocomposites of Zn-Ti-Fe oxide using zinc as a host with different ratios of precursor salts were prepared by co-precipitation method to use as semiconductors for dye sensitized solar cell (DSSC). The as-synthesized nanocomposites were characterized using XRD, SEM-EDX, TEM and UV-Vis spectrophotometer. DSSCs based on the new semiconductors and di-tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) (N719) dye has been constructed and characterized[81].

(Asoufi,et.al,2018), A green route for synthesis iron oxide (Hematite, α -Fe₂O₃) from ferrous chloride tetrahydrate (FeCl₂·4H₂O) and *Ailanthus excelsa* leaves extract, which act as reducing and stabilizing agent. Biosynthesized Fe₂O₃NPs were synthesized were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-vis absorption spectroscopy (UV-vis) [82].

(Siddiqui,et.al,2019),The aim of the present study was to make effort to provide sustainable and affordable water purification technique for complete cleaning of polluted water. For this purpose, an economical organic-inorganic advance nanohybrid composite, binary iron-zirconium oxide decorated Black cumin seed, was prepared by following one step co-precipitation method. The prepared composite was used for inhibition of growth of bacterial cells, and remediation of arsenic, and dyes, from water. The nanohybrid composite was characterized by using Fourier-transform infrared spectroscopy, energy dispersive X-Ray spectroscopy, X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, thermogravimetry, and differential scanning calorimetry etc. techniques[83].

(Siddiqui,et.al,2019)In this work, an advance approach is reported for the water treatment technology using nanohybrid composite Fe₂O₃-SnO₂/BC prepared by incorporation of iron-tin binary oxide into the cellulosic framework of medicinally active *Nigella sativa* (Black cumin) seed powder. The co-precipitation method was followed to prepare the nanohybrid composite which was subjected to investigate its physiochemical properties using spectroscopic and microscopic techniques. Fourier-transform infrared spectroscopy analysis confirmed the formation of highly functionalized nanocomposite through the hydrogen and electrostatic interactions between the functional groups of seeds and Fe₂O₃-SnO₂. X-ray and selected area electron diffraction pattern revealed the presence of cubic phase of γ -Fe₂O₃ and tetragonal phase of SnO₂ in the composite[84].

(**Noufal KombyAbdulla,et.al,2019**), This study reports the incorporation of magnetic γ -Fe₂O₃ nanoparticles into the carbon framework of highly abundant, house hold medicinal plant, *Psidium guajava*, commonly known as Guava through co-precipitation. The prepared nanocomposite, γ -Fe₂O₃@GL was characterized with several spectroscopic and microscopic techniques, and showed the nano-porous structure having extensive oxygenous functional groups at the surface. The saturation magnetic moment of γ -Fe₂O₃@GL was found to be 0.72 emug⁻¹. Nanocomposite was used for the adsorption of methylene blue from water for which batch experiments were carried out under the change of various process parameters, and exhibited the fast and 99% removal of methylene blue from its solution having 10 mg L⁻¹ concentrations with 1.0 gL⁻¹ amount of γ -Fe₂O₃@GL. The maximum monolayer adsorption capacity was found to be in range 69.93 to 91.74 mgg⁻¹, at 27–45 °C. The magnetically separable γ -Fe₂O₃@GL showed the high reusability and adsorption rate without significant loss after sixth adsorption-desorption cycles. Therefore, the prepared magnetic γ -Fe₂O₃@GL can be useful technique for water treatment having low cost and high adsorption capacity[85].

(**Pallela,et.al,2019**), The aim of the work is to synthesize iron oxide (α -Fe₂O₃) nanoparticles using *Sida cordifolia* plant extract along with evaluation of its antibacterial activity. The presence of phytochemicals in *Sida cordifolia* methanolic plant extract was investigated by HPTLC and LC-MS/TOF. The probable mechanism for formation of α -Fe₂O₃ nanoparticles in mediation with plant extract was demonstrated. The green synthesized iron oxide nanoparticles (α -Fe₂O₃ NPs) were characterized by using X-ray diffraction, scanning, and transmission electronic microscopy[86].

(**Karade,et.al,2019**), The *Gardenia*, traditional medicinal plant used from ancient time to increase appetite and other medicinal uses has been employed for the synthesis of superparamagnetic α -Fe₂O₃ nanoparticles (NPs). The plant extracts unveiled its bifunctional nature through the reducing ferric ions by phenolic groups and capping nature through the –OH bonding over the NPs surface. The prepared NPs exhibits α -Fe₂O₃ phase among iron oxides and spherical morphology with an average size around 5 nm[87].

(Islam,et.al,2019), Hematite nanoparticles (NPs) are chemically and thermodynamically more stable among iron oxide NPs therefore these are considered highly suitable for biomedical applications. This work explores *Rhus punjabensis* extract potential as both reducing and capping agent for phytomediated synthesis of NPs from ferric chloride precursor. The structural, morphological and compositional investigations were carried out with XRD, SEM, TEM, EDS, and FFT. The synthesized NPs were hematite (Fe_2O_3) with rhombohedral crystal structure of an approximate size of 41.5 ± 5 nm. TEM, FTIR, and TG/DTA indicated phase-pure Fe_2O_3 formation with controlled size through use of capping agent[88].

(Susanta Kumar Biswal,et.al,2020), An environmental friendly and cost effective method was used for the preparation of silver-iron oxide ($\alpha\text{-Fe}_2\text{O}_3\text{-Ag}$) nanocomposite using guava (*Psidium guajava*) leaf extract, which can be used as an adsorbent for decontamination of chromium (VI) ions from aqueous media. XRD analysis revealed that both Iron oxide and silver nanoparticles are crystalline in nature with face-centered cubic and rhombohedral geometry respectively. The FESEM micrographs of $\text{Fe}_2\text{O}_3\text{-Ag}$ nanocomposite displayed irregular shaped particles with an average size of 50–90 nm. BET surface area analysis suggests that the prepared $\text{Fe}_2\text{O}_3\text{-Ag}$ nanocomposites are mesoporous in nature with surface area of $122.72 \text{ m}^2/\text{g}$. The adsorption of Cr(VI) was pH dependent and maximum adsorption occurred at pH = 4 with maximum adsorption capacity of 71.34 mg/g. Thermodynamic parameters reveals that the Cr(VI) adsorption on $\text{Fe}_2\text{O}_3\text{-Ag}$ surface is endothermic and spontaneous in nature[89].

(Vinayagam,et.al,2020), Microporous $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were synthesized by employing the extract of *Spondias dulcis* leaves by green-synthesis technique for the first time. The nanoparticles were characterized by many techniques. A continual absorption band without any peak in UV-vis spectrum and a strong signal for iron and oxygen atoms in EDS confirmed the formation of iron-oxide nanoparticles. Rod-like structures with few aggregations due to magnetic interactions were witnessed in FE-SEM image. Specific peaks belonging to $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were observed in XRD spectrum, and they were very pure and crystalline with a mean particle diameter of 11.38 nm. XPS analysis confirmed oxidation state of Fe and O and portrayed the presence of $\alpha\text{-Fe}_2\text{O}_3$. A relatively higher surface area ($190.84 \text{ m}^2/\text{g}$) than reported green-synthesized $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles has been obtained by BET analysis, and the

pores were microscopic (0.465 nm) in nature. Signature bands for Fe-O (1136 cm^{-1}) and organic moieties stretching vibrations were confirmed by FTIR spectrum. The point of zero charge was determined as 7.97 which is concordant with the published value for $\alpha\text{-Fe}_2\text{O}_3$. The thermal stability was ascertained by TGA which showed 28% weight loss[90].

(SaimaNoreen,et.al,2020), In view of eco-benign nature of green synthesis, *Dombeya wallichii* and *Pyrus comminis* leaves extracts were used for the fabrication of iron oxide Fe_2O_3 NPs. The nanoadsorbents thus prepared were successfully applied for the adsorption of anionic dye from aqueous solution. The process variables such as pH, adsorbent dose, contact time, temperature and concentration of dye significantly affected the dye adsorption and optimum conditions were pH 3, 0.01 g adsorbent dose, 200 mg/L initial dye concentration, 80 min contact time and 65°C . The adsorption of dye on to nanoadsorbents was an endothermic and favorable. Langmuir model and pseudo-second-order explained well the dye adsorption data. The presence of salts and surfactants reduced the dye adsorption and sodium hydroxide can desorb the dye from the nanoadsorbents. Nanoadsorbent prepared via green route are efficient for the removal of anionic dye and could possibly be used for the remediation of textile effluents contains dyes[91].

(Vinayagam,et.al,2020), Microporous $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were synthesized by employing the extract of *Spondias dulcis* leaves by green-synthesis technique for the first time. The nanoparticles were characterized by many techniques. A continual absorption band without any peak in UV-vis spectrum and a strong signal for iron and oxygen atoms in EDS confirmed the formation of iron-oxide nanoparticles. Rod-like structures with few aggregations due to magnetic interactions were witnessed in FE-SEM image. Specific peaks belonging to $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were observed in XRD spectrum, and they were very pure and crystalline with a mean particle diameter of 11.38 nm. XPS analysis confirmed oxidation state of Fe and O and portrayed the presence of $\alpha\text{-Fe}_2\text{O}_3$. A relatively higher surface area ($190.84\text{ m}^2/\text{g}$) than reported green-synthesized $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles has been obtained by BET analysis, and the pores were microscopic (0.465 nm) in nature[92].

(Noreen,et.al,2020),Textile sector is one of the major industries responsible for water pollution and the remediation of dyes is necessary to safe guard the water resources. Adsorption using nanoadsorbents have been emerged as one of viable techniques to eliminate the dyes from wastewater. Iron oxide was prepared via green route using Fan palm (F.P), *Dombeya wallichii* (D.W)

and *Pyrus comminis* (P.C) as a reducing, capping and stabilizing agents. The adsorption of anionic dye using nanoadsorbents was studied and pH, adsorbent dose, contact time, temperature and concentration of dye were optimized. The maximum dye adsorption was achieved at pH 3, 0.01 g/50 mL adsorbent dose, 200 mg/L initial concentration at 65 °C[93].

(Al-Hakkani,et.al,2021),The aim of the current work is the introduction of a quick and simple literature survey about the bio-fabrication of the Alpha Hematite nanoparticles (α -Fe₂O₃) using the plant extracts green method. The survey manifested the utilities of the environmentally friendly biosynthesis methods *via* extracting different plant species, some of its important physicochemical properties, various instrumental analysis characterization tools, and potential applications[94].

(Noreen,et.al,2021),In the present investigation, ZnO, CuO and Fe₂O₃ were prepared via green route and utilized for the sequestration of DGY (Direct Golden Yellow) dye. Affecting variables i.e., temperature, contact time, adsorbent dose and pH were optimized for maximum sequestration of dye from aqueous medium. The pH 2, adsorbent dose 0.1 g/50 mL dye solution, temperature 30 °C and 50 mg/L dye initial concentration were best levels for efficient dye adsorption and equilibrium was attained in 30 min reaction time. The dye sequestration on to ZnO, CuO and Fe₂O₃ was an exothermic process. Freundlich and Temkin adsorption isotherms explained well the dye adsorption onto nanoadsorbents and dye adsorption followed pseudo first order kinetic model. Effect of electrolytes and heavy metal ions was also investigated and both affected the adsorption process significantly. In the presences of surfactant/detergent, the removal of dye was reduced and 0.5 N NaOH efficiently desorbed the dye from nanoadsorbents. Findings depicted that the nanoadsorbents are effectual for the sequestration of DGY dye, which can be employed for the remediation of textile effluents[95].

(Weldegebrieal,et.al,2021),Hematite (α -Fe₂O₃) nanoparticles (NPs) was biosynthesized using *Vernonia amygdalina* (*V. amygdalina*) leaves extract and Fe(NO₃)₃.9H₂O precursor and characterized using X-ray diffraction (XRD), Ultraviolet–visible (UV-Vis), Fourier transform infrared (FTIR), and scanning electron microscopy (SEM) techniques. Moreover, the photocatalytic activity of synthesized sample calcined at 550 and 650 °C for the degradation of methyl orange (MO) and methylene blue (MB) dyes was studied and results indicated good catalytic activity towards MB at natural pH and efficient degradation at alkaline pH under sunlight irradiation. However, MO was efficiently degraded

only in the presence of a small amount of H_2O_2 oxidant and that this disparity in photodegradation between the two dyes at similar experimental parameters could be due to difference in their molecular structure stability and HOMO-LUMO energy gap compared to VB-CB positions of catalyst $\alpha\text{-Fe}_2\text{O}_3$ NPs[96].

(Anuj KumarPrajapati,et.al,2021),In this study, ternary phase $\text{Fe}_2\text{O}_3\text{-Mn}_2\text{O}_3\text{-Mn}_3\text{O}_4$ (FMM) nanocomposites (NCs) were synthesized via a facile co-precipitation method. The surface of synthesized NCs was modified by cationic CTAB surfactant to increase surface functionality and surface area without any phase change. The existence of the ternary phase in NCs was confirmed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) techniques. Additionally, characterization techniques such as Fourier transform infrared spectroscopy (FT-IR), Brunauer–Emmett–Teller (BET) surface area analysis, point of zero charge, Field Emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM) were examined for FMM NCs and CTAB modified FMM NCs. The FT-IR and BET surface area analysis confirmed that CTAB modified FMM NCs showed excellent functionality and 19.11% higher surface area than unmodified FMM NCs. Thus, the prepared both NCs were used for congo red (CR) dye adsorption from aqueous solution by varying batch experimental parameters, such as initial pH, contact time and temperature with varying the initial concentration of dye[97].

. **(AmritKaur,et.al,2021)**, $\text{Fe}(\text{OH})_3$ nanoparticles (NPs), have been prepared employing an aqueous extract of *Acacia catechu* leaves as green reducing as well as stabilizing agent. The annealing of $\text{Fe}(\text{OH})_3$ NPs results in the formation of highly crystalline $\alpha\text{-Fe}_2\text{O}_3$ NPs. Thus prepared $\text{Fe}(\text{OH})_3$ and $\alpha\text{-Fe}_2\text{O}_3$ NPs have been characterized for crystallinity, shape, size and porosity and tested for adsorptive removal of $\text{Cr}(\text{VI})$ from aqueous solution at varying pH, dose of NPs and initial concentration of $\text{Cr}(\text{VI})$. Removal efficacy of both forms of NPs ($\text{Fe}(\text{OH})_3$ and $\alpha\text{-Fe}_2\text{O}_3$) towards $\text{Cr}(\text{VI})$ has been correlated with their structural aspects. Under optimal conditions, $\text{Fe}(\text{OH})_3$ NPs and $\alpha\text{-Fe}_2\text{O}_3$ NPs have been found to remove 84.9 % and 22 % of $\text{Cr}(\text{VI})$ from aqueous solutions[98].

(Noukelag,et.al,2021),Biosynthesized hematite phase $\alpha\text{Fe}_2\text{O}_3$ nanoparticles (NP s) have been successfully demonstrated via an entirely green process mediated aqueous extract of *Rosmarinus officinalis* (rosemary) leaves acting as both stabilizing and capping agents. The synthesis was free of solvents and surfactants to adhere to green chemistry principles and the impartation of environmental benignity. To achieve the goal of this study, the main physical

properties of the biosynthesized α -Fe₂O₃ NPs were carried-out using complementary techniques namely, field emission scanning electron microscopy (FESEM) which revealed the self-assembled, highly agglomerated NPs, and the average size was found to peak at 6.531 ± 0.148 nm while X-ray diffraction (XRD) exhibited several Bragg diffraction peaks in line with the rhombohedral structure and the crystallinity nature of α -Fe₂O₃ NPs with an average size within the range of 7.412–10.742 nm in agreement with the FESEM results. The energy-dispersive X-ray spectroscopy (EDS) [99].

(Ramesh,et.al,2021),In this investigation α -Fe₂O₃ nanoparticles were successfully synthesized by biogenic route using *Plectranthus amboinicus* leaf extract. The XRD studies confirmed the rhombohedral structure and the SEM analysis revealed the spherical nature with the average size of the 100 nm. Desired elements Fe and O were identified using the EDAX spectrum. The chemical groups present in the sample were identified from the FTIR spectroscopy and the strong absorption band at 560 cm^{-1} and 466 cm^{-1} is due to the existence of Fe-O bonding. The optical property of the specimen was analysed using UV–Visible spectroscopy and the calculations showed that the energy gap(E_g) is around 3.2 eV[100].

1.12 Aims of the Study

1. Preparation of $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ nanoparticles using a friendly environmentally method.
2. Preparation of binary composite with paraffin and activated carbon ($\alpha\text{-Fe}_2\text{O}_3$ / paraffin , $\gamma\text{-Al}_2\text{O}_3$ /paraffin, $\alpha\text{-Fe}_2\text{O}_3$ / activated carbon and $\gamma\text{-Al}_2\text{O}_3$ / activated carbon.
3. Using the obtained metal oxide nanoparticles and their nanocomposite to remove methyl orange dye from its aqueous solutions.

Chapter Two

(Experimental part)

2. The Experimental Part

2.1 Chemicals Materials

The chemicals used in this study are shown below in Table (2-1).

Table (2-1) of chemicals in terms of purity and the company

No	Chemicals Name	Formula	Purity %	Origin
1	Absolute ethanol	C_2H_5OH	99.9	GCC
2	activated charcoal			
3	Aluminium Chloride hexahydrate	$AlCl_3.6H_2O$	99	CDH
4	Aluminium Sulphate hexadecahydrate	$Al_2(SO_4)_3.16H_2O$	99.5	CDH
5	eucalyptus leaves from Diyala governorate			
6	Ferrous Chloride	$FeCl_2.2H_2O$	99	CDH
7	Ferrous Sulphate	$FeSO_4.7H_2O$	99	Alpha Chemika
8	Methyl Orange	$C_{14}H_{14}N_3NaO_3S$	99	MERK
9	Paraffin			
10	Sodium hydroxide	$NaOH$	99	Alpha chemical

2.2 Instruments Used

The devices used in the study are shown in Table. (2-2).

Table (2-2) of the Instruments used

No	Instrument	Details and Origin	Location
1	Electric balance	Kern Acjiacs , ACS 120-40, WB 12AEO308, Max 120g, d = 0.1 mg, (Germany) Binder	for Pure Science Department of Chemistry, University of
2		Oven BINDER, Germany	

	Oven	10-300 °C	
3	pH Meter	pH / Ion Benchtop WTW inolab pH Meter 7110 Benchtop Meter, (Germany)	
4	Hot plate magnetic stirrer	Hot Plate and Megnetic stirrer, LMS-100, Korea	
5	Water bath with shaker	BS-11,230 VAC-50Hz, (KOREA)	
6	Centerifuge	Hermie Laborti Chink Type Z 200 A, 6000rpm, (Germany)	
7	Distillation device	Luzpe A viso Agua Insuficicente, (Germany)	
8	Electric furnace	Type - Nabentherm, Max Temperature 1300 °C, 400V, IS.OA, 50160 HZ, (Germany)	
9	Ultrasonic Instrument	(Ningbo Runyes Medical Instrument, made in china)	
10	UV-Visible	(UV-Visible, spectrophotometer, Double beam(v-650), Japan).	
11	X-ray Diffraction spectroscopy XRD	XRD - 6000CU KA (1=1.5406A9) 220/50, HZ, Shimadzu, (Japan)	Ministry of Science and Technology
12	Field Emission Scanning Electron Microscope (FESEM)	Image Topography of Materials	MIRA3 TESCAN, College of Sharif University of Technology, Tehran, Iran
13	BET (Brunauer- Emmett-Teller)	Q-surf 9600 USA	Petroleum Research and Development Center inIraq

2.3 Preparation of Plant Extract

The plant extract was prepared by taking eucalyptus leaves from trees in Diyala governorate, and they were washed well with plain water and then with deionize water. The leaves were dried for two days in the shade, then they were cut and ground well, and 5 g was taken in 50 mL of distilled water, and heated for 30 min at a temperature of 70 °C with stirring, the extract is left to cool and then put it in a centrifuge for 5 min at a speed of 1600 rpm to get rid of the remaining living materials, and collected in a vial and kept at 25 °C.



Figure 2.1. Preparation of Plant Extract

2.4 Preparation of Metal Oxides Nanoparticles

2.4.1 . Preparation of Aluminum Oxide Nanoparticles

(0.3 g) of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ was dissolved in 50 mL of deionized water and stirred well using a magnetic stirrer. Take 10 mL of the extract and put it in a burette and gradually add to the mixture drop by drop at a temperature of 25 °C. Raise the temperature to 80°C and gradually add (0.1M) of sodium hydroxide was added gradually until the solution becomes basic (pH=8) and a precipitate is formed. Water and ethanol are used to wash the sediment and remove pollutants. The precipitate is dried at a temperature of 60°C for three hours, where nanopowder of aluminum hydroxide is formed, The formed powder is calcination for 5 hours at a temperature of 550°C, where nanopowder of aluminum oxide is formed.



Figure 2.2. Preparation of γ - Al_2O_3 nanoparticles from aqueous $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$



Figure 2.3. Preparation of γ - Al_2O_3 nanoparticles from aqueous $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$

2.4.2. Preparation of α - Fe_2O_3 Nanoparticles

(0.3 g) of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 50 mL of deionize water and stirred well using a magnetic stirrer. Take 10ml of the extract and put it in a burette and gradually add to the mixture drop by drop at a temperature of 25 °C. Raise the temperature to 80°C and gradually add 0.1M of sodium hydroxide until the solution becomes basic (pH=8) and a precipitate is formed. Water and ethanol are used to wash the sediment and remove pollutants. The precipitate is dried at a temperature of 60°C for three hours, where nano iron hydroxide powder is formed, the formed powder is calcination for 5 hours at a temperature of 550°C, where iron oxide nanoparticles is formed.



Figure 2.4. Preparation of α - Fe_2O_3 nanoparticles from aqueous $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ salt



Figure 2.5. Preparation of α -Fe₂O₃ nanoparticles from aqueous FeSO₄·7H₂O

2.4.3. Preparation of α -Fe₂O₃ / Paraffin Nanocomposite

(0.3 g) of nano iron oxide was taken and dispersion in 20 mL of ethanol and placed in the ultrasonic bath for 30 min and then 20 mL of paraffin was taken and placed in the ultrasonic device for 30 min at a temperature of 50 °C. Then the nano-oxide suspension was gradually added to the paraffin and placed in the ultrasonic device for (2h) and left to dry.



Figure 2.6. Preparation of the α -Fe₂O₃ / paraffin nanocomposite produced from FeSO₄·7H₂O and paraffin



Figure 2.7. Preparation of the α - Fe_2O_3 / paraffin nanocomposite from $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ with paraffin

2.4.4. Preparation of γ - Al_2O_3 /Paraffine Nanocomposite

(0.7 g) of nano iron oxide was taken and dispersion in 20 mL of ethanol and placed in the ultrasonic device for 30 min and then 20 mL of paraffin was taken and placed in the ultrasonic device for 30 min at a temperature of 50 °C. The nano oxide suspension was gradually added to the Paraffin is placed in the ultrasound machine for 2hrs and left to dry.



Figure 2.8. Preparation of the γ - Al_2O_3 /paraffine nanocomposite produced from $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ and paraffin



Figure 2.9. Preparation of γ - Al_2O_3 /paraffine nanocomposite produced from $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and paraffin

2.4.5 Preparation of α - Fe_2O_3 /AC Nanocomposite

(0.3 g) of nano iron oxide from iron sulfate was taken in 20 mL of ethanol and placed in the ultrasound machine for 30 min and then (0.3 g) of activated charcoal was taken and dispersion in 20 mL of ethanol and placed in the ultrasonic device for a period 30 min at a temperature of 50 °C The nano-oxide suspension is gradually added to the activated charcoal and placed in the ultrasound machine for 2hrs and left to dry.



Figure 2.10. Preparation of the α - Fe_2O_3 /AC nanocomposite produced from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and activated charcoal

2.4.6 Preparation of γ - Al_2O_3 /AC Nanocomposites

(0.7 g) of nanoporous aluminum oxide, sourced from aluminum sulfate, was taken in 20 mL of ethanol and placed in the ultrasonic device for 30 min and then (0.3 g) of activated charcoal was taken and dispersion in 20 mL of ethanol and placed in the ultrasonic device for a period 30 min at a temperature of 50 °C The nano-oxide suspension is gradually added to the activated charcoal and placed in the ultrasound machine for 2hrs and left to dry.



Figure 2.11. Preparation of the γ - $\text{Al}_2\text{O}_3/\text{AC}$ nanocomposites produced from $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ and activated charcoal

2.5 Determination of the Calibration Curve for Methyl Orange M.O

A solution of methyl orange M.O dye was prepared at a concentration of (1000 ppm) by dissolving (1 g) of the dye in (1000 mL) of deionize water. From this solution, solutions of different concentrations were prepared by taking the appropriate volume of the solution and diluting it with distilled water. In order to determine the wavelength at which the highest absorption (λ_{max}) occurs, a UV-visible spectrometer was used within the range (200-800nm) for the purpose of recording the absorption spectrum using a quartz cell whose cross-section length is (1 cm). The wavelength (λ_{max}) was determined as in Figure (1-3) at 465 nm. Then the absorbance of these solutions was measured at a wavelength (465 nm) using a UV-visible spectrophotometer, and then Lambert - Bear law was applied by plotting the

absorbance versus the concentration to extract the molar absorption coefficient.

$$A = \epsilon b c \quad \dots\dots\dots (2-1)$$

Since:-

A: - absorbency

ϵ :- molar absorption coefficient

b:- cell thickness

C:- concentration

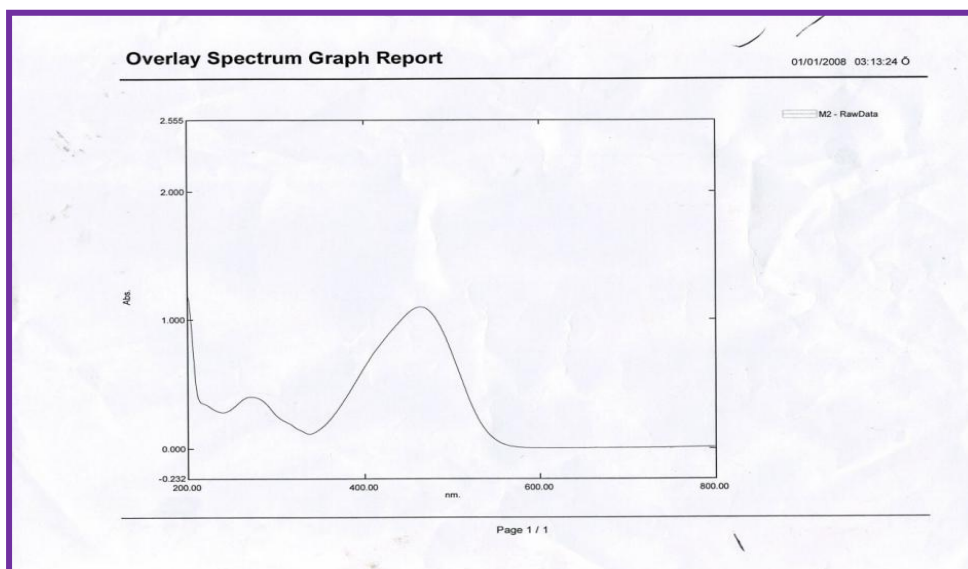


Figure 2.12. UV Visible Absorption Spectrum for methyl orange M.O dye

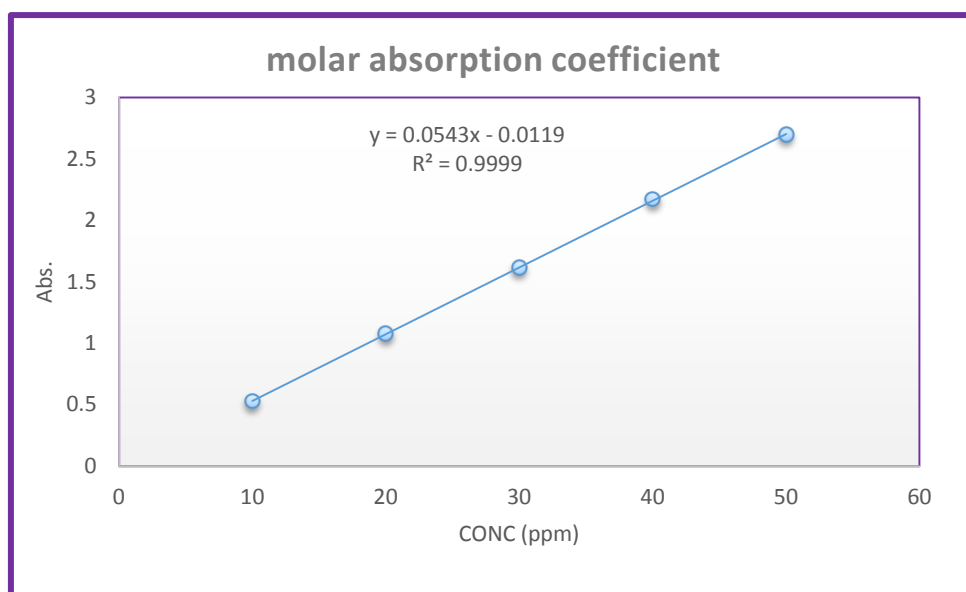


Figure 2.13. Determination of the molar absorption coefficient of methyl orange M.O dye at ($\lambda=465$ nm)

2.6. Determining the Optimum Conditions for Removing the Methyl Orange Dye

2.6.1. Determination of equilibrium time

Six volumetric flasks, each with a volume of 100 ml, were used to test the amount of time needed for the adsorption process to reach equilibrium at 298 K. Each flask contained 30 ml of methyl orange dye solution, which had an initial concentration of (50ppm), and 0.1 g of either nano oxides ($\gamma\text{-Al}_2\text{O}_3$), ($\alpha\text{-Fe}_2\text{O}_3$), ($\alpha\text{-Fe}_2\text{O}_3$ /paraffine, $\gamma\text{-Al}_2\text{O}_3$ /paraffine, $\alpha\text{-Fe}_2\text{O}_3$ /AC and $\gamma\text{-Al}_2\text{O}_3$ /AC) was added into each flask and covered them with glass stopper and placed in a water bath shaker at constant temperature of (298) K at speed of (150) rpm at various time intervals (10, 20, 30, 40, 50,60 min) . and the adsorbed quantities were found using spectroscopic methods by following the adsorption process at the maximum wavelength of the dye 465nm. The results are that the time required to reach the equilibrium state is (60 min).

2.6.2.Determination of Adsorbent Weight

The impact of adsorbent quantity was investigated using (0.02,0.04,0.06,0.08,0.1 gm) From the adsorbent surface (γ -Al₂O₃), (α -Fe₂O₃), (α -Fe₂O₃/paraffine, γ -Al₂O₃/paraffine, α -Fe₂O₃/AC and γ -Al₂O₃/AC) put into each flask and covered them with glass stopper and placed in a water bath shaker at constant temperature of (298) K at speed of (150) rpm and time fixed at 60 min . The adsorbed quantities were found using spectroscopic methods by following the adsorption process at the maximum wavelength of the dye 465nm, , as it was found that the optimal amount of adsorption was (0.1 g) for the compounds under study.

2.6.3 Effect of Heat

The study to the effect of temperature on the adsorption of methyl orange dye is determined by preparing four volumetric bottles of 100mL capacity) containing equal volumes (30mL) of the dye at a concentration of (50ppm) and (0.1g) of (γ -Al₂O₃), (α -Fe₂O₃), (α -Fe₂O₃/paraffine, γ -Al₂O₃/paraffine, α -Fe₂O₃/AC and γ -Al₂O₃/AC) These volumetric put in a water bath shaker (at 185 rpm) at (50) minute to reach equilibrium at different temperatures (30,50,70,90) After continuous shaking, the adsorbent surface was separated by using the centrifugal method (center fuge) at a time of 60 min.

Chapter Three

(Results and Discussion)

3.1. Characterization of the Nanomaterials

3.1.1. Fourier Transform Infrared (FTIR) Spectrum Analysis

The FTIR spectroscopy was used to confirm the synthesized products

3.1.1.1. FTIR of FeSO₄, FeCl₂, Fe(OH)₂ and α -Fe₂O₃ Nanoparticles

Figure 1 (a) shows the FTIR spectrum of Fe₂O₃ show two broad bands at (555 and 463) cm⁻¹, These peaks may correspond to Fe-O stretching and bending vibration mode. Figure 1 (b) the IR spectrum for FeSO₄ shows two broad bands at (3455 and 3144) cm⁻¹. The band at (3455) cm⁻¹ can be assigned to the stretching modes of surface H₂O molecules or to an envelope of hydrogen-bonded surface OH groups. The band at (3144) cm⁻¹ can be assigned to the OH stretching mode in the structure. The band at (1643) cm⁻¹ is close to the position of H₂O bending vibrations. Infrared spectrum figure 1(C) for Fe(OH)₂ showed two broad bands related to ν OH from iron species and adsorbed water in region near (3402 and 3152) cm⁻¹. The band corresponding to Fe-O stretching mode of Fe₂O₃ is seen at 576 cm. Figure 2 (a) shows the FTIR spectrum of Fe₂O₃ show two broad peaks at 555 and 463 cm⁻¹. These peaks may correspond to Fe-O stretching and bending vibration mode. Figure 2 (a) the FTIR spectrum of Fe₂O₃ shows clearly the characteristic absorption band at 576 cm⁻¹ attributed to the stretching vibration of the Fe-O bond of Fe₃O₄. Additional, the broad bands at around 3449 and 1634 cm⁻¹ can be attributed respectively to the stretching and bending vibrations of -OH groups on the surface of nanoparticles. Figure 2 (b) the IR spectrum for FeCl₂ shows two broad bands at 3455 and 3144 cm⁻¹. The IR band at 3455 cm⁻¹ can be assigned to the stretching modes of surface H₂O molecules or to an envelope of hydrogen-bonded surface OH groups. The IR band at 3144 cm⁻¹ can be assigned to the OH stretching mode in the goethite structure. The IR band at 1643 cm⁻¹ is close to the position of H₂O bending vibrations. A smaller-intensity bands at 1193 and 1126 cm⁻¹. Infrared spectrum figure 2(C) for Fe(OH)₂ showed two broad bands related to ν OH from iron species and

adsorbed water in region near 3402 and 3152 cm^{-1} . The band corresponding to Fe-O stretching mode of Fe_2O_3 is seen at 576 cm^{-1} . Figure 2 (a) shows the FTIR spectrum of Fe_2O_3 show two broad peaks at 555 and 463 cm^{-1} . These peaks may correspond to Fe-O stretching and bending vibration mode.

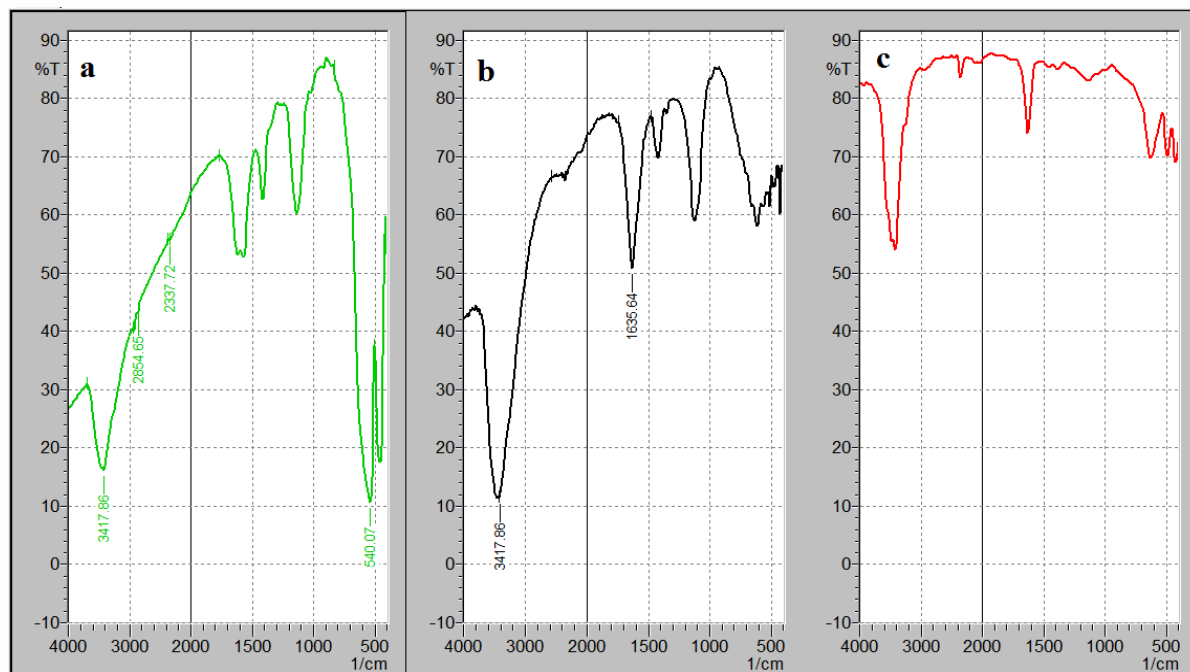


Figure 3.1. FTIR spectrum of (a) $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles (b) FeSO_4 salt and (c) Fe(OH)_2 nanoparticles

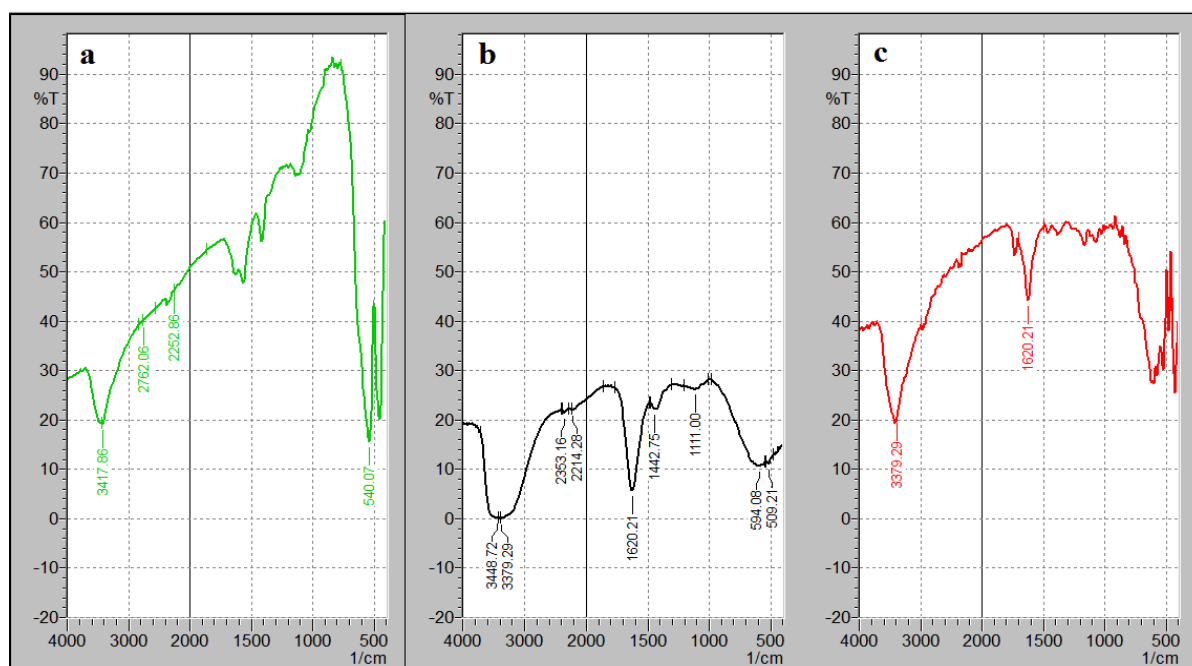


Figure 3.2. FTIR spectrum of (a) $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles (b) FeCl_2 salt and (c) Fe(OH)_2 nanoparticles

3.1.1.2. FTIR Analysis of $\text{Al}(\text{SO}_4)_3$, AlCl_3 , $\text{Al}(\text{OH})_3$ and $\gamma\text{-Al}_2\text{O}_3$ Nanoparticles

The Figure (3) a of Al_2O_3 shows two broad bands, the absorption bands are due to the vibration of the octahedral (Al-O) bond (Al-O) (507cm^{-1}) and the tetrahedral (626 cm^{-1}) which represents the The image approximately in the range 3150 cm^{-1} appears on the near-image on the hydroxyl (OH) groups. The Figure (3) b of $\text{Al}_2(\text{SO}_4)_3$ show absorbance at (940 and 713) cm^{-1} , assigned to $\nu\text{Al-SO}_3$ and $\nu\text{Al-O}$, respectively.

The Figure (3) C of $\text{Al}(\text{OH})_3$ nanoparticles exhibit peaks at 510 and 1082 cm^{-1} that correspond to the Al-O bonds. A large band around 3400 cm^{-1} is also observed, due to the -OH groups adsorbed on the nanoparticle surface. The Figure (4) a of Al_2O_3 shows two broad bands, the absorption bands are due to the vibration of the octahedral (Al-O) bond (Al-O) (507cm^{-1}) and the tetrahedral (626 cm^{-1}) which represents the The image approximately in the range 3150 cm^{-1} appears on the near-image on the hydroxyl (OH) groups. The Figure (4) b of AlCl_3 show absorbance at 614 , assigned to Al-O and also large band around 3400 cm^{-1} is also observed refered to OH, respectively. The Figure (4) C of $\text{Al}(\text{OH})_3$ nanoparticles exhibit peaks at 510 and 1082 cm^{-1} that correspond to the Al-O bonds. A large band around 3400 cm^{-1} is also observed, due to the -OH groups adsorbed on the nanoparticle surface.

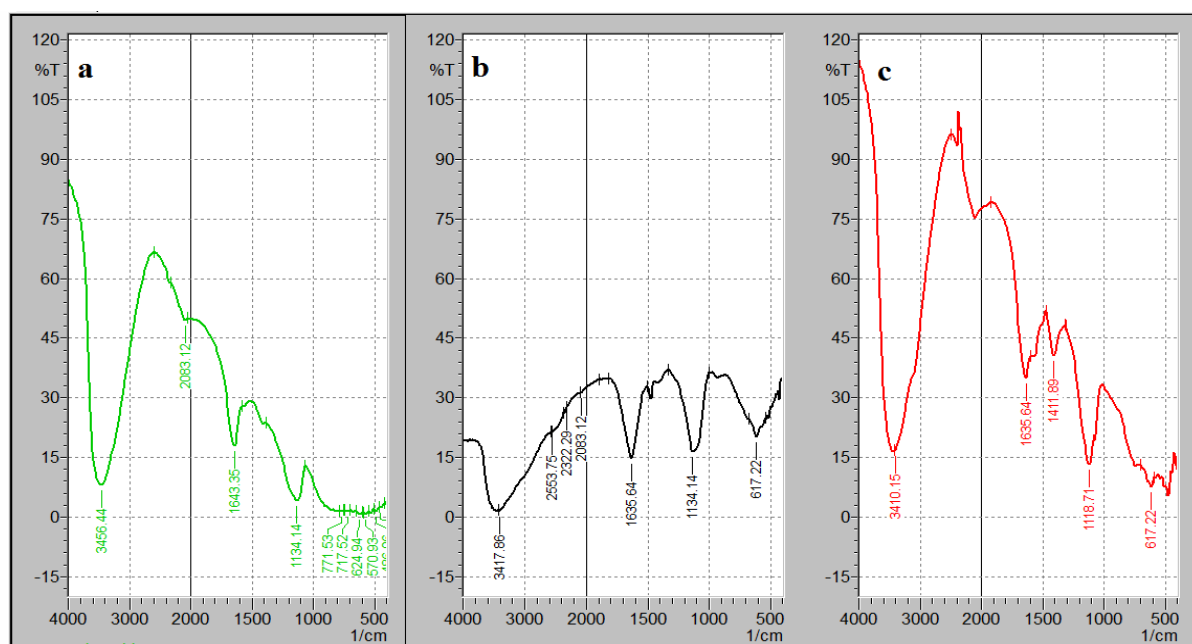


Figure 3.3. FTIR spectrum of (a) $\gamma\text{-Al}_2\text{O}_3$ nanoparticles (b) $\text{Al}(\text{SO}_4)_3$ salt and (c) $\text{Al}(\text{OH})_3$ nanoparticles

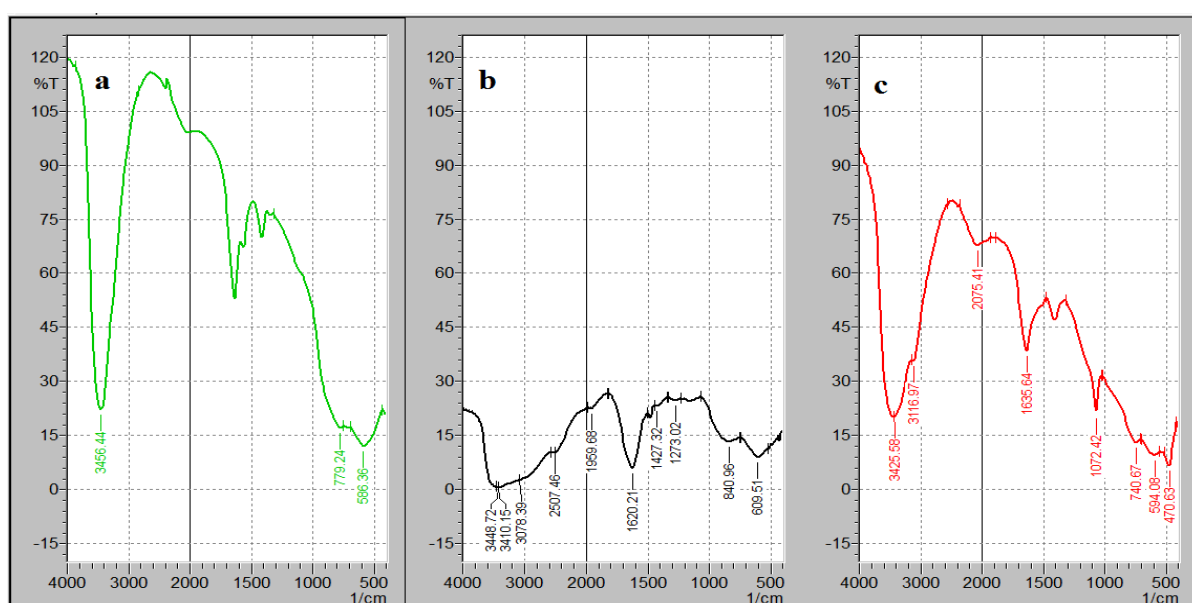


Figure 3.4. FTIR spectrum of (a) $\gamma\text{-Al}_2\text{O}_3$ nanoparticles (b) AlCl_3 salt and (c) $\text{Al}(\text{OH})_3$ nanoparticles

3.1.2. X-Ray Diffraction Analysis of α -Fe₂O₃ and γ -Al₂O₃ Nanoparticles

To study the fine structure of the material and know its crystal structure, this technique is used. To calculate the average size of the prepared crystals, The Debye–Scherrer equation is used.

$$D = \frac{K\lambda}{\beta \cos \theta} \dots\dots\dots (1-3)$$

$$\beta = \frac{\text{FWHM} \times 3.14}{180} \dots\dots\dots (2-3)$$

D = average crystal grain size

k = constant and represents the form factor and depends on the shape of the crystal of the objects and its value is often (0.94)

λ = X-ray wavelength and is about 0.1546 nm

β = width of the beam at average maximum height

Cos θ = cosine of the angle

1. X-Ray Diffraction α -Fe₂O₃

The X-ray diffraction examination of the Iron oxide nanoparticles α -Fe₂O₃ as shown in Figure (3-5 a) showing the presence of three strong peaks at (24.3 , 33.3 , 35.8). All diffraction data are in good agreement with Ref. Code files **No. 00-013-0534**. The size of the nanoparticles was also determined by the Debye-Scherrer equation and it was found that the size of the nanoparticles is (40.8 nm). The X-ray diffraction examination of the Iron oxide nanoparticles α -Fe₂O₃ as shown in Figure (3-5 b) showing the presence of three strong peaks at (24.3 , 31.9 , 33.4).). All diffraction data are in good agreement with Ref. Code files **No. 00-013-0534**. The size of the nanoparticles was also determined by the Debye-Scherrer equation and it was found that the size of the nanoparticles is (48.4 nm).

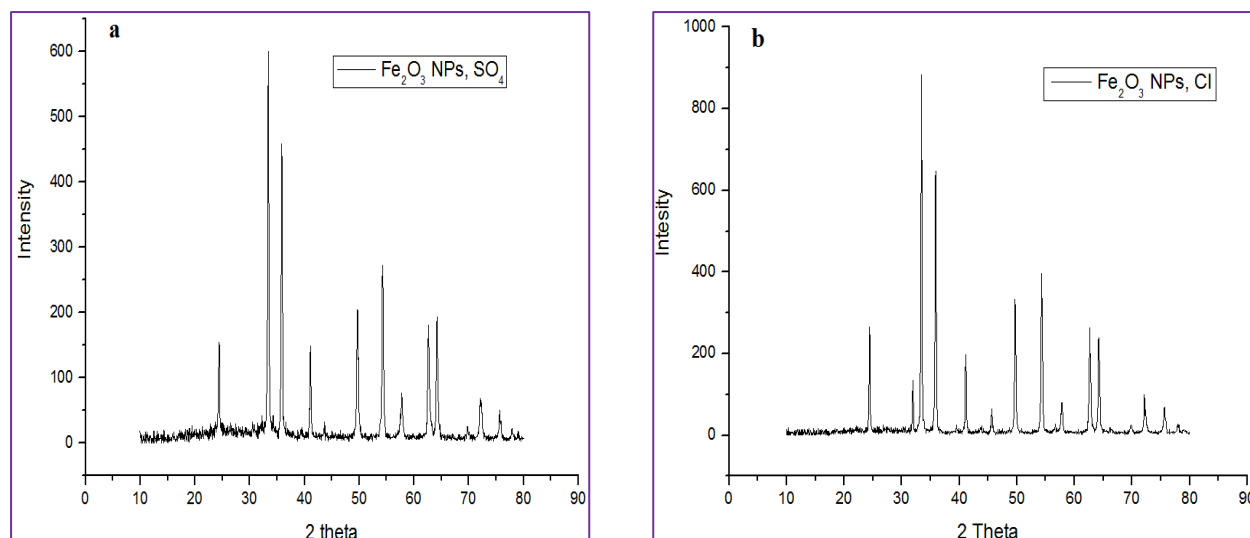


Figure 3.5. XRD pattern of (a) α - Fe_2O_3 NPs from FeSO_4 precursor, (b) α - Fe_2O_3 NPs from FeCl_2 precursor

2.X-Ray Diffraction γ - Al_2O_3

The X-ray diffraction examination of the aluminum oxide nanoparticles γ - Al_2O_3 as shown in Figure (3-6 a) and have three strong peaks at (37.9 , 46.2 , 66.9).).All diffraction data are in good agreementwith Ref.Code files **No. 01-075-00921**.The size of the nanoparticles was also determined by the Debye-Scherrer equation and it was found that the size of the nanoparticles is (9.2 nm). The X-ray diffraction examination of the aluminum oxide nanoparticles γ - Al_2O_3 as shown in Figure (3-6 b) showing the presence of three strong peaks at (31.9 , 45.6 , 56.6).).All diffraction data are in good agreementwith Ref.Code files **No. 01-075-0921**.The size of the nanoparticles was also determined by the Debye-Scherrer equation and it was found that the size of the nanoparticles is (37.47 nm).

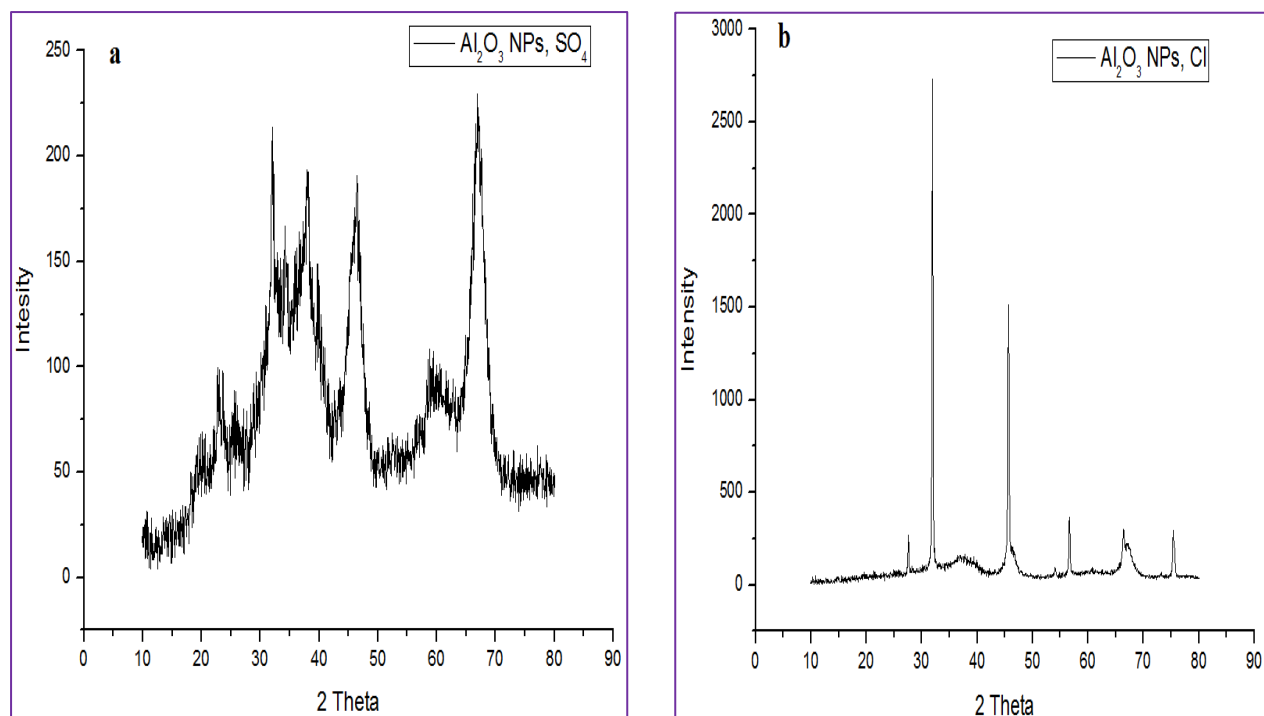


Figure 3.6. XRD pattern of (a) γ - Al_2O_3 NPs from $\text{Al}(\text{SO}_4)_3$ precursor, (b) γ - Al_2O_3 NPs from AlCl_3 precursor

3.1.3. FESEM Image of all Samples Nanoparticles

3.1.3.1. FESEM Image of $\text{Fe}(\text{OH})_2$ and α - Fe_2O_3 Nanoparticles

FESEM images of the $\text{Fe}(\text{OH})_2$ nanoparticles are shown in figures (3-7 a&b) and revealed spherical nanoparticles. The spherical nanoparticles belong to the $\text{Fe}(\text{OH})_2$ nanoparticles from sulfate and chloride precursor with average diameters (122.46-45.28nm), respectively. FESEM images of the α - Fe_2O_3 nanoparticles are shown in Figures (3-8 a&b) and revealed spherical nanoparticles spherical nanoparticles belong to the α - Fe_2O_3 nanoparticles from sulfate and chloride precursor with average diameters (163.2-389.3nm), respectively. And their distribution is irregular and also the appearance of clusters of some nanoparticles can be observed.

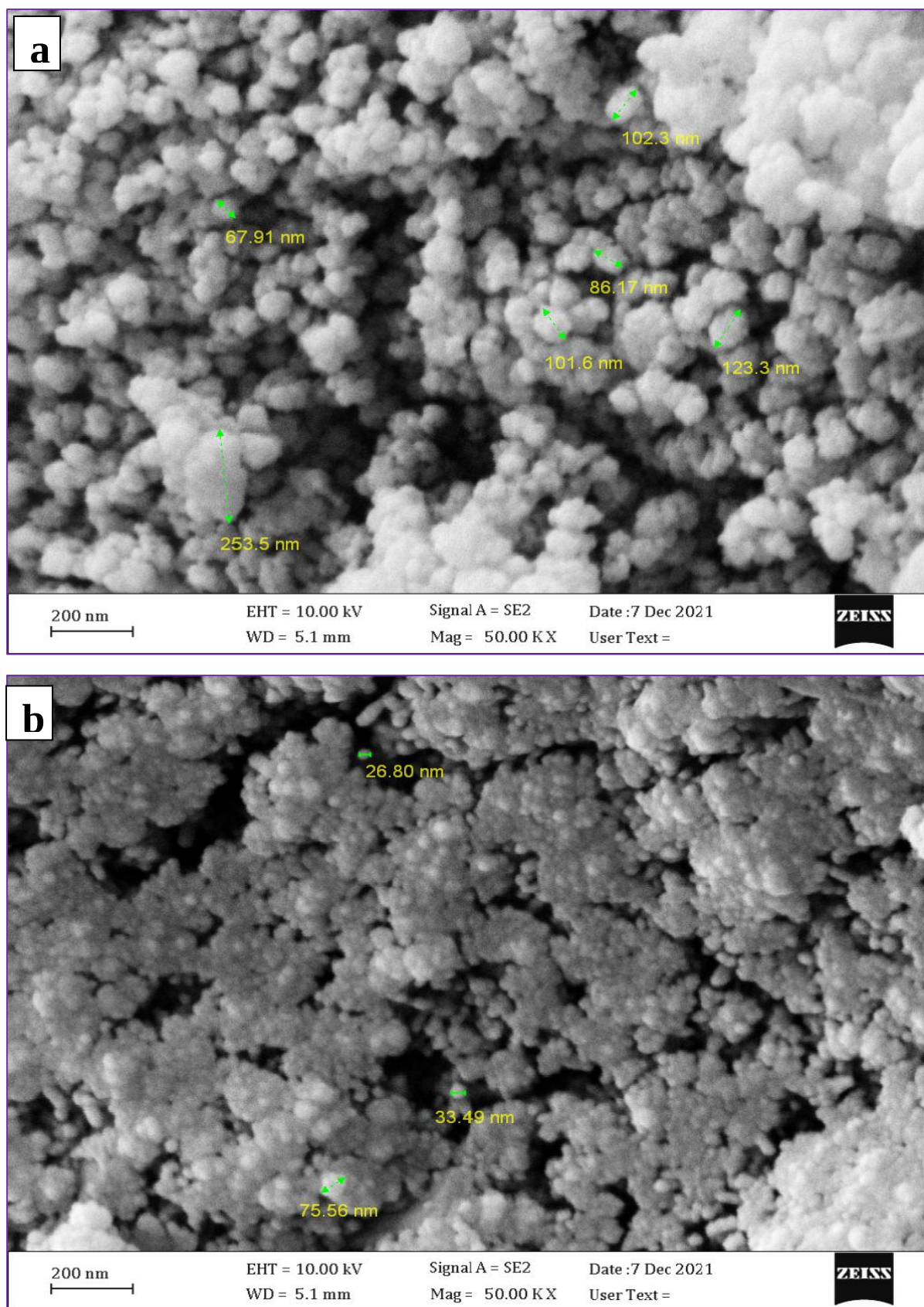


Figure 3. 7. FESEM images precursor of (a) $\text{Fe}(\text{OH})_2$ NPs from FeSO_4 precursor, (b) $\text{Fe}(\text{OH})_2$ NPs from FeCl_2

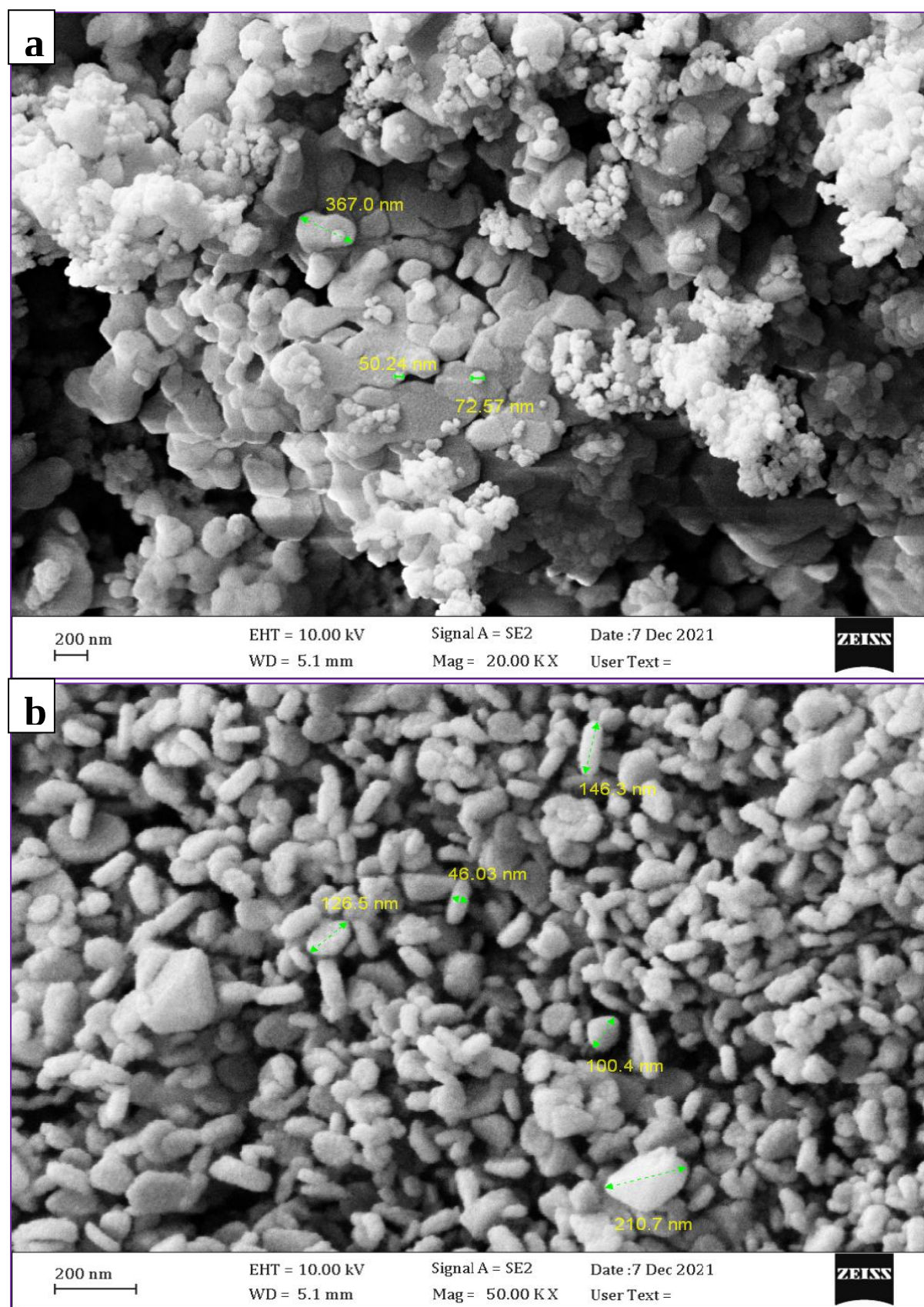
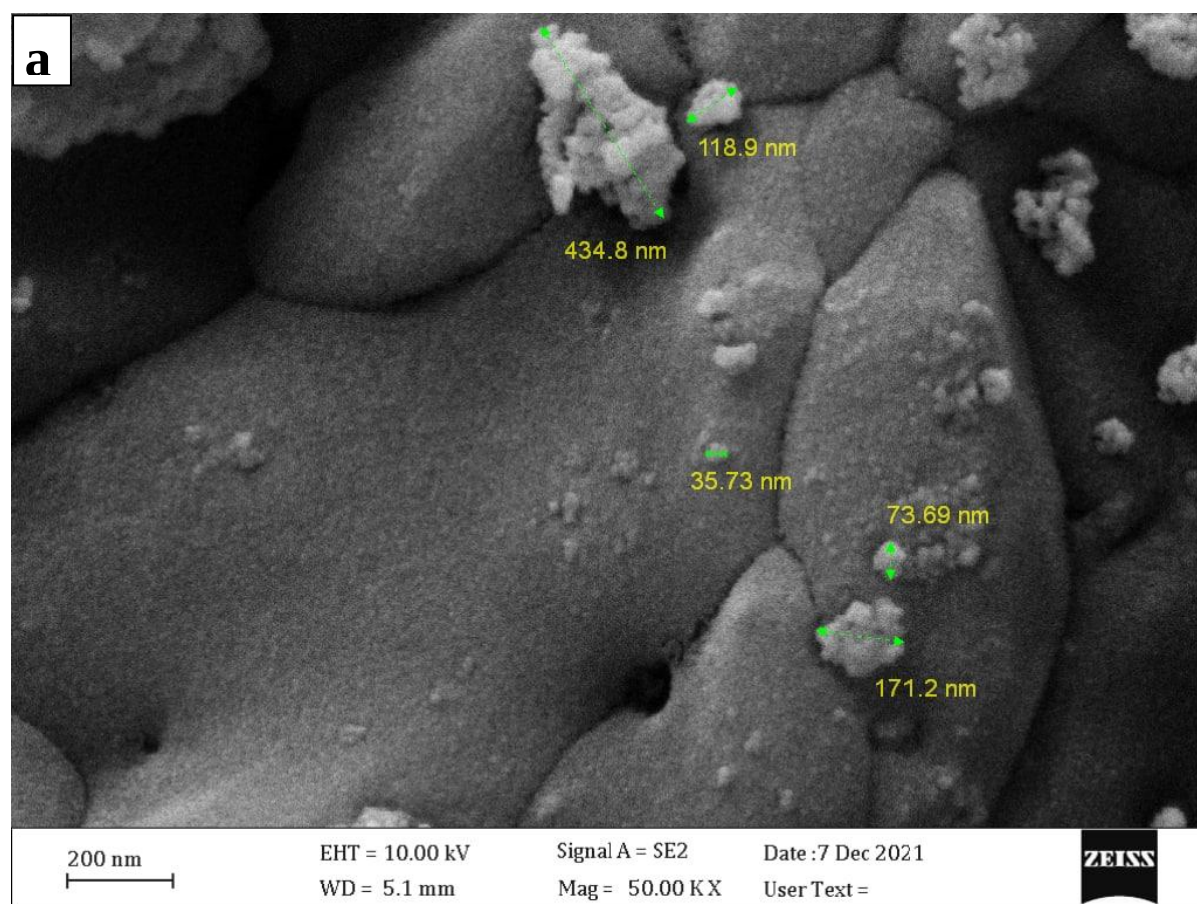


Figure 3.8. FESEM images of (a) α -Fe₂O₃ NPs from FeSO₄ precursor, (b) α -Fe₂O₃ NPs from FeCl₂ precursor

3.1.3.2. FESEM Image of $\text{Al}(\text{OH})_3$ and $\gamma\text{-Al}_2\text{O}_3$ Nanoparticles

Scanning electron microscopy examination of aluminum hydroxide produced from aluminum sulfate and aluminum chloride (a) $\text{Al}(\text{OH})_3$ NPs from $\text{Al}(\text{SO}_4)_3$ precursor, (b) $\text{Al}(\text{OH})_3$ NPs from AlCl_3 precursor

From figures (3-9) (a,b) the nanoparticles are in the form of clumps and scales, and the size of the nanoparticles is within (a) (166.8 nm) and (b) (299.1 nm) and their distribution is in the form of It is irregular and clumps of some nanoparticles can also be observed. Scanning electron microscopy examination of aluminum oxide produced from aluminum sulfate and aluminum chloride (a) $\gamma\text{-Al}_2\text{O}_3$ NPs from $\text{Al}(\text{SO}_4)_3$ precursor, (b) $\gamma\text{-Al}_2\text{O}_3$ NPs from AlCl_3 precursor are shown in Figure (3-10) (a,b) and show that the nanoparticles are in the form of cavities and that the size of the nanoparticles is within (a) (405.8 nm) and (b) (146.2 nm) and that their distribution is in the form of It is irregular and clumps of some nanoparticles can also be observed .



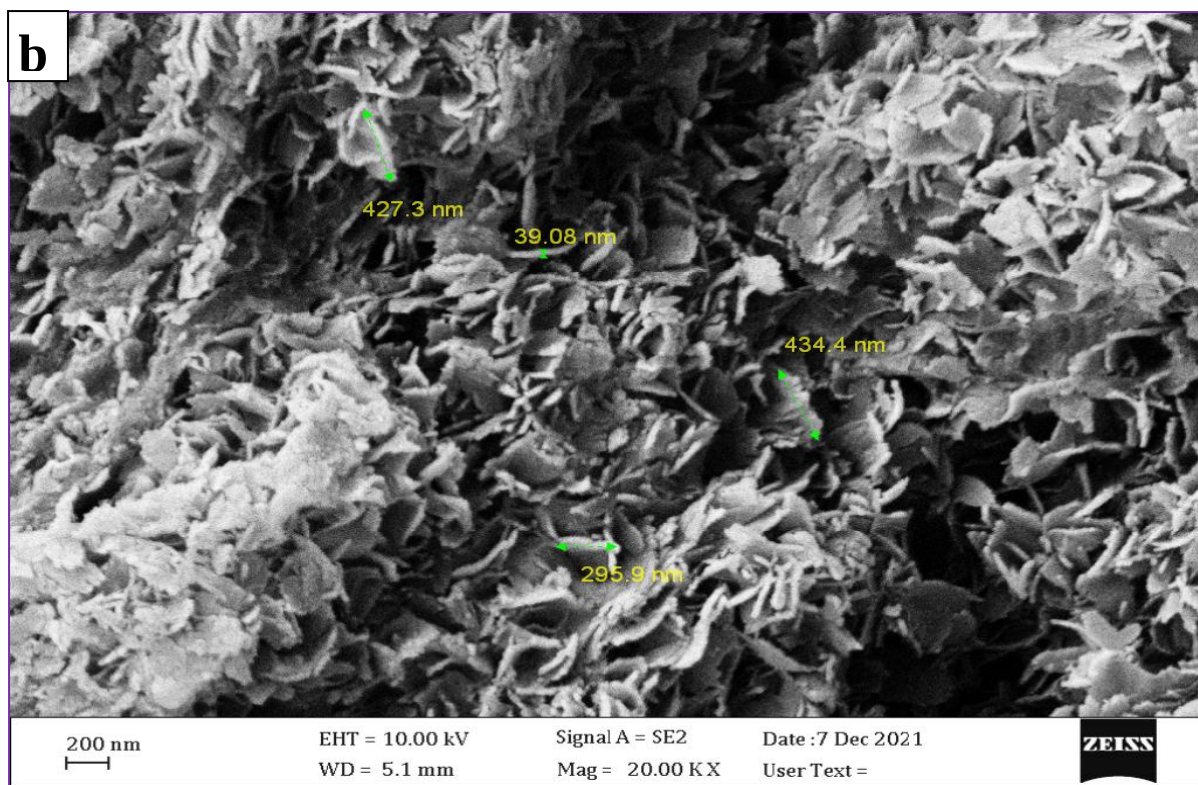
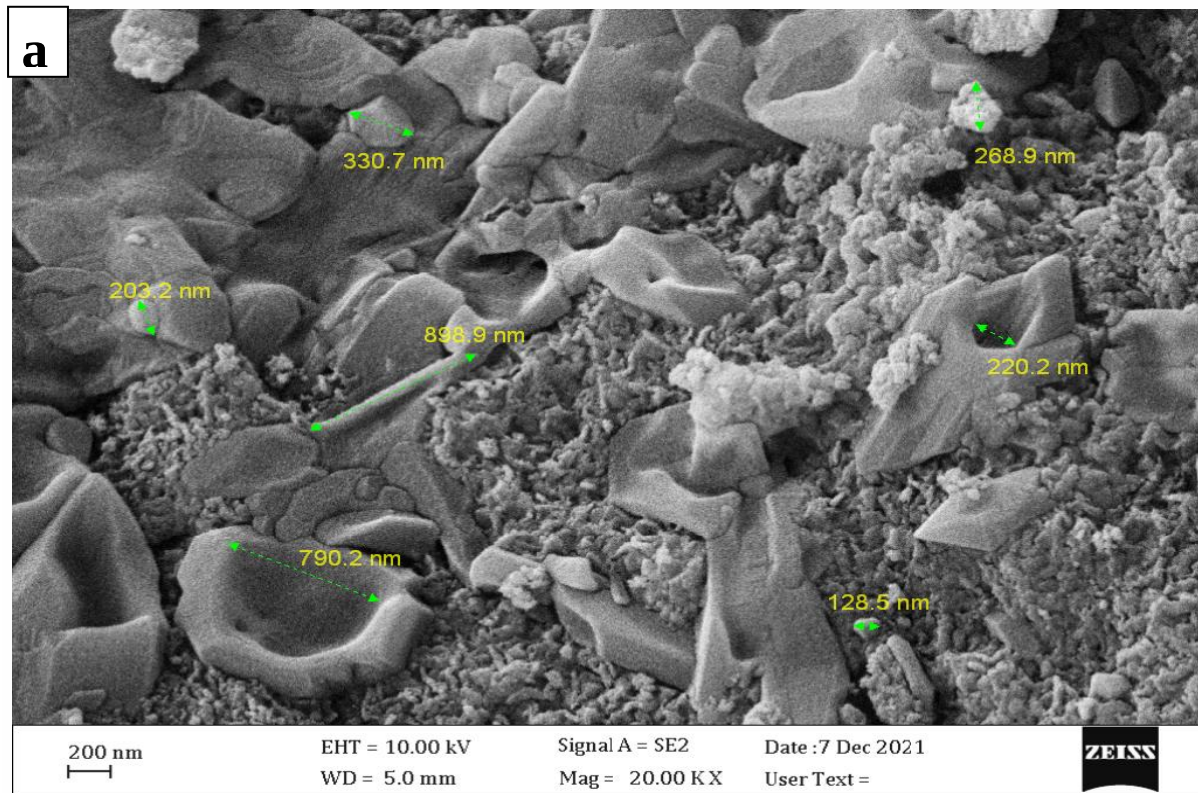


Figure 3.9..FESEM images of (a) $\text{Al}(\text{OH})_3$ NPs from $\text{Al}(\text{SO}_4)_3$ precursor, (b) $\text{Al}(\text{OH})_3$ NPs from AlCl_3 precursor



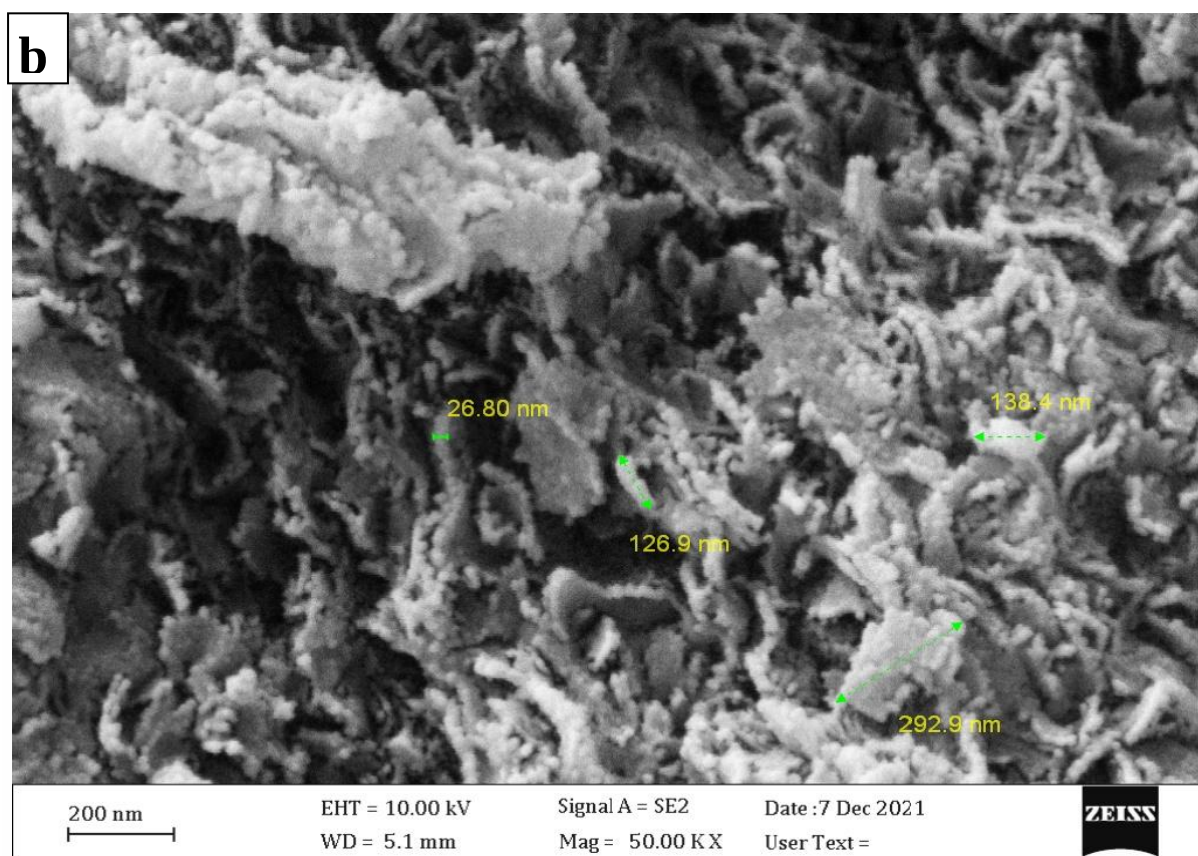


Figure 3.10. FESEM images of (a) γ - Al_2O_3 NPs from $\text{Al}(\text{SO}_4)_3$ precursor, (b) γ - Al_2O_3 NPs from AlCl_3 precursor

3.1.3.3. FESEM Image of the α - Fe_2O_3 /AC Nanocomposite

Scanning electron microscopy examination of iron oxide produced from iron sulfate with activated charcoal Fe_2O_3 /AC NPs from $\text{Fe}(\text{SO}_4)_2$ precursor. As shown in Figure (3-11) they show that the nanoparticles are in the form of clumps and scales, and that the size of the nanoparticles is within (50.24 nm, 201 nm) and their distribution is in the form of. It is irregular and clumps of some nanoparticles can also be observed.

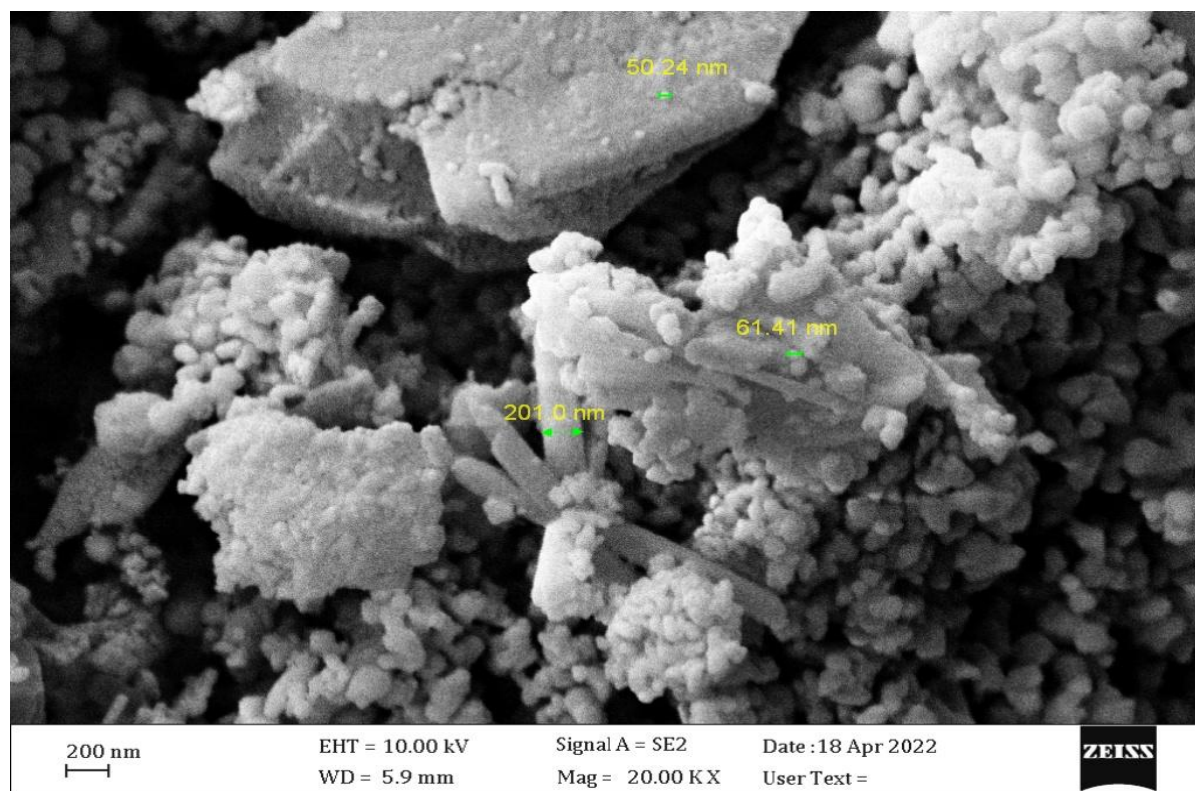


Figure 3.11. FESEM image of the α -Fe₂O₃ /AC nanocomposite produced from Fe(SO₄)₂ and activated charcoal

3.1.3.4. FESEM Image of γ -Al₂O₃ NPs/ activated charcoal Nanocomposite

Scanning electron microscopy examination of iron oxide produced from iron sulfate with activated charcoal γ -Al₂O₃ /AC NPs from Al₂(SO₄)₂ precursor As shown in Figure (3-12) they show that the nanoparticles are in the form of clumps and scales, and that the size of the nanoparticles is within (27.9nm, 139nm) and their distribution is in the form of It is irregular and clumps of some nanoparticles can also be observed.

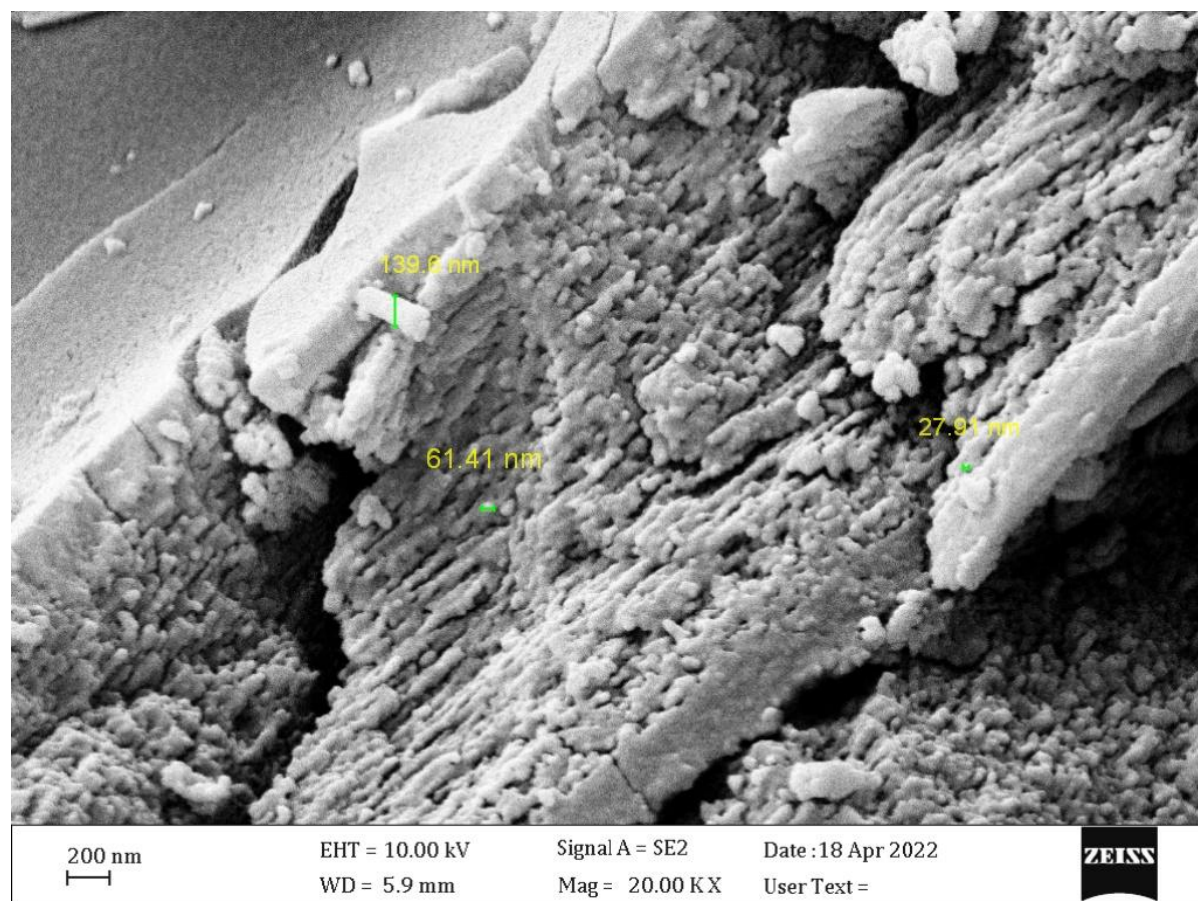


Figure 3.12. FESEM image of the γ - Al_2O_3 NPs/ activated charcoal nanocomposite produced from $\text{Al}(\text{SO}_4)_3$ with activated charcoal

3.1.4. The Surface Area (BET)

The surface area of nano-oxides were (α - Fe_2O_3 NPs from FeSO_4 precursor, α - Fe_2O_3 NPs from FeCl_2 precursor, γ - Al_2O_3 NPs from $\text{Al}(\text{SO}_4)_3$ precursor γ - Al_2O_3 NPs from AlCl_3 precursor), measured using BET and shear method) (Branuuer - Emmette - Teller), which includes the use of liquid nitrogen at a temperature of (77 K). The (BET) theory is currently used as a standard equation for isothermic adsorption analysis in order to obtain a specific surface area for solids. The surface area of nano-oxide (α - Fe_2O_3) NPs from FeSO_4 precursor) is ($10.616 \text{ m}^2/\text{g}$) Figure 3.13 (a) and nano-oxide (α - Fe_2O_3) NPs from FeCl_2 precursor) is ($3.3469 \text{ m}^2/\text{g}$) Figure 3.13 (b) and nano-oxide (γ - Al_2O_3 NPs from $\text{Al}(\text{SO}_4)_3$ precursor) is ($67.7 \text{ m}^2/\text{g}$) Figure 3.14(a) and nano-oxide (γ - Al_2O_3 NPs from AlCl_3 precursor) is ($102.8 \text{ m}^2/\text{g}$) Figure 3.14(b) . The surface

area of iron oxide complex produced from iron sulfate with activated charcoal(α -Fe₂O₃ NPs from FeSO₄ precursor/AC) is(184.43 m²/g) Figure 3.15 . the aluminum oxide produced from aluminum sulfate with activated charcoal(γ -Al₂O₃ NPs from Al(SO₄)₃ precursor/AC) is(142.21 m²/g) Figure 3.16.

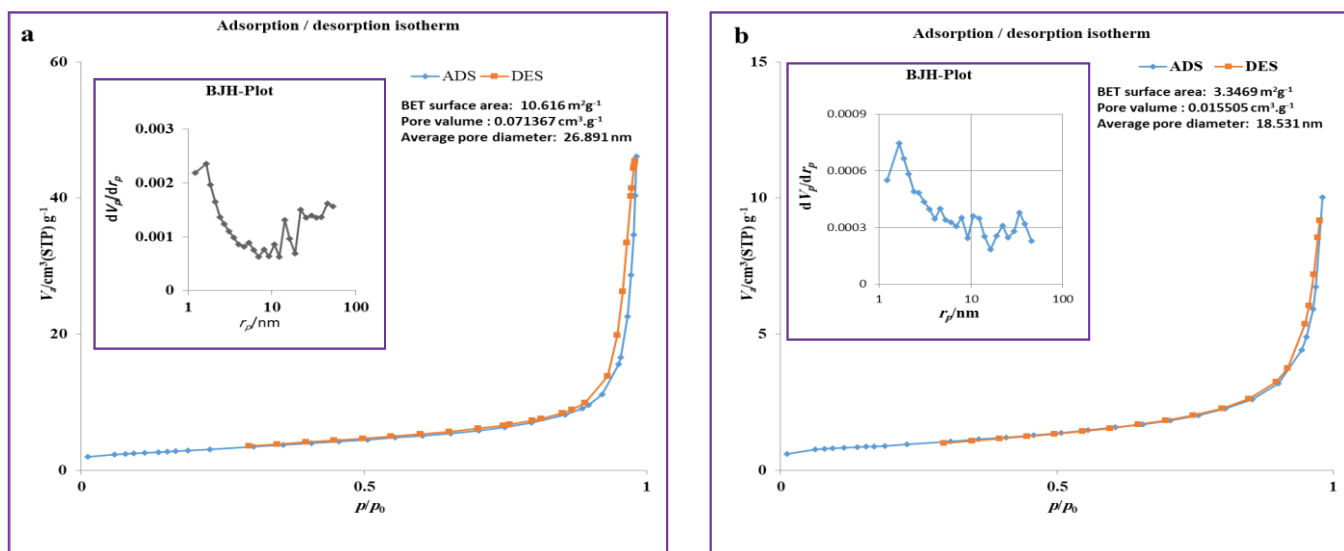


Figure 3.13. BET curve of (a) α -Fe₂O₃ NPs from FeSO₄ precursor, (b) α -Fe₂O₃ NPs from FeCl₂ precursor. (inset) BJH plot showing distribution of pores

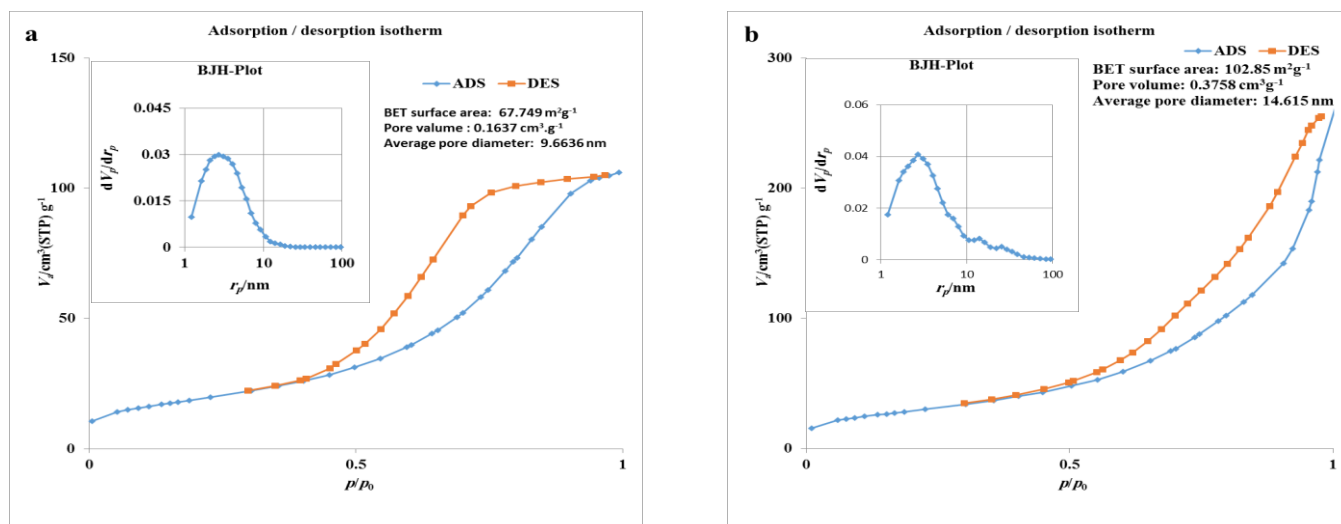


Figure 3.14. BET curve of (a) γ -Al₂O₃ NPs from Al(SO₄)₃ precursor, (b) γ -Al₂O₃ NPs from AlCl₃ precursor. (Inset) BJH plot showing distribution of pores

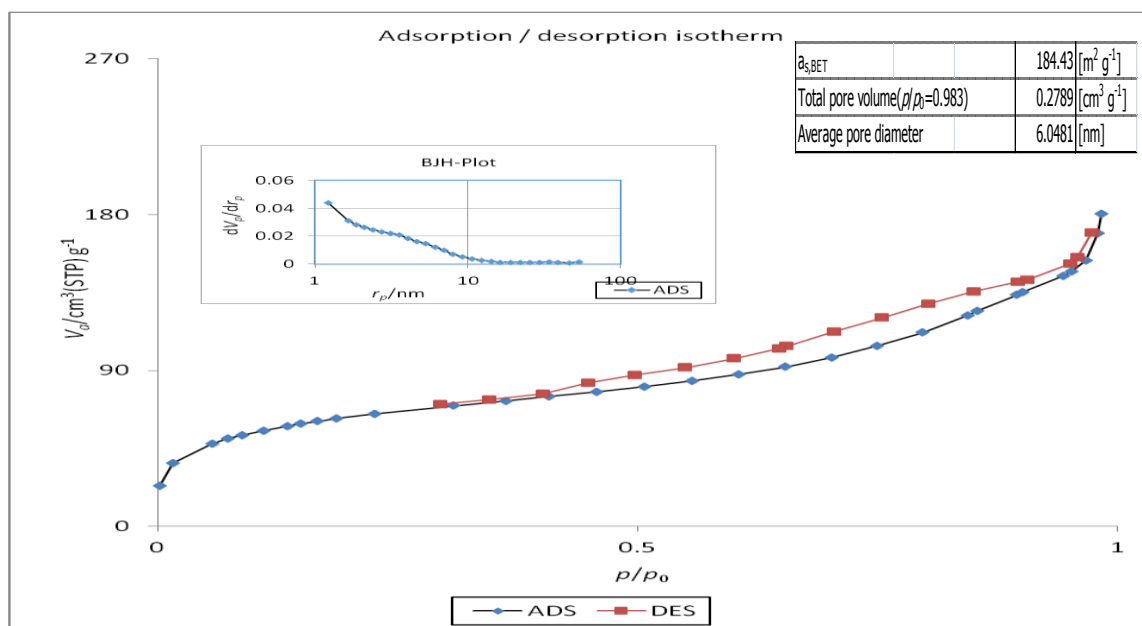


Figure 3.15. BET curve of α -Fe₂O₃/AC nanocomposite from FeSO₄ as a precursor

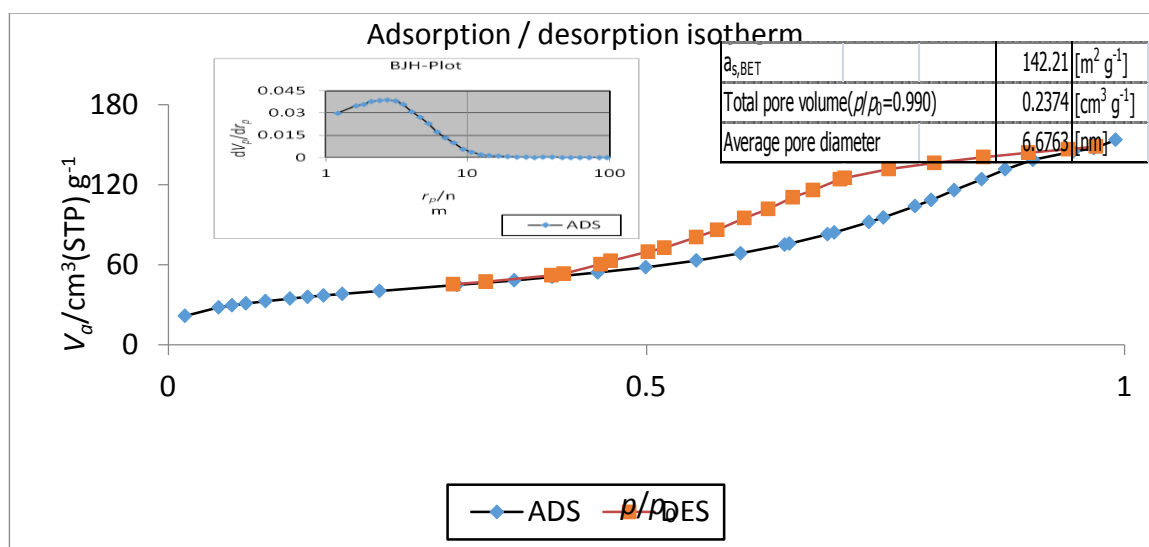


Figure 3.16. BET curve of γ -Al₂O₃ /AC nanocomposite from Al(SO₄)₃ as a precursor

3.1.5. DLS Study of α -Fe₂O₃ and γ -Al₂O₃ Nanoparticles

DLS Analysis Figures 3.17 A and B, shows DLS data for α -Fe₂O₃ which were prepared from sulfate and chloride iron. The diameter of 573 and 2690 nm with average nanoparticle size was found to be 691 nm for α -Fe₂O₃ which were prepared from sulfate and 587 and 125 nm with average nanoparticle size was

found to be 227 nm for α -Fe₂O₃ which was prepared from chloride precursor respectively. Obviously, all the nanoparticles were not same size, and the increase in the nanoparticle size can be attributed to the agglomeration of smaller nanoparticles, as well in case α -Fe₂O₃ that prepared from chloride precursor gave smaller nanoparticles

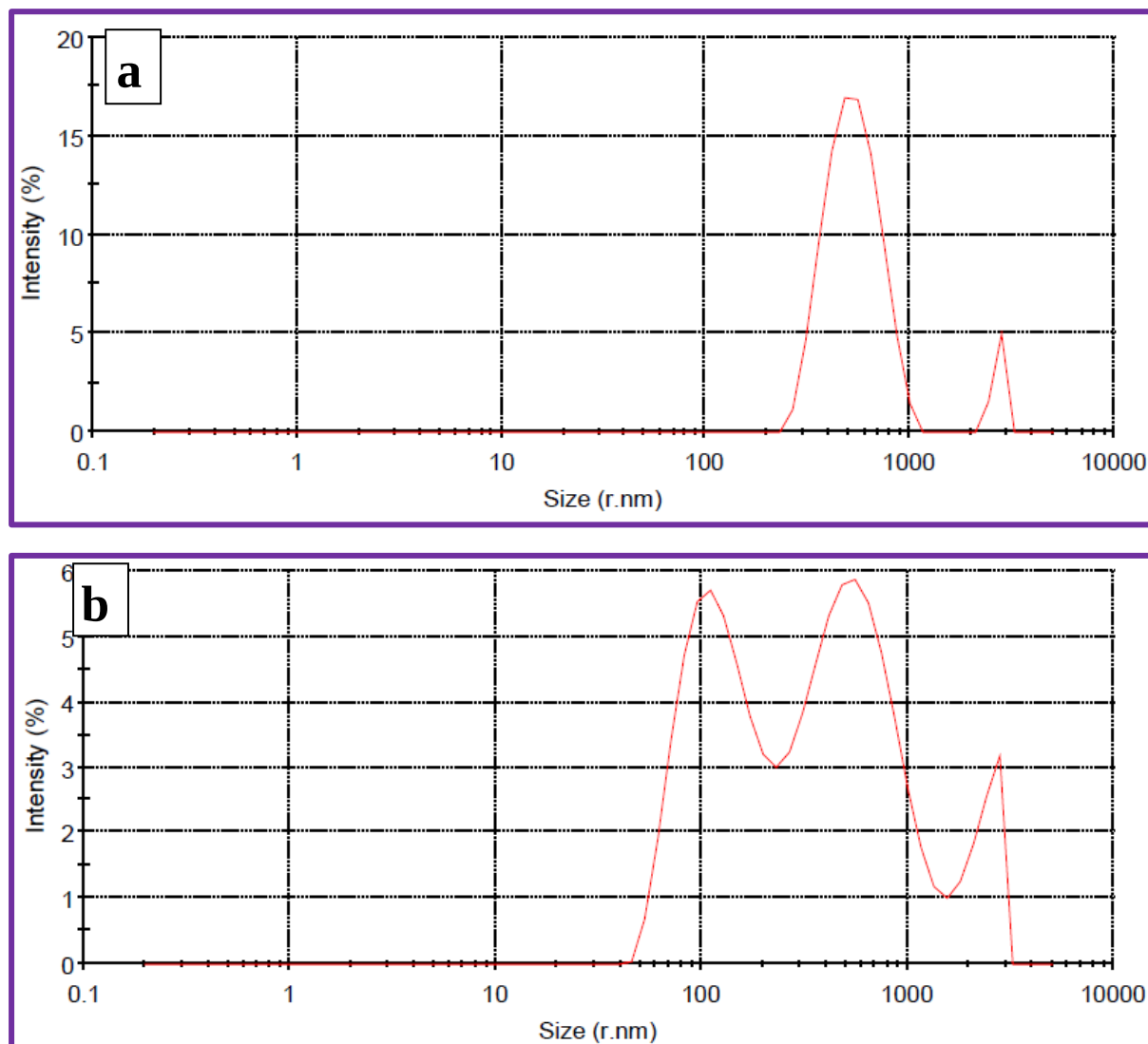


Figure 3.17. Particle size distribution for the (a) α -Fe₂O₃ NPs from FeSO₄ precursor, (b) α -Fe₂O₃ NPs from FeCl₂ precursor.

Figures 3.18 A and B, shows DLS data for γ -Al₂O₃ which were prepared from sulfate and chloride aluminum. The diameter of 174.7 nm with average nanoparticle size was found to be 652.3 nm for γ -Al₂O₃ which were prepared from sulfate and 256 nm with the average nanoparticle size was found to be 434nm for γ -Al₂O₃ which was prepared from chloride precursor respectively.

Showing that, all the nanoparticles were not same size, and the increase in the nanoparticle size can be attributed to the agglomeration of smaller nanoparticles, as well in case $\gamma\text{-Al}_2\text{O}_3$ that prepared from chloride precursor gave smaller nanoparticles.

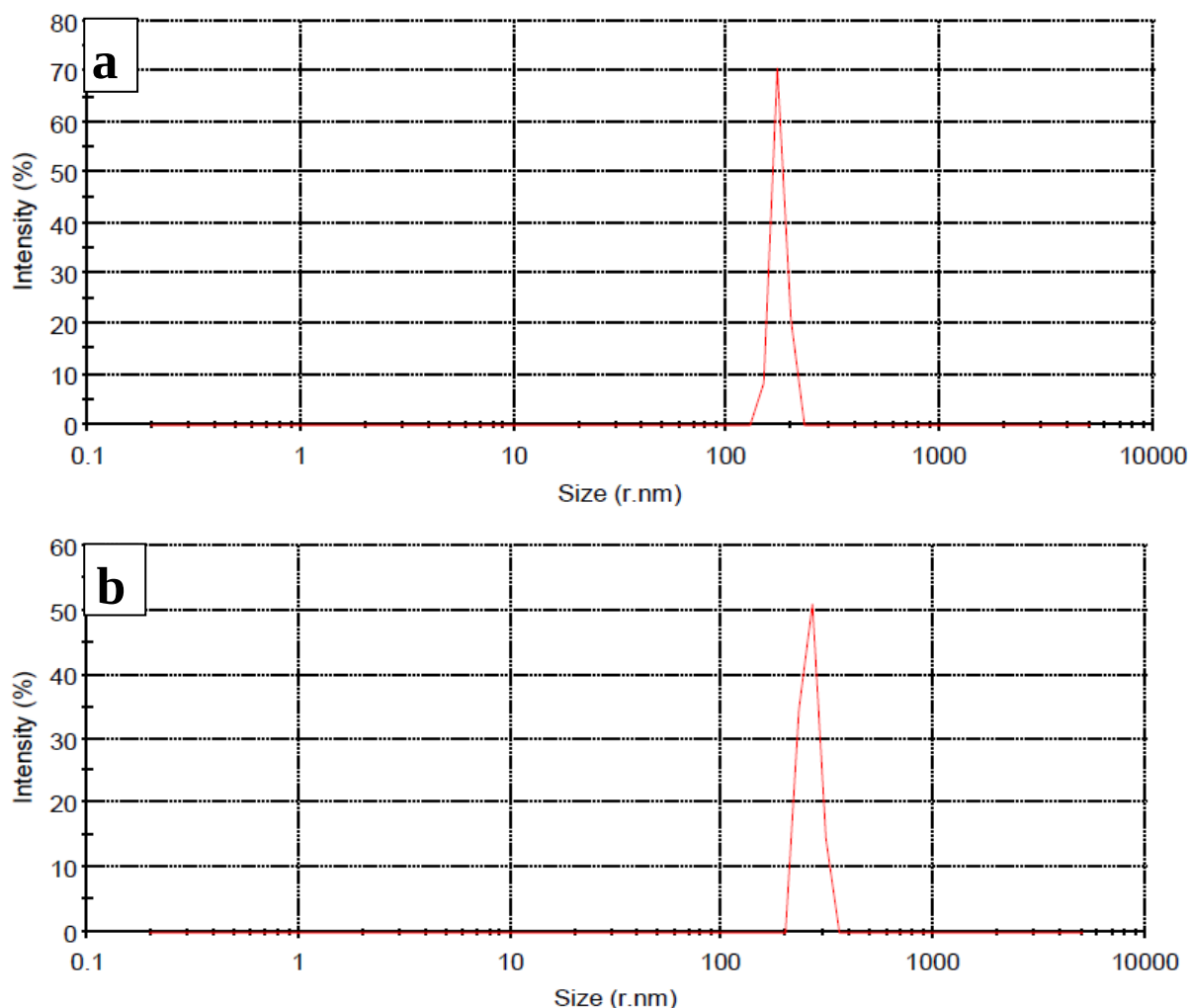


Figure 3.18. Particle size distribution for the (a) $\gamma\text{-Al}_2\text{O}_3$ NPs from $\text{Al}(\text{SO}_4)_3$ precursor, (b) $\gamma\text{-Al}_2\text{O}_3$ NPs from AlCl_3 precursor.

3.2. Adsorption of Methyl Orange Dye

The effect of contact time, adsorbent quantity and temperature effect on methyl orange dyes adsorption was studied using iron oxide and aluminum oxide nanoparticles that prepared from plant sources, in addition to metal oxide nanoparticles and the binary composite prepared from Fe_2O_3 and Al_2O_3 nanoparticles/ Activated carbon or paraffin. Initial concentration of methyl

orange dyes before carrying out the adsorption process by uv-visible was 50 mg/L.

3.2.1. Effect of Adsorbent Quantity on Adsorption

The effect of the weight of the adsorbent surface on the adsorption of methyl orange) was studied by changing the weight of Metal oxide nanoparticles and their nanocomposite (α -Fe₂O₃,SO₄NPs, α -Fe₂O₃,SO₄ NPs/AC, α - Fe₂O₃,Cl NPs α - Fe₂O₃,Cl NPs /AC, α - Fe₂O₃,SO₄ NPs/Pr, α - Fe₂O₃,Cl NPs /Pr, AC , pr, γ - Al₂O₃,SO₄ NPs, γ - Al₂O₃,Cl NPs, γ - Al₂O₃,SO₄ NPs/AC, γ - Al₂O₃ ,Cl NPs /AC, γ - Al₂O₃,SO₄ NPs/pr, γ - Al₂O₃,Cl NPs /Pr) with the original concentration of methyl orange remaining constant (50 ppm) at room temperature and constant time (30min). The highest percentage of removal of Metal oxide nanoparticles and their nanocomposite was at the weight (0.1 g).

Tables (3.1): Effect of nanoadsorbent dose on the adsorption of methyl orange at 298 K by all samples prepared

α - Fe ₂ O ₃ ,SO ₄ NPs				α - Fe ₂ O ₃ ,Cl NPs			
W, g	C ₀ mg/L	C _t mg/L	R%	W, g	C ₀ mg/L	C _t mg/L	R%
0.01	50	42.17	15.66	0.01	50	45.03	9.94
0.02		34.33	31.34	0.02		39.12	21.76
0.04		27.16	45.68	0.04		31.36	37.28
0.06		24.45	51.1	0.06		28.05	43.9
0.08		21.09	57.82	0.08		24.73	50.54
0.1		18.91	62.18	0.1		20.91	58.18
α - Fe ₂ O ₃ ,SO ₄ NPs /AC				α - Fe ₂ O ₃ ,Cl NPs /AC			
W, g	C ₀ mg/L	C _t mg/L	R%	W, g	C ₀ mg/L	C _t mg/L	R%
0.01	50	41.87	16.26	0.01	50	47.16	5.68
0.02		35.09	29.82	0.02		43.13	13.74
0.04		31.12	37.76	0.04		37.12	25.76
0.06		27.17	45.66	0.06		32.29	35.42
0.08		20.82	58.36	0.08		23.82	52.36
0.1		18.04	63.92	0.1		18.01	63.98
α - Fe ₂ O ₃ ,SO ₄ NPs /Pr				α - Fe ₂ O ₃ ,Cl NPs /Pr			
W, g	C ₀ mg/L	C _t mg/L	R%	W, g	C ₀ mg/L	C _t mg/L	R%
0.01	50	48.63	2.74	0.01	50	48.12	3.76
0.02		45.01	9.98	0.02		47.44	5.12
0.04		41.9	16.2	0.04		39.34	21.32
0.06		38.08	23.84	0.06		34.88	30.24

0.08		29.93	40.14	0.08		29.76	40.48
0.1		27.31	45.38	0.1		24.26	51.48
AC				Pr			
W, g	C ₀ mg/L	C _t mg/L	R%	W, g	C ₀ mg/L	C _t mg/L	R%
0.01	50	44.31	11.38	0.01	50	48.94	2.12
0.02		39.34	21.32	0.02		48.65	2.7
0.04		36.12	27.76	0.04		46.79	6.42
0.06		30.15	39.7	0.06		46.68	6.64
0.08		23.35	53.3	0.08		45.13	9.74
0.1		19.09	61.82	0.1		45.01	9.98
γ- Al ₂ O ₃ ,SO ₄ NPs				γ- Al ₂ O ₃ ,Cl NPs			
W, g	C ₀ mg/L	C _t mg/L	R%	W, g	C ₀ mg/L	C _t mg/L	R%
0.01	50	46.23	7.54	0.01	50	48.45	3.1
0.02		44.53	10.94	0.02		46.42	7.16
0.04		39.21	21.58	0.04		39.01	21.98
0.06		31.67	36.66	0.06		34.93	30.14
0.08		27.15	45.7	0.08		29.52	40.96
0.1		25.08	49.84	0.1		26.01	47.98
γ- Al ₂ O ₃ ,SO ₄ NPs /AC				γ- Al ₂ O ₃ ,Cl NPs /AC			
W, g	C ₀ mg/L	C _t mg/L	R%	W, g	C ₀ mg/L	C _t mg/L	R%
0.01	50	44.12	11.76	0.01	50	46.17	7.66
0.02		39.34	21.32	0.02		43.67	12.66
0.04		36.13	27.74	0.04		39.09	21.82
0.06		31.25	37.5	0.06		34.58	30.84
0.08		24.04	51.92	0.08		25.07	49.86
0.1		19.03	61.94	0.1		18.92	62.16
γ- Al ₂ O ₃ ,SO ₄ NPs /Pr				γ- Al ₂ O ₃ ,Cl NPs /Pr			
W, g	C ₀ mg/L	C _t mg/L	R%	W, g	C ₀ mg/L	C _t mg/L	R%
0.01	50	48.18	3.64	0.01	50	48.95	2.1
0.02		47.05	5.9	0.02		46.17	7.66
0.04		43.11	13.78	0.04		45.44	9.12
0.06		41.03	17.94	0.06		42.07	15.86
0.08		39.45	21.1	0.08		38.18	23.64
0.1		37.98	24.04	0.1		37.09	25.82

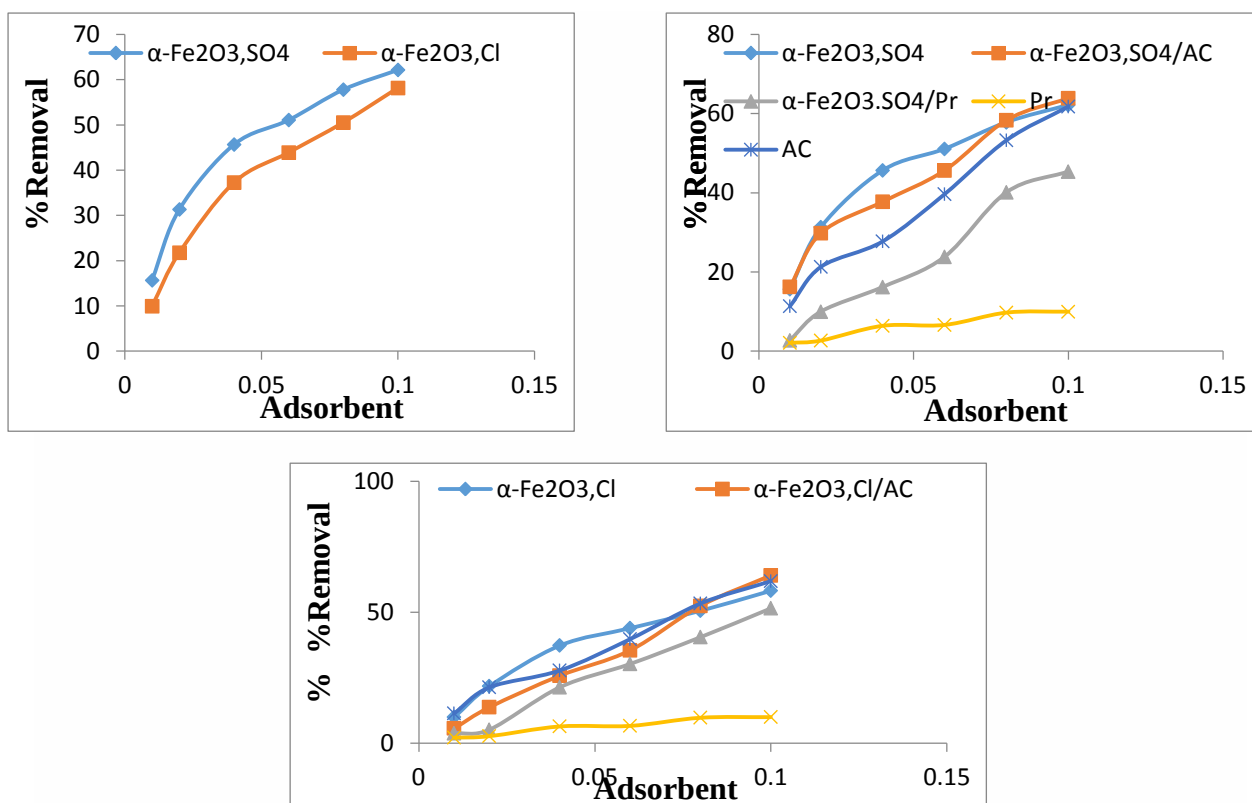


Figure 3.19. The effect of nano adsorbent dosage on the % removed of methyl orange dye by α -Fe₂O₃ NPs and their composite

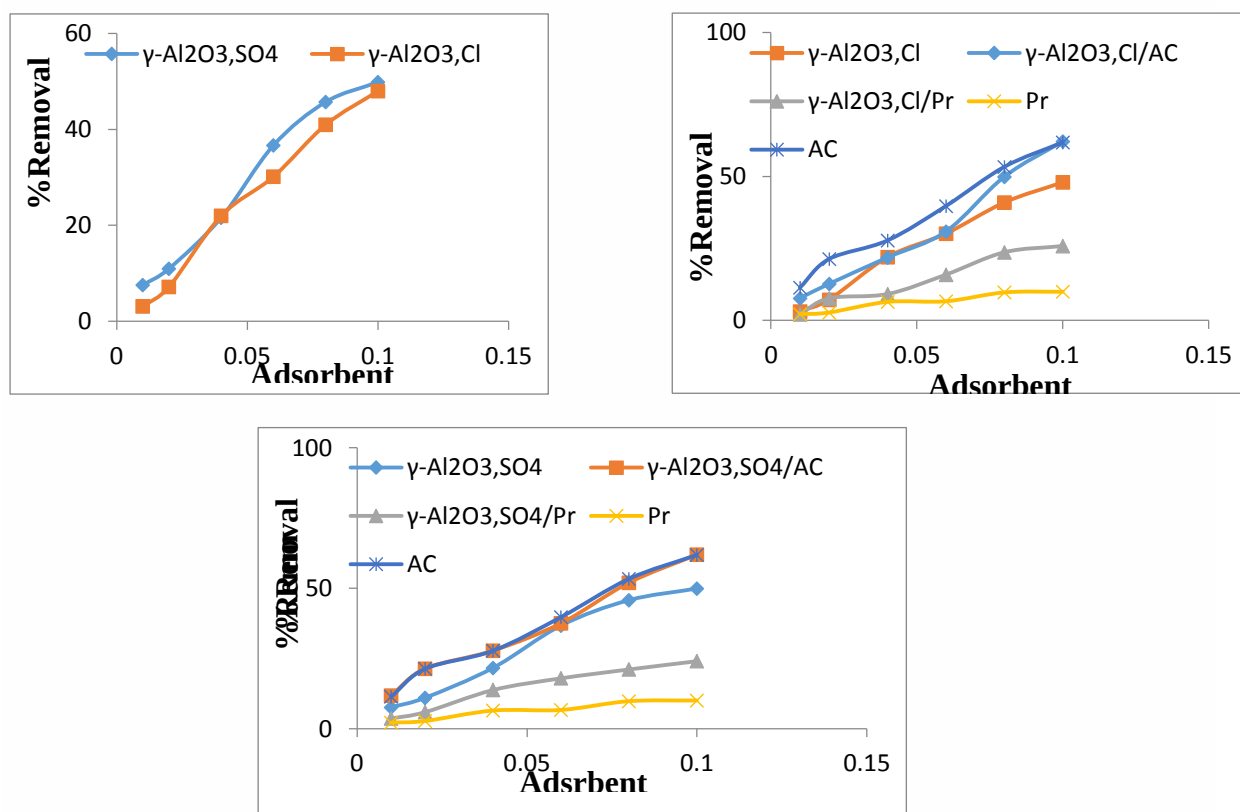


Figure 3.20. The effect of nano adsorbent dosage on the % removal of methyl orange dye by γ -Al₂O₃ NPs and their composite

3.2.2. Effect of Contact Time on Adsorption

It is clear from table (3.1) and figure 3.21 that the adsorption process was enhanced by the activated carbon. The percent removal of methyl orange increased from 29.5% to 83.7% for α -Fe₂O₃/AC, whereas for γ -Al₂O₃/AC, the percent removal increased from 15.3 to 62.2%. In the case of α -Fe₂O₃ and Al₂O₃, there was less change in the percent removed. The Figure 3.22 also showed that the adsorption reached equilibrium after 60 min in the all cases.

The effect of equilibrium time on the removal of methyl orange) was studied using oxides and nanocomposites (α - Fe₂O₃, SO₄ NPs/AC, α - Fe₂O₃, SO₄ NPs/AC, α - Fe₂O₃, Cl NPs α - Fe₂O₃, Cl NPs /AC α). - Fe₂O₃,SO₄ NPs/Pr, α - Fe₂O₃,Cl NPs/Pr, AC,pr, γ - Al₂O₃,SO₄ NPs, γ - Al₂O₃,Cl NPs, γ - Al₂O₃,SO₄ NPs/AC, γ - Al₂O₃,Cl NPs /AC, γ - Al₂O₃,SO₄ NPs, γ - Al₂O₃,Cl NPs /Pr) at room temperature and using a fixed concentration of dye (50 ppm and (0.1g) of the adsorbent and at different times (10,20,30, 40,50,60 min. The results showed, as shown in Table (3-2) and Figure (41-4), that the equilibrium time for oxides and nanocomposites is (60 min) .

Tables (3.2): Effect of nanoadsorbent dose on the adsorption of methyl orange at 298 K by all samples prepared

α -Fe ₂ O ₃ , SO ₄				α -Fe ₂ O ₃ , Cl			
time,min	C ₀ mg/L	C _t mg/L	R%	time,min	C ₀ mg/L	C _t mg/L	R%
10	50	40.34	19.32	10	50	39.13	21.74
20		31.11	37.78	20		33.02	33.96
30		23.22	53.56	30		25.49	49.02
40		18.19	63.62	40		18.86	62.28
50		12.86	74.28	50		13.55	72.9
60		12.04	75.92	60		13.16	73.68
α -Fe ₂ O ₃ , SO ₄ /AC				α -Fe ₂ O ₃ , Cl/AC			
time,min	C ₀ mg/L	C _t mg/L	R%	time,min	C ₀ mg/L	C _t mg/L	R%
10	50	35.22	29.56	10	50	36.15	27.7
20		28.09	43.82	20		31.24	37.52
30		21.17	57.66	30		23.33	53.34
40		16.18	67.64	40		17.82	64.36
50		8.14	83.72	50		10.04	79.92
60		8.12	83.76	60		9.58	80.84

α -Fe ₂ O ₃ , SO ₄ /Pr				α -Fe ₂ O ₃ , Cl/Pr			
time,min	C ₀ mg/L	C _t mg/L	R%	time,min	C ₀ mg/L	C _t mg/L	R%
10	50	44.08	11.84	10	50	46.22	7.56
20		43.23	13.54	20		44.34	11.32
30		39.45	21.1	30		41.12	17.76
40		31.42	37.16	40		36.59	26.82
50		25.71	48.58	50		31.86	36.28
60		24.08	51.84	60		26.12	47.76
γ -Al ₂ O ₃ , SO ₄				γ -Al ₂ O ₃ , Cl			
time,min	C ₀ mg/L	C _t mg/L	R%	time,min	C ₀ mg/L	C _t mg/L	R%
10	50	46.53	6.94	10	50	43.42	13.16
20		39.21	21.58	20		39.01	21.98
30		37.67	24.66	30		33.93	32.14
40		29.15	41.7	40		26.52	46.96
50		21.68	56.64	50		22.71	54.58
60		20.33	59.34	60		21.23	57.54
γ -Al ₂ O ₃ , SO ₄ /AC				γ -Al ₂ O ₃ , Cl/AC			
time,min	C ₀ mg/L	C _t mg/L	R%	time,min	C ₀ mg/L	C _t mg/L	R%
10	50	42.34	15.32	10	50	43.67	12.66
20		36.13	27.74	20		38.09	23.82
30		31.25	37.5	30		29.58	40.84
40		26.04	47.92	40		24.07	51.86
50		19.03	61.94	50		20.92	58.16
60		18.89	62.22	60		19.67	60.66
γ -Al ₂ O ₃ , SO ₄ /Pr				γ -Al ₂ O ₃ , Cl/Pr			
time,min	C ₀ mg/L	C _t mg/L	R%	time,min	C ₀ mg/L	C _t mg/L	R%
10	50	47.05	5.9	10	50	48.17	3.66
20		45.11	9.78	20		44.44	11.12
30		42.03	15.94	30		36.07	27.86
40		38.45	23.1	40		31.18	37.64
50		32.98	34.04	50		27.09	45.82
60		31.11	37.78	60		26.57	46.86
AC				Pr			
time,min	C ₀ mg/L	C _t mg/L	R%	time,min	C ₀ mg/L	C _t mg/L	R%
10	50	37.12	25.76	10	50	48.69	2.62
20		31.43	37.14	20		47.09	5.82
30		25.56	48.88	30		45.17	9.66
40		21.79	56.42	40		45.01	9.98
50		16.34	67.32	50		44.88	10.24
60		14.07	71.86	60		41.64	16.72

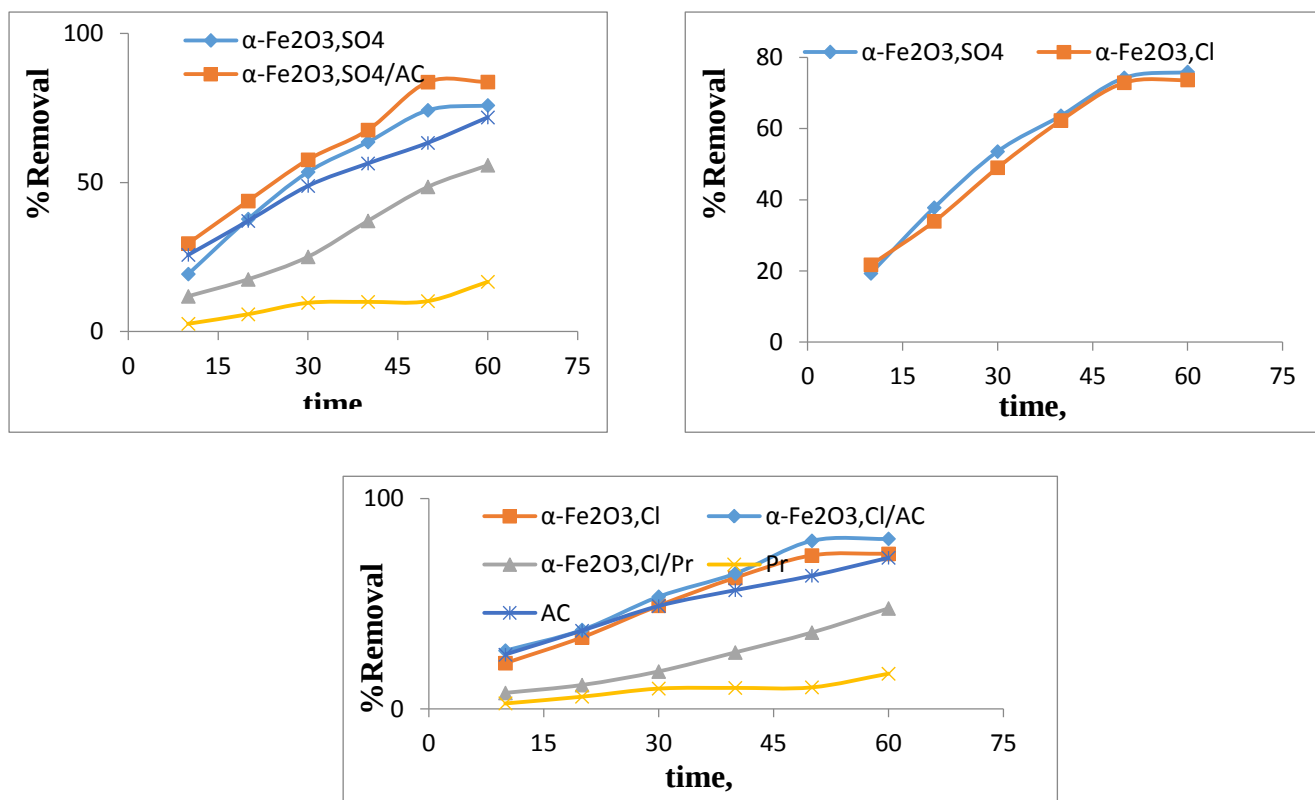


Figure 3.21. The effect of contact time on the % removed of methyl orange dye by α -Fe₂O₃NPs and their composite

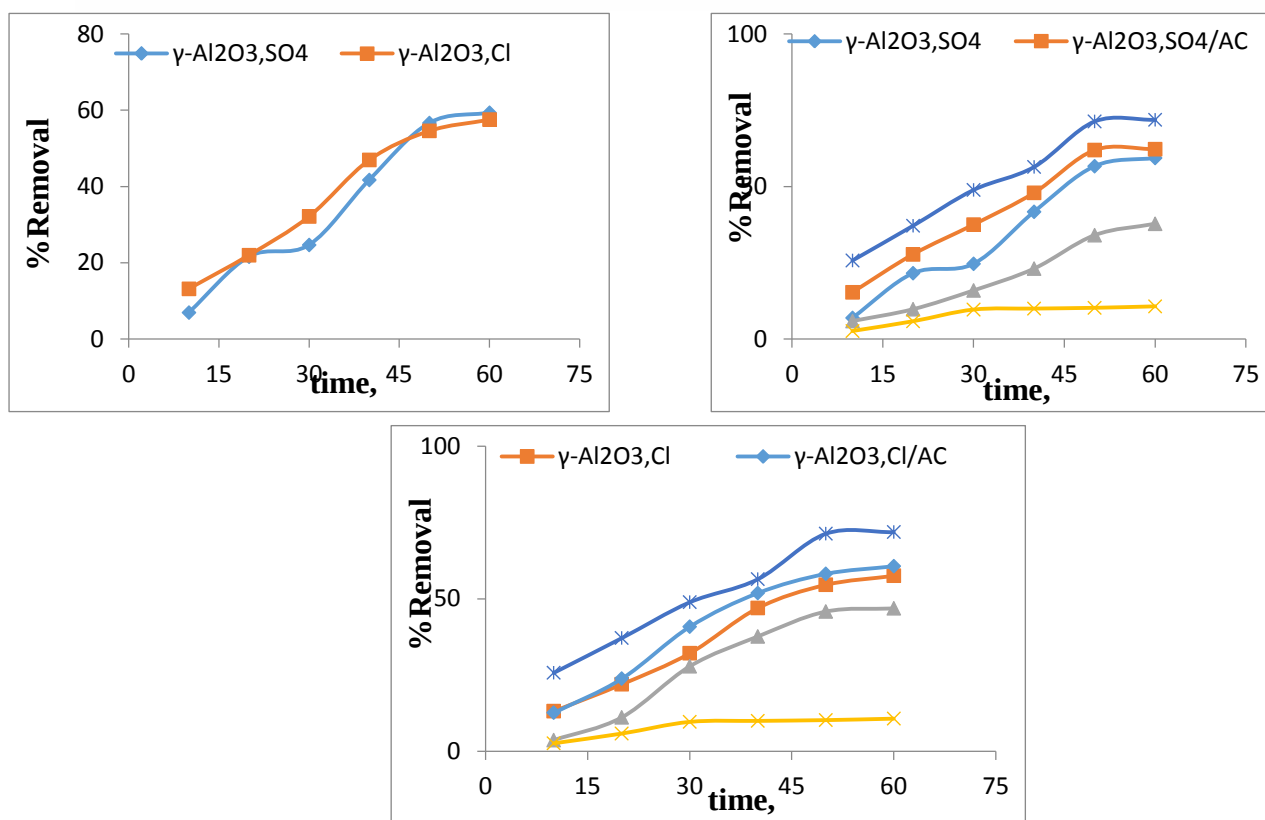


Figure 3.22. The effect of contact time on the % removed of methyl orange dye by γ -Al₂O₃NPs and their composite

3.2.3. Effect of Temperature on the Methyl Orange Adsorption

The effect of temperature on methyl orange dye removal was investigated with 30° C to 90° C temperature range for 60 min at pH 8 with 0.1 g adsorbent dose. As the temperature increased the methyl orange dye removal increased from >10% to >50% as depicted in table (3.4) , Fig. (3.17) and (3.18) indicating the process to be endothermic in nature. Methyl orange dye removal pertains to physical as well as chemical sorption. This may be due to busting of internal bonds at higher temperature resulting in increased active sites at the nanoadsorbent surface. Similar trends were observed by Fan et al. 2008.

Tables (3.3): Effect of temperature on the adsorption of methyl orange at 0.1 g for each sample and contact time 60 min.

α -Fe ₂ O ₃ ,SO ₄ NPs				α -Fe ₂ O ₃ ,Cl NPs			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
303	50	42.41	15.18	303	50	41.52	16.96
323		36.57	26.86	323		33.82	32.36
343		27.03	45.94	353		28.58	42.84
363		21.01	57.98	373		16.07	67.86
α -Fe ₂ O ₃ ,SO ₄ NPs/AC				α -Fe ₂ O ₃ ,Cl NPs/AC			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
303	50	43.88	12.24	303	50	39.47	21.06
323		35.12	29.76	323		36.16	27.68
343		26.6	46.8	353		24.96	50.08
363		22.9	54.2	373		18.13	63.74
α -Fe ₂ O ₃ ,SO ₄ NPs/Pr				α -Fe ₂ O ₃ ,Cl NPs/Pr			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
303	50	46.62	6.76	303	50	45.17	9.66
323		38.54	22.92	323		35.34	29.32
343		33.91	32.18	353		28.04	43.92
363		27.53	44.94	373		20.34	59.32
AC				Pr			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
303	50	43.76	12.48	303	50	48.23	3.54
323		39.15	21.7	323		46.25	7.5
343		28.48	43.04	353		45.88	8.24
363		22.78	54.44	373		45.12	9.76

$\gamma\text{-Al}_2\text{O}_3\text{,SO}_4$ NPs				$\gamma\text{-Al}_2\text{O}_3\text{,Cl}$ NPs			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
303	50	43.87	12.26	303	50	41.49	17.02
323		37.18	25.64	323		37.57	24.86
343		29.71	40.58	353		31.79	36.42
363		24.81	50.38	373		24.12	51.76
$\gamma\text{-Al}_2\text{O}_3\text{,SO}_4$ NPs/AC				$\gamma\text{-Al}_2\text{O}_3\text{,Cl}$ NPs/AC			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
303	50	40.62	18.76	303	50	39.83	20.34
323		33.68	32.64	323		33.75	32.5
343		27.18	45.64	353		29.23	41.54
363		23.06	53.88	373		24.91	50.18
$\gamma\text{-Al}_2\text{O}_3\text{,SO}_4$ NPs/Pr				$\gamma\text{-Al}_2\text{O}_3\text{,Cl}$ NPs/Pr			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
303	50	45.55	8.9	303	50	46.32	7.36
323		42.17	15.66	323		40.09	19.82
343		35.89	28.22	353		36.17	27.66
363		29.09	41.82	373		30.31	39.38

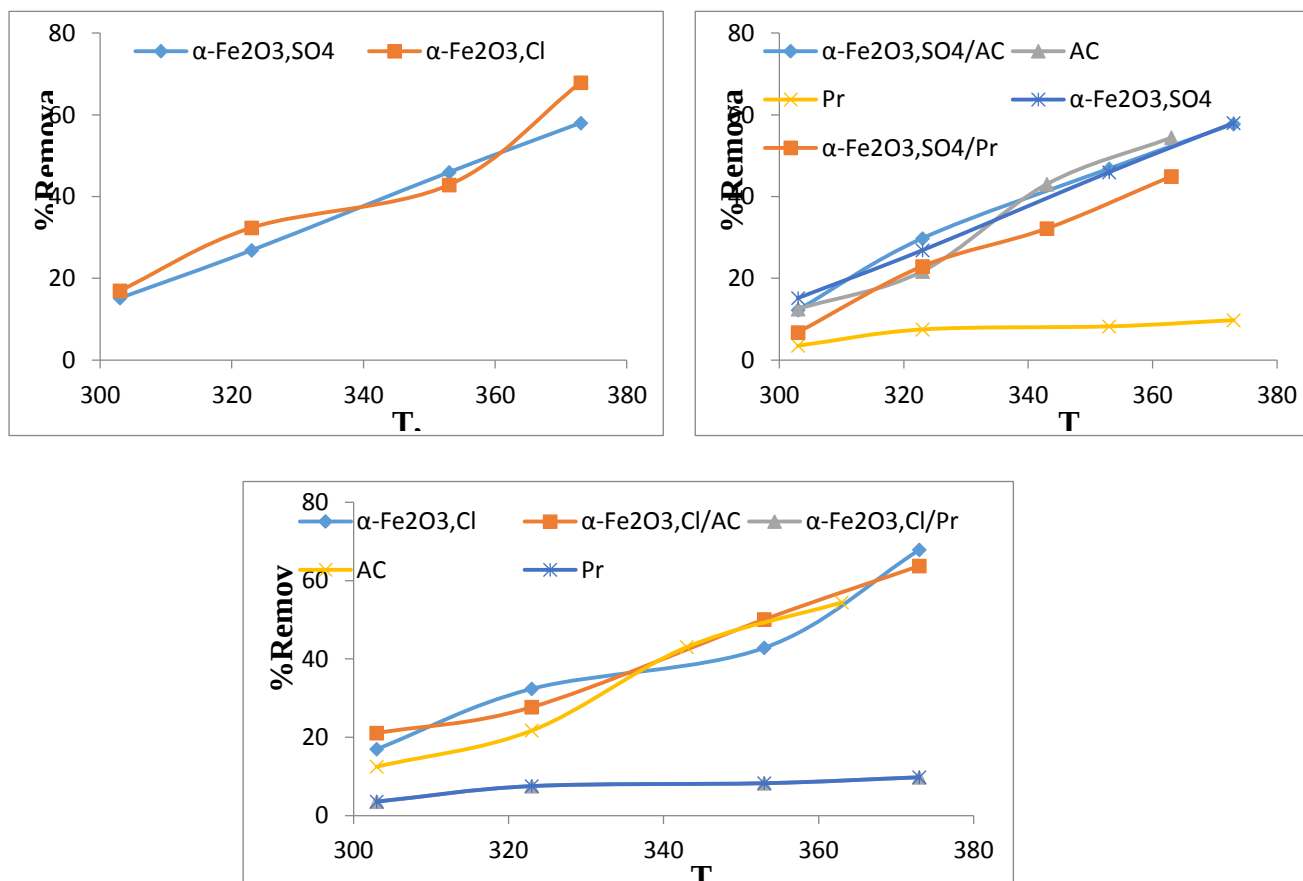


Figure 3.23. The effect of temperature on the % removed of methyl orange dye by $\alpha\text{-Fe}_2\text{O}_3\text{NPs}$ and their composite

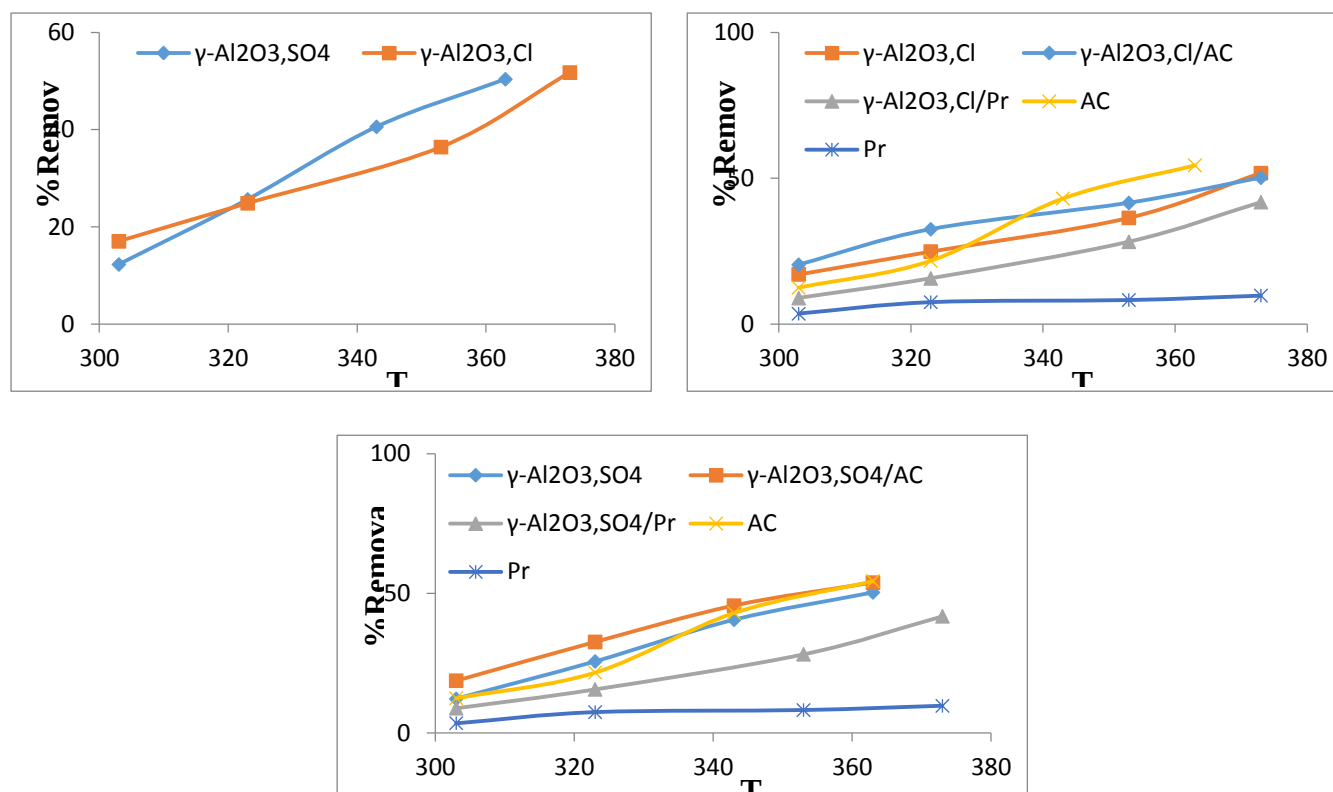


Figure 3.24. The effect of temperature on the % removed of methyl orange dye by $\gamma\text{-Al}_2\text{O}_3\text{NPs}$ and their composite

3.3. Kinetics Studies of Adsorption Process for Methyl Orange

3.3.1. Adsorption Kinetics

The kinetic study of adsorption methyl orange dye was carried out of each sample by using experimental conditions of initial concentration (50 mg/L), temperatures (298 K) and intervals times (10, 20,30,40,50 and 60)minute.

The adsorption percentage (%Removal) and adsorption capacity values at equilibrium and t time (q_e and q_t mg g^{-1}) were calculated using the following equations:

where C_0 , C_e and C_t (mg L^{-1}) are the MO dye concentrations at initial, equilibrium and t time, respectively, V (0.03L) is the solution volume and m (0.1g) is the mass of used adsorbent. The MO dye concentrations (C) were

obtained through Beer–Lambert law in which the absorbance value ($\lambda_{\max} = 464$ nm) for MO versus concentration obeys a linear relationship.

These data was applied for three model (the pseudo first – order, the pseudo second – order and the Elovich model) expressed by its equations to calculate the value of k as shown in figures (3.25) and (3.26) for the adsorption of methyl orange dye.

Table (3.4) The adsorption data for methyl orange dye removal by α -Fe₂O₃ and their composite at 298K.

α-Fe₂O₃,SO₄ NPs						
time	C _t	qt	qe-qt	ln(qe-qt)	Int	t/qt
10	40.34	2.898	8.49	2.138889	2.302	3.450656
20	31.11	5.667	5.721	1.744144	2.995	3.529204
30	23.22	8.034	3.354	1.210154	3.401	3.73413
40	18.19	9.543	1.845	0.612479	3.688	4.191554
50	12.86	11.142	0.246	-1.40242	3.912	4.487525
60	12.04	11.388	0	0	4.094	5.268704
α-Fe₂O₃,SO₄ NPs/AC						
time	C _t	qt	qe-qt	ln(qe-qt)	Int	t/qt
10	35.22	4.434	8.13	2.095561	2.302	2.2553
20	28.09	6.573	5.991	1.790258	2.995	3.042751
30	21.17	8.649	3.915	1.364815	3.401	3.468609
40	16.18	10.146	2.418	0.882941	3.688	3.94244
50	8.14	12.558	0.006	-5.116	3.912	3.981526
60	8.12	12.564	0	0	4.094	4.775549
α-Fe₂O₃,SO₄ NPs/Pr						
time	C _t	qt	qe-qt	ln(qe-qt)	Int	t/qt
10	44.08	1.776	6	1.791759	2.302	5.630631
20	43.23	2.031	5.745	1.74833	2.995	9.847366
30	39.45	3.165	4.611	1.528445	3.401	9.478673
40	31.42	5.574	2.202	0.789366	3.688	7.176175
50	25.71	7.287	4.473	1.498059	3.912	6.861534
60	24.08	7.776	0	0	4.094	7.716049
AC						
time	C _t	qt	qe-qt	ln(qe-qt)	Int	t/qt
10	37.12	3.864	6.915	1.933693	2.302	2.587992
20	31.43	5.571	5.208	1.650196	2.995	3.59002
30	25.56	7.332	3.447	1.237504	3.401	4.091653
40	21.79	8.463	2.316	0.839842	3.688	4.726456
50	18.34	9.498	1.281	0.247641	3.912	5.264266
60	14.07	10.779	0	0	4.094	5.566379

Pr						
time	C_t	qt	qe-qt	$\ln(qe-qt)$	Int	t/qt
10	48.69	0.393	2.115	0.749055	2.302	25.44529
20	47.09	0.873	1.635	0.491643	2.995	22.90951
30	45.17	1.449	1.059	0.057325	3.401	20.70393
40	45.01	1.497	1.011	0.01094	3.688	26.72011
50	44.88	1.536	0.972	-0.0284	3.912	32.55208
60	41.64	2.508	0	0	4.094	23.92344
α -Fe ₂ O ₃ ,Cl NPs						
time	C_t	qt	qe-qt	$\ln(qe-qt)$	Int	t/qt
10	39.13	3.261	7.791	2.052969	2.302	3.066544
20	33.02	5.094	5.958	1.784735	2.995	3.926188
30	25.49	7.353	3.699	1.308063	3.401	4.079967
40	18.86	9.342	1.71	0.536493	3.688	4.281738
50	13.55	10.935	0.117	-2.14558	3.912	4.572474
60	13.16	11.052	0	0	4.094	5.428882
α -Fe ₂ O ₃ ,Cl/AC NPs						
time	C_t	qt	qe-qt	$\ln(qe-qt)$	Int	t/qt
10	36.15	4.155	7.971	2.07581	2.302	2.406739
20	31.24	5.628	6.498	1.871494	2.995	3.55366
30	23.33	8.001	4.125	1.417066	3.401	3.749531
40	17.82	9.654	2.472	0.905028	3.688	4.14336
50	10.04	11.988	0.138	-1.9805	3.912	4.170838
60	9.58	12.126	0	0	4.094	4.948046
α -Fe ₂ O ₃ ,Cl/Pr NPs						
time	C_t	qt	qe-qt	$\ln(qe-qt)$	Int	t/qt
10	46.22	1.134	6.03	1.796747	2.302	8.818342
20	44.34	1.698	5.466	1.698547	2.995	11.77856
30	41.12	2.664	4.5	1.504077	3.401	11.26126
40	36.59	4.023	3.141	1.144541	3.688	9.942829
50	31.86	5.442	1.722	0.543486	3.912	9.187799
60	26.12	7.164	0	0	4.094	8.375209

Table (3.5) The adsorption data for methyl orange dye removal by $\gamma\text{-Al}_2\text{O}_3$ and their composite at 298K.

$\gamma\text{-Al}_2\text{O}_3$, SO_4 NPs						
time	C_t	qt	qe-qt	$\ln(\text{qe-qt})$	Int	t/qt
10	46.53	1.041	7.86	2.061787	2.302	9.606148
20	39.21	3.237	5.664	1.73413	2.995	6.17856
30	37.67	3.699	5.202	1.649043	3.401	8.1103
40	29.15	6.255	2.646	0.973049	3.688	6.394884
50	21.68	8.496	0.405	-0.90387	3.912	5.885122
60	20.33	8.901	0	0	4.094	6.740816
$\gamma\text{-Al}_2\text{O}_3$, SO_4 NPs /AC						
time	C_t	qt	qe-qt	$\ln(\text{qe-qt})$	Int	t/qt
10	42.34	2.298	7.035	1.950898	2.302	4.35161
20	36.13	4.161	5.172	1.643259	2.995	4.806537
30	31.25	5.625	3.708	1.310493	3.401	5.333333
40	26.04	7.188	2.145	0.76314	3.688	5.56483
50	19.03	9.291	0.042	-3.17009	3.912	5.381552
60	18.89	9.333	0	0	4.094	6.428801
$\gamma\text{-Al}_2\text{O}_3$, SO_4 NPs /Pr						
time	C_t	qt	qe-qt	$\ln(\text{qe-qt})$	Int	t/qt
10	47.05	0.885	4.782	1.564859	2.302	11.29944
20	45.11	1.467	4.2	1.435085	2.995	13.63327
30	42.03	2.391	3.276	1.186623	3.401	12.54705
40	38.45	3.465	2.202	0.789366	3.688	11.54401
50	32.98	5.106	0.561	-0.57803	3.912	9.792401
60	31.11	5.667	0	0	4.094	10.58761
$\gamma\text{-Al}_2\text{O}_3$, Cl NPs						
time	C_t	qt	qe-qt	$\ln(\text{qe-qt})$	Int	t/qt
10	43.42	1.974	6.657	1.895669	2.302	5.065856
20	39.01	3.297	5.334	1.674101	2.995	6.066121
30	33.93	4.821	3.81	1.337629	3.401	6.222775
40	26.52	7.044	1.587	0.461845	3.688	5.678592
50	22.71	8.187	0.444	-0.81193	3.912	6.107243
60	21.23	8.631	0	0	4.094	6.951686
$\gamma\text{-Al}_2\text{O}_3$, Cl/AC NPs						
time	C_t	qt	qe-qt	$\ln(\text{qe-qt})$	Int	t/qt
10	43.67	1.899	7.2	1.974081	2.302	5.265929
20	38.09	3.573	5.526	1.709464	2.995	5.597537
30	29.58	6.126	2.973	1.089572	3.401	4.89716
40	24.07	7.779	1.32	0.277632	3.688	5.142049
50	20.92	8.724	0.375	-0.98083	3.912	5.731316
60	19.67	9.099	0	0	4.094	6.594131
$\gamma\text{-Al}_2\text{O}_3$, Cl NPs/Pr						
time	C_t	qt	qe-qt	$\ln(\text{qe-qt})$	Int	t/qt

10	48.17	0.549	6.48	1.868721	2.302	18.21494
20	44.44	1.668	5.361	1.679151	2.995	11.99041
30	36.07	4.179	2.85	1.047319	3.401	7.178751
40	31.18	5.646	1.383	0.324255	3.688	7.084662
50	27.09	6.873	0.156	-1.8579	3.912	7.274844
60	26.57	7.029	0	0	4.094	8.536065

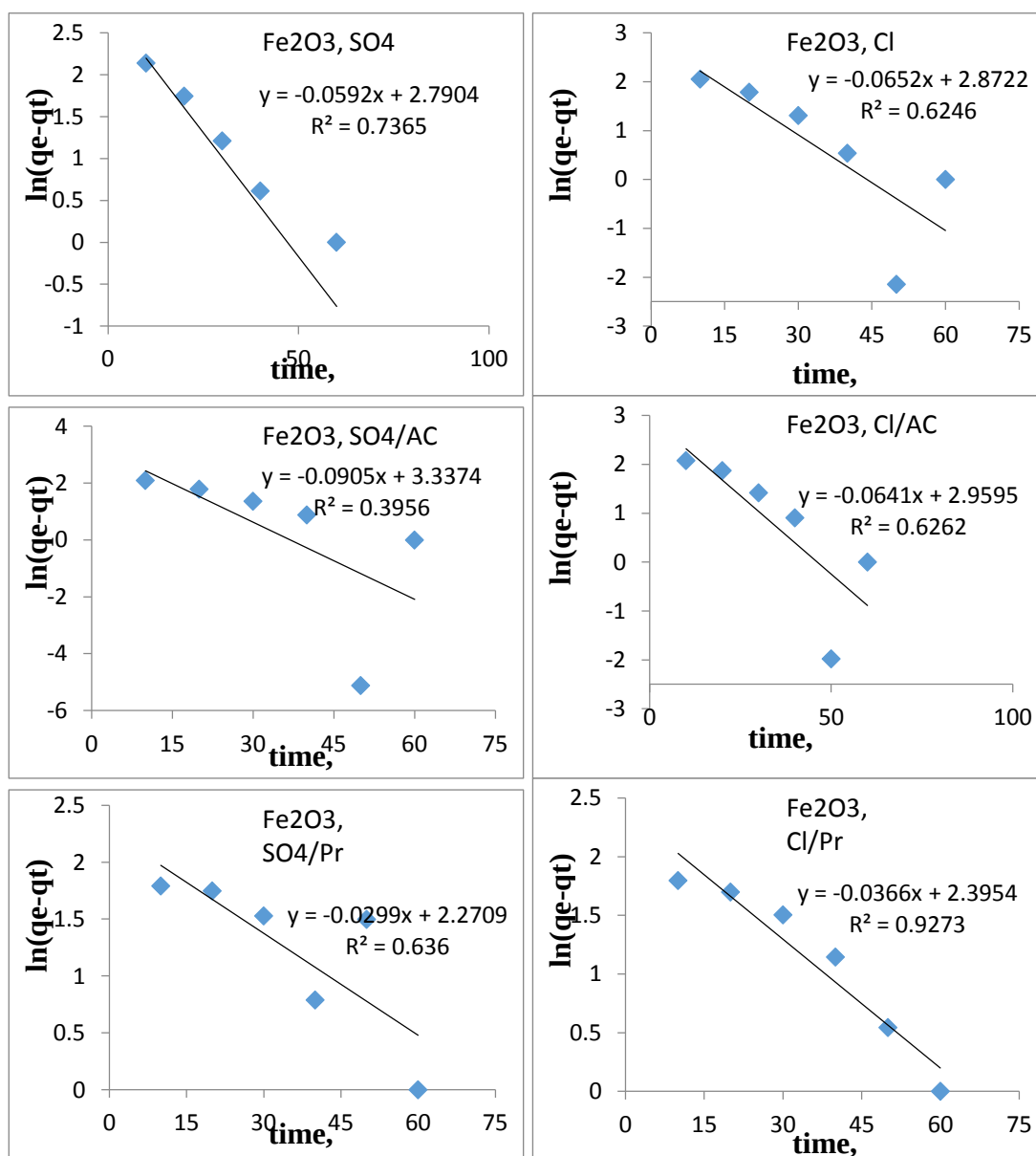


Figure 3.25. The Pseudo First - Order Kinetic Model for methyl orange adsorbed by α - Fe_2O_3 NPs and their composite

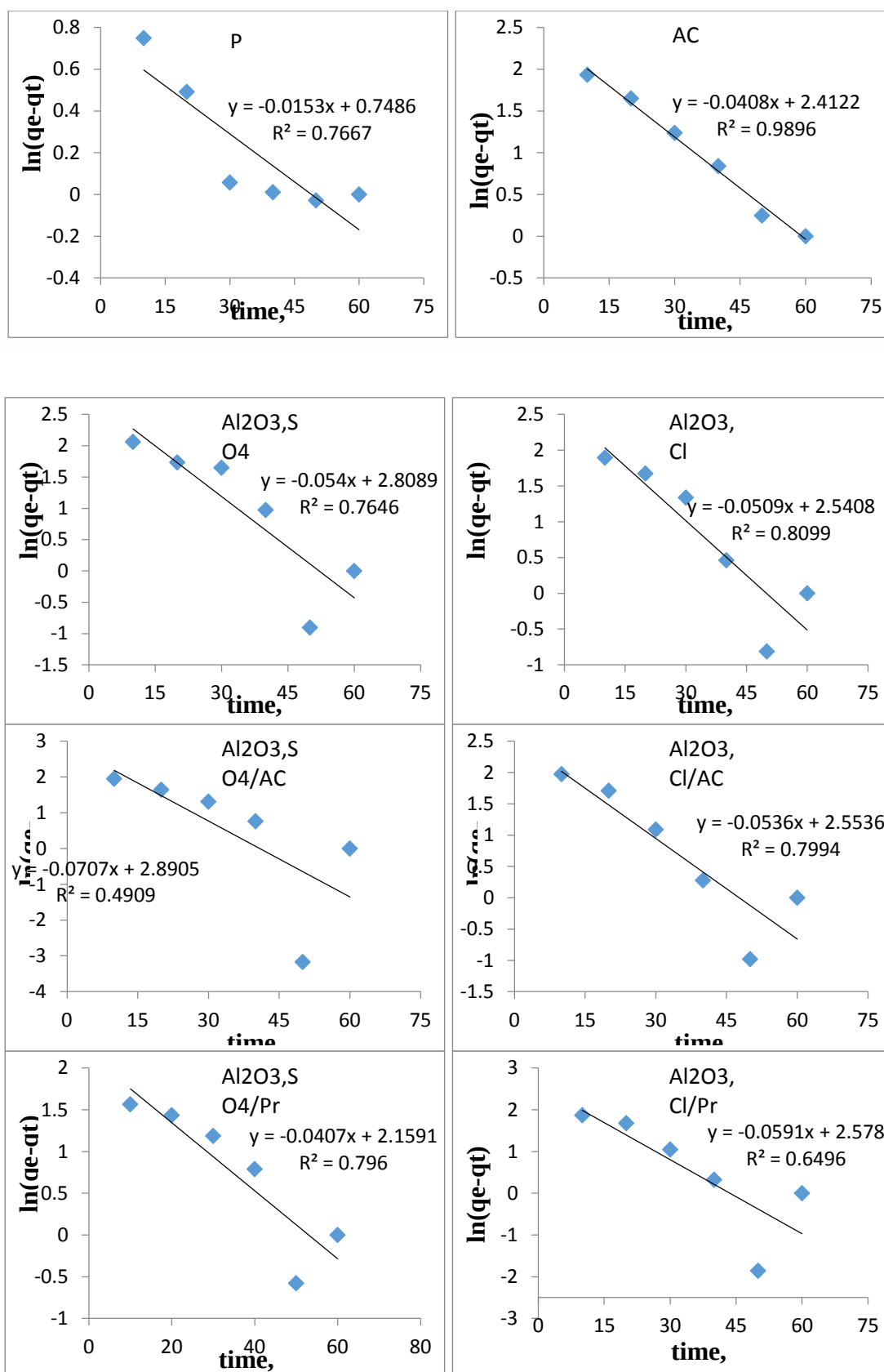


Figure 3.26. The Pseudo First - Order Kinetic Model for methyl orange adsorbed by γ -Al₂O₃NPs and their composite

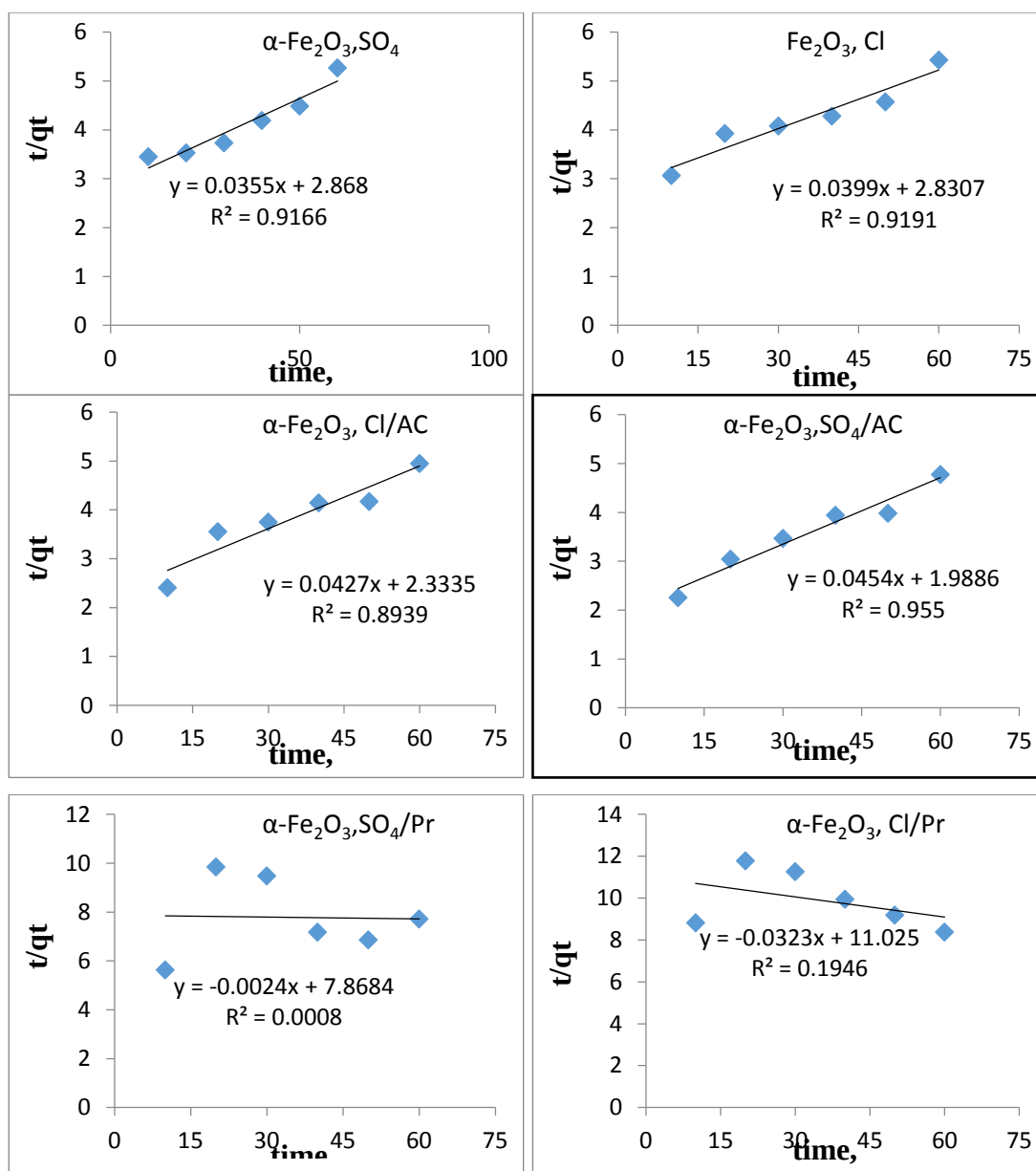


Figure 3.27. The Pseudo Second – Order Kinetic Model for methyl orange dye adsorption on $\alpha\text{-Fe}_2\text{O}_3$ NPs and their composite

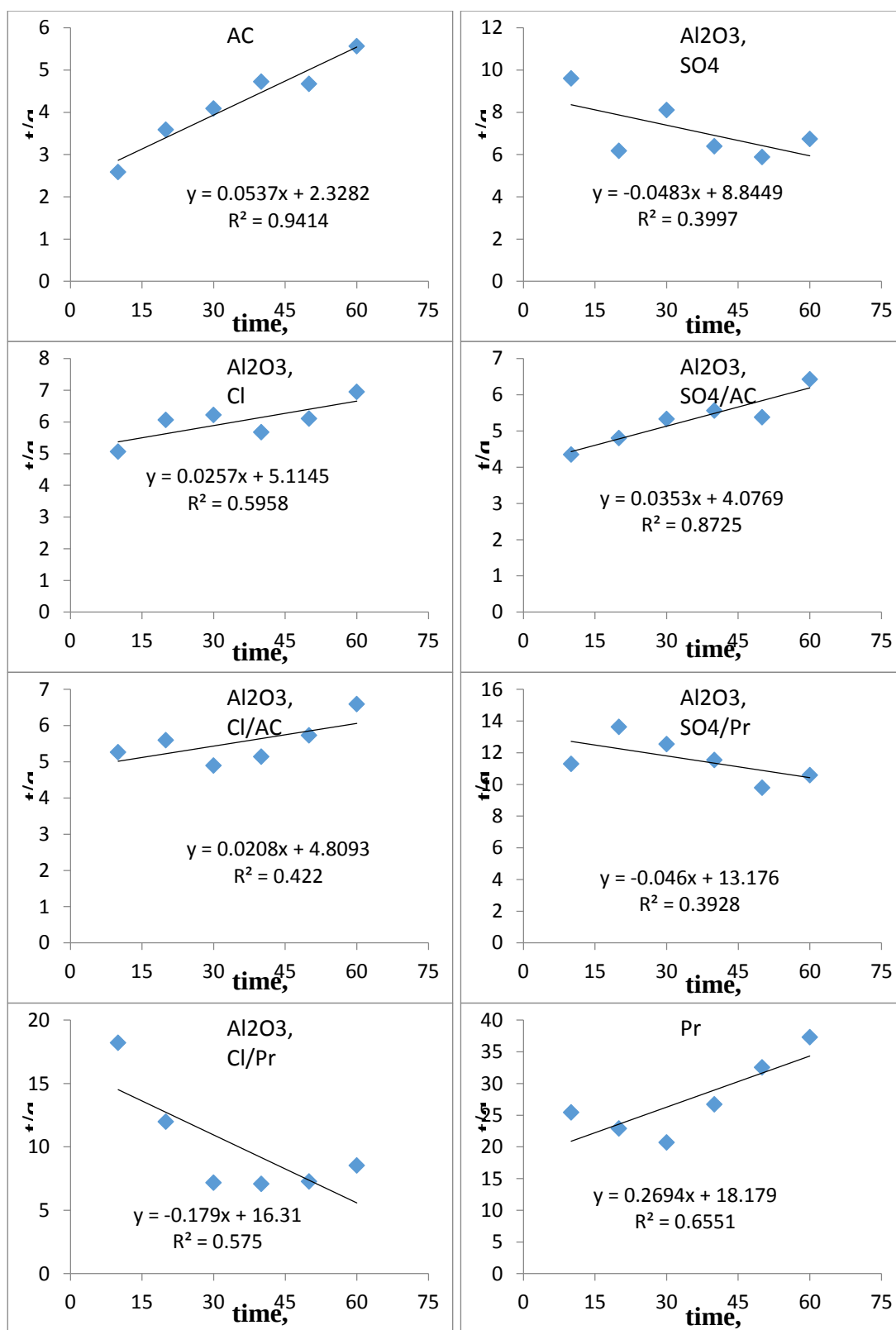


Figure 3.28. The Pseudo Second – Order Kinetic Model for methyl orange dye adsorption on γ -Al₂O₃NPs and their composite

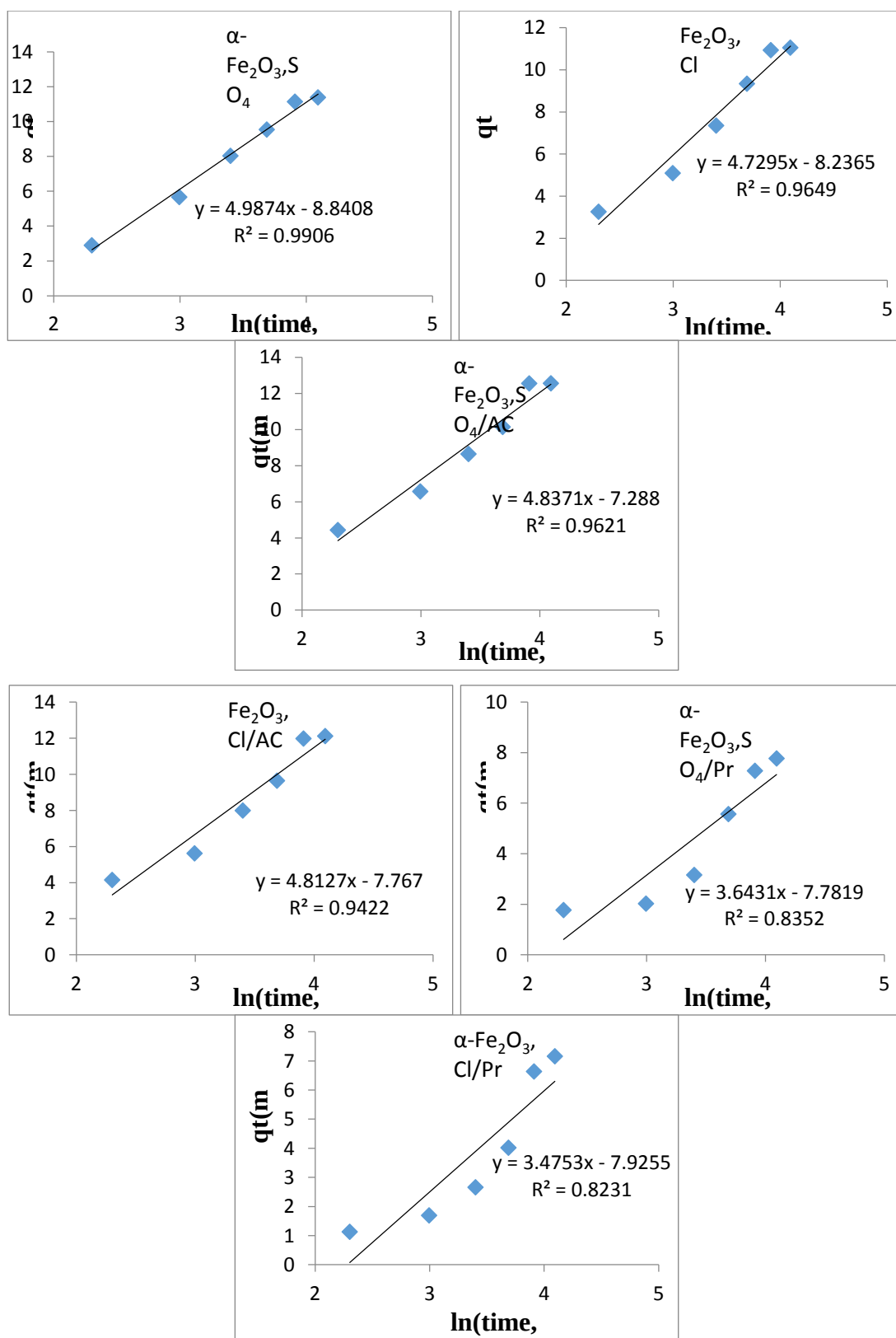


Figure 3.29. The Elovich Model for methyl orange dye adsorption on α -Fe₂O₃NPs and their composite

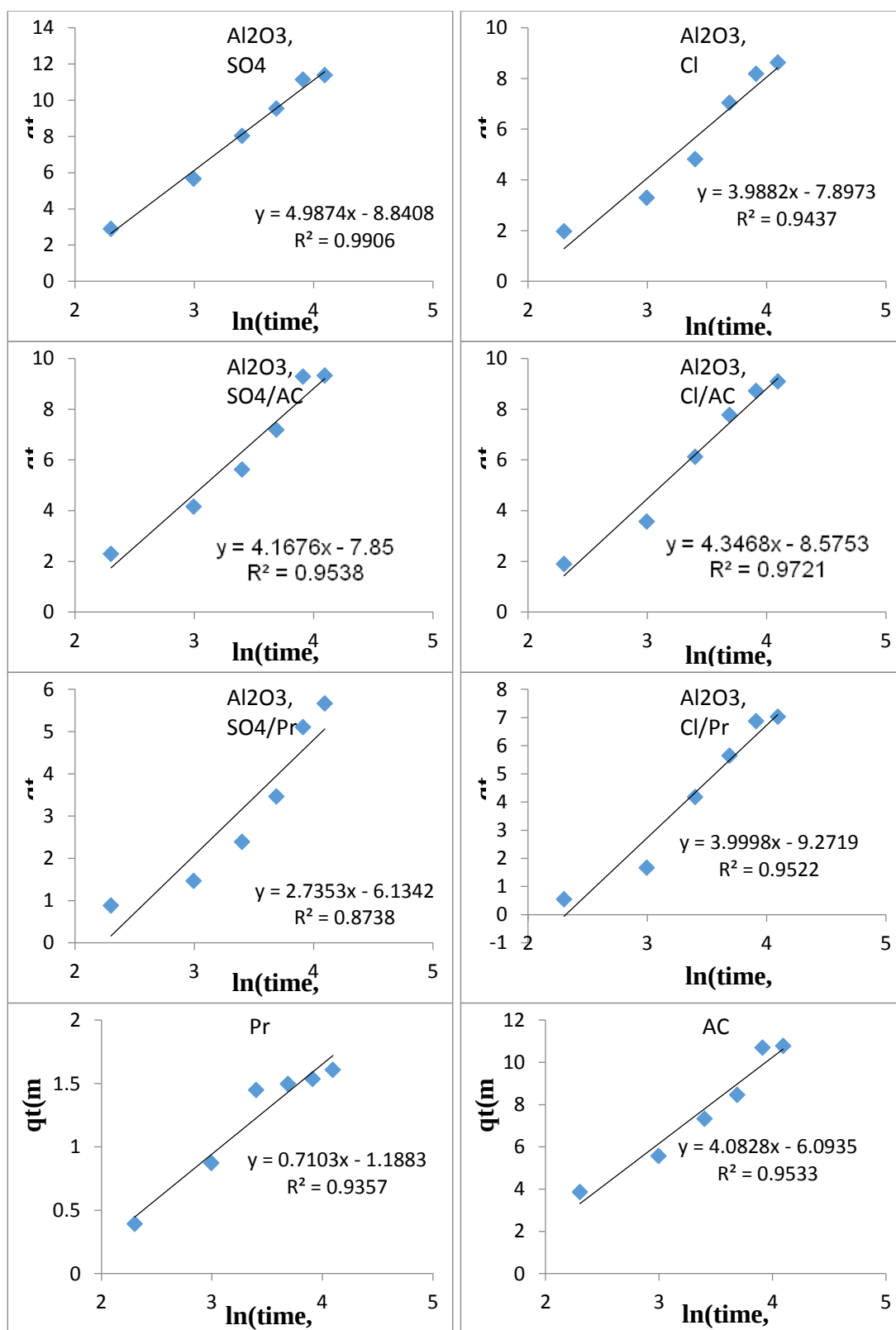


Figure 3.30. The Elovich Model for methyl orange dye adsorption on $\gamma\text{-Al}_2\text{O}_3\text{NPs}$ and their composite

The calculated values of k_1 , k_2 and k_{elovich} with their correlation coefficient of adsorption for methyl orange dye on $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ and their composite adsorbents are given in table (3.6). The results show the correlation coefficient of Elovich model is higher than the pseudo-first-order and pseudo-second order.

Table (3.6): Adsorption kinetics constants for methyl orange adsorption on $\alpha\text{-Fe}_2\text{O}_3, \gamma\text{-Al}_2\text{O}_3$ nanoparticles and their composite

Sample	qe	pseudo-first-order		pseudo-second order		Elovich model	
		K_1, min^{-1}	R^2	$K_2, \text{g/mg.min}$	R^2	K_{elovich}	R^2
$\alpha\text{-Fe}_2\text{O}_3, \text{SO}_4$	16.287	-0.059	0.736	4.471×10^{-5}	0.916	4.987	0.99
$\alpha\text{-Fe}_2\text{O}_3, \text{Cl}$	17.675	-0.065	0.624	6.334×10^{-5}	0.919	4.729	0.964
$\alpha\text{-Fe}_2\text{O}_3, \text{SO}_4/\text{AC}$	28.147	-0.090	0.395	9.360×10^{-5}	0.955	4.837	0.962
$\alpha\text{-Fe}_2\text{O}_3, \text{Cl}/\text{AC}$	19.288	-0.064	0.626	7.796×10^{-5}	0.893	4.812	0.942
$\alpha\text{-Fe}_2\text{O}_3, \text{SO}_4/\text{Pr}$	10.490	-0.030	0.680	2.346×10^{-5}	0.095	3.732	0.884
$\alpha\text{-Fe}_2\text{O}_3, \text{Cl}/\text{Pr}$	10.972	-0.036	0.927	9.465×10^{-5}	0.194	3.194	0.836
Pr	2.114	-0.015	0.766	0.00026	0.128	0.995	0.854
AC	11.158	-0.040	0.989	0.00157	0.974	3.802	0.973
$\gamma\text{-Al}_2\text{O}_3, \text{SO}_4$	16.591	-0.053	0.764	0.00026	0.339	4.517	0.990
$\gamma\text{-Al}_2\text{O}_3, \text{Cl}$	12.689	-0.050	0.809	0.0044	0.595	3.988	0.943
$\gamma\text{-Al}_2\text{O}_3, \text{SO}_4/\text{AC}$	28.147	-0.090	0.490	9.360×10^{-5}	0.872	4.837	0.953
$\gamma\text{-Al}_2\text{O}_3, \text{Cl}/\text{AC}$	19.288	-0.064	0.799	7.769×10^{-5}	0.422	4.812	0.972
$\gamma\text{-Al}_2\text{O}_3, \text{SO}_4/\text{Pr}$	10.490	-0.030	0.796	2.346×10^{-6}	0.392	3.723	0.873
$\gamma\text{-Al}_2\text{O}_3, \text{Cl}/\text{Pr}$	10.972	-0.036	0.649	9.465×10^{-5}	0.595	3.194	0.952

By comparing the results that obtained from the application of different chemical reaction models; the Lagergren pseudo-first-order model, the pseudo-

second-order model and the Elovich model to fit the experimental data, it can conclude that the adsorption of methyl orange dye by all samples could be expressed well by the intra-particle diffusion model. Fitting the experimental data with the Elovich model gave straight lines with excellent regression coefficients ($R^2 = 0.83$ to 0.99) and good agreement between experimental and calculated amount of adsorbed methyl orange dye per unit mass of sample at equilibrium.

3.4. Thermodynamic Study of Methyl Orange Dye Adsorption

In any adsorption procedure, values of thermodynamic parameters such as Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and entropy (ΔS°) must be taken into consideration in order to determine the thermodynamic nature of a process. Values of thermodynamic parameters are the actual indicators for practical application of a process. Adsorption of methyl orange dye onto nanoadsorbents based on thermodynamic studies was calculated at a range of temperature (303, 323, 343, and 363 K). The Gibbs free energy (ΔG°) was calculated by the following equation.

$$G^\circ = -RT \ln K_c$$

k_c (L/mg) is the equilibrium constant ($= q_e/C_e$)

$$k_c = q_e/C_e$$

Where R , T and K_c are commonly gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), absolute temperature (K), and the equilibrium adsorption constant, respectively

The Arrhenius equation was used to determine kinetic of adsorption reactions. It can be expressed as the following equation

Standard enthalpy (ΔH°) and entropy (ΔS°) were determined from the Van't Hoff isotherm equation as follow:

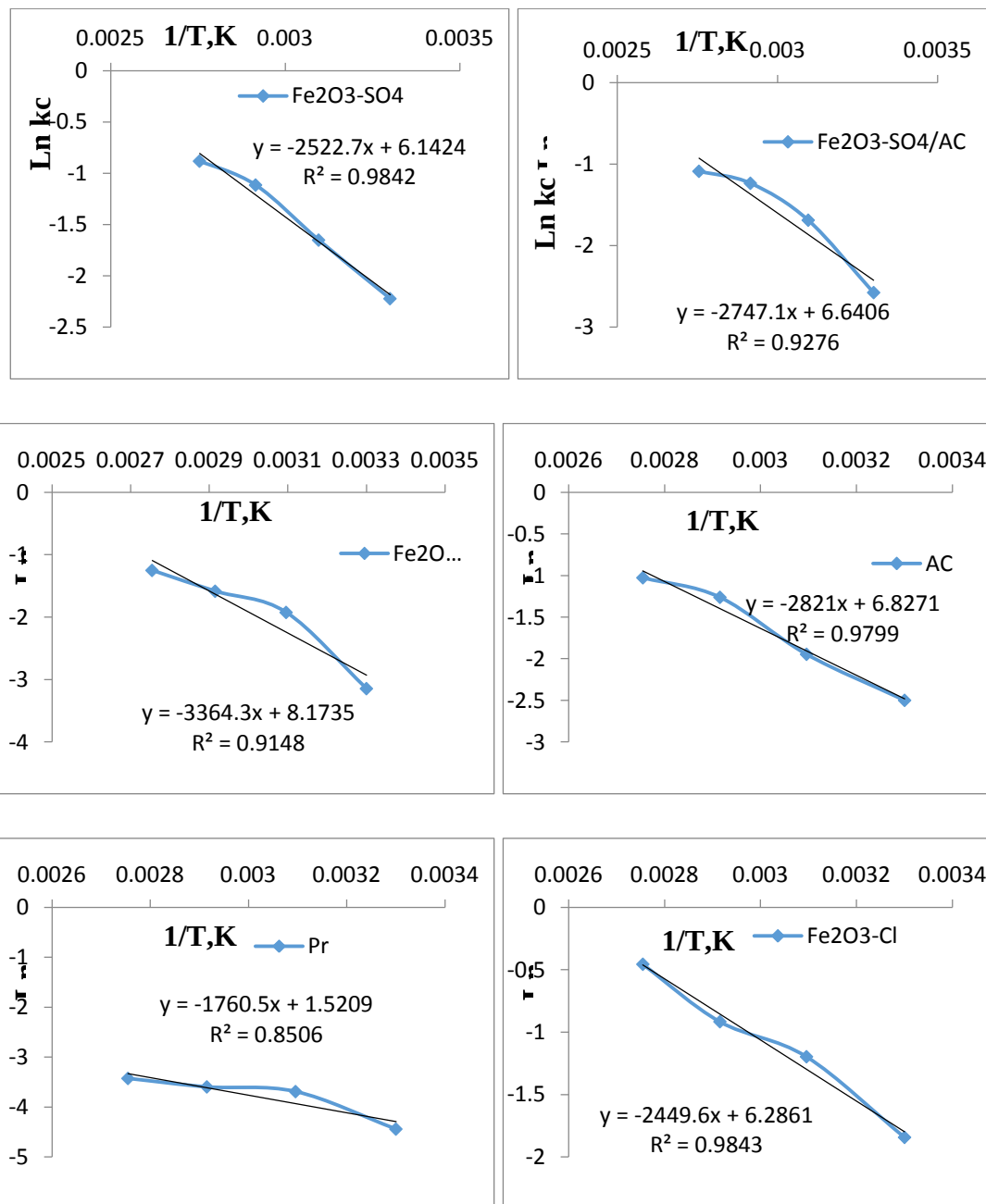
$$\ln k_c = \Delta S^\circ/R - \Delta H^\circ/RT$$

ΔH° and ΔS° were obtained from the slope and intercept of the plot of $\ln K_c$ vs $1/T$ figures (3.31, 3.32).

Thereafter, ΔG° can be calculated using Equation;

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The obtained values for ΔG° , ΔH° and ΔS° are listed in Table (3.8).



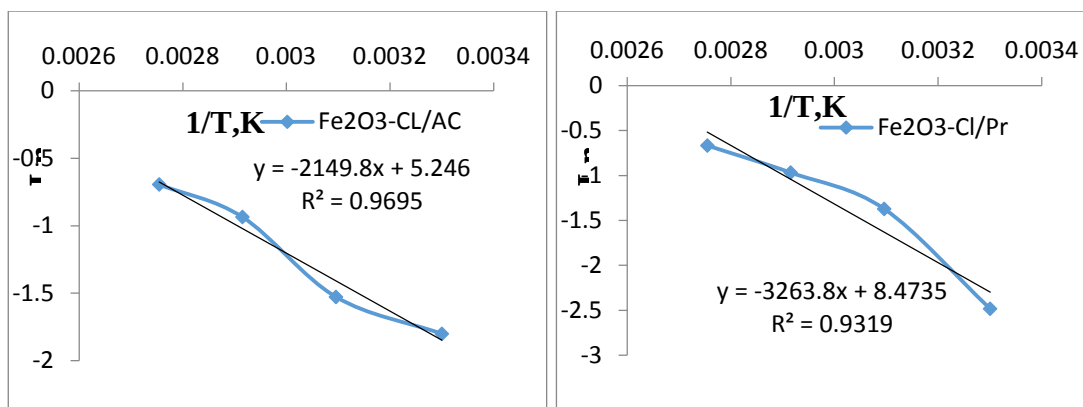
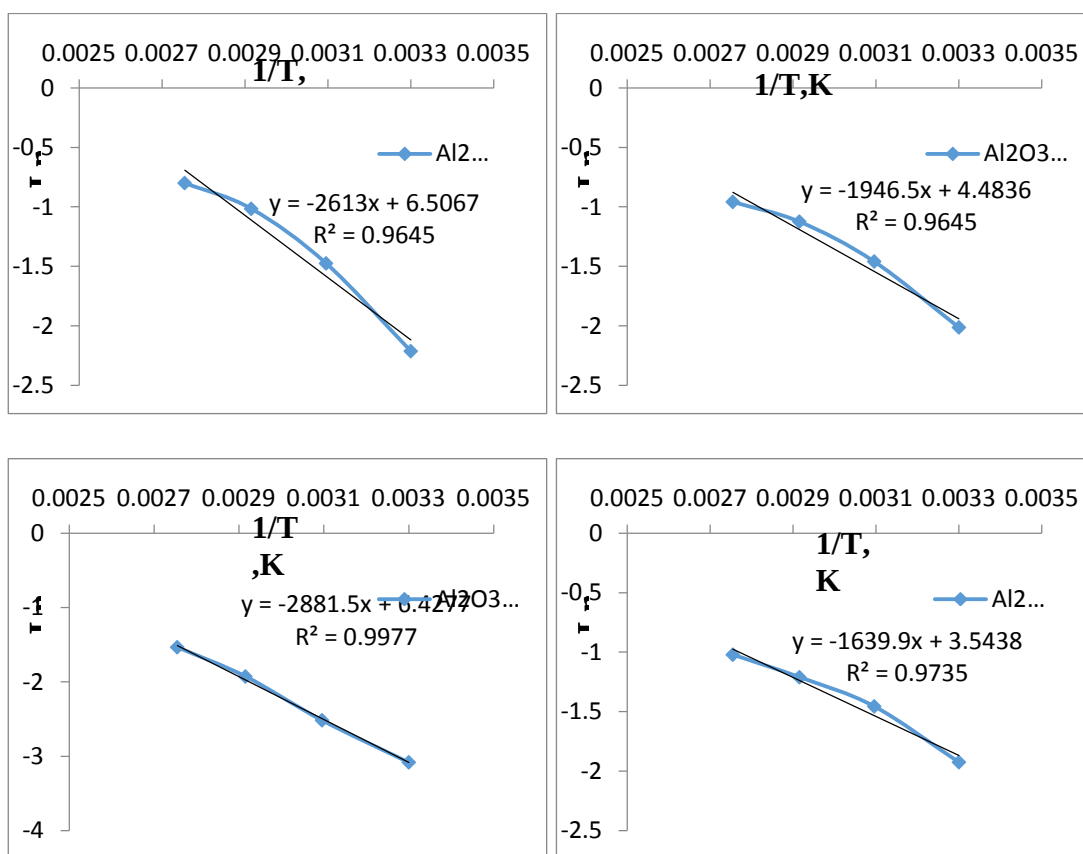


Figure 3.31. Plot of $\ln K_c$ versus $1/T$ to estimate the thermodynamic parameters for the adsorption of methyl orange dye on $\alpha\text{-Fe}_2\text{O}_3$ NPs and their campiest



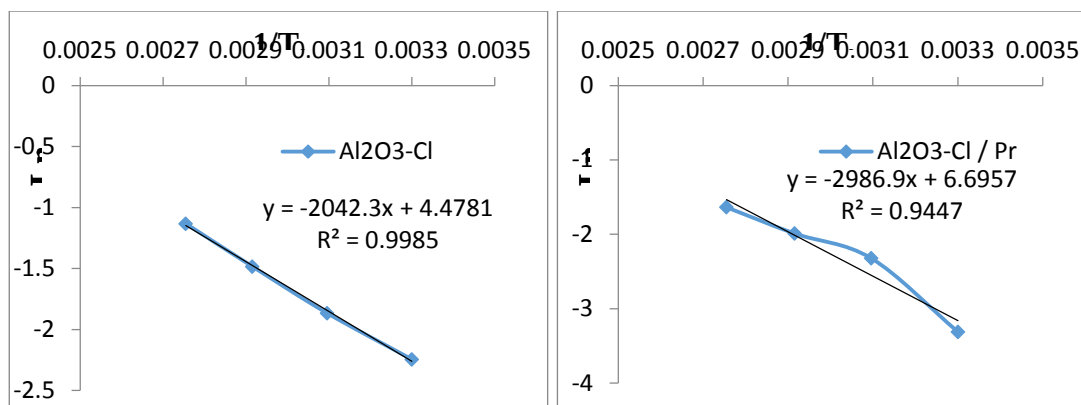


Figure 3.32. Plot of $\ln K_c$ versus $1/T$ to estimate the thermodynamic parameters for the adsorption of methyl orange dye on $\gamma\text{-Al}_2\text{O}_3$ and their composite

The thermodynamic parameters were determined for feasibility and spontaneity of the adsorption process at different temperature values. The Gibbs's free energy (ΔG°) and ΔH° and ΔS° have been calculated using thermodynamic relationship (Table 3.7).

Table(3.7) - Thermodynamic parameters of methyl orange dye adsorption onto samples

	T,k	ΔG , J/mol	ΔH , J/mol	ΔS , J mol ⁻¹ k ⁻¹
Fe2O3-SO4	303	3833.026	17939.72	46.55673
	323	2901.892		
	343	1970.757		
	363	1039.622		
Fe2O3-SO4/AC	303	6045.666	19405.29	44.09117
	323	5163.842		
	343	4282.019		
	363	3400.195		
Fe2O3-SO4/Pr	303	6445.077	30125.01	78.1516
	323	4882.045		
	343	3319.013		
	363	1755.981		
Fe2O3-Cl	303	4458	17160.03	41.9209
	323	3619.582		
	343	2781.164		
	363	1942.746		
Fe2O3-Cl/AC	303	4630.597	15425.76	35.62761

	323	3918.045		
	343	3205.493		
	363	2492.941		
Fe2O3-Cl/Pr	303	5765.639	19692.52	45.96331
	323	4846.373		
	343	3927.107		
	363	3007.84		
AC	303	6255.311	23453.77	56.76059
	323	5120.099		
	343	3984.888		
	363	2849.676		
Pr	303	10743.37	12229.79	4.905674
	323	10645.26		
	343	10547.15		
	363	10449.03		
Al2O3-SO4	303	5197.774	24513.24	63.74742
	323	3922.825		
	343	2647.877		
	363	1372.928		
Al2O3-SO4 /AC	303	4907.968	17551.52	41.7279
	323	4073.41		
	343	3238.852		
	363	2404.294		
Al2O3-Cl /AC	303	4907.968	17551.52	41.7279
	323	4073.41		
	343	3238.852		
	363	2404.294		
Al2O3-Cl /AC	303	4733.449	14013.52	30.62731
	323	4120.903		
	343	3508.357		
	363	2895.811		
Al2O3-Cl	303	5653.679	14461.35	29.06823
	323	5072.315		
	343	4490.95		
	363	3909.586		
Al2O3-SO4 / Pr	303	7706.725	20460.48	42.09161
	323	6864.893		
	343	6023.061		
	363	5181.229		
Al2O3-Cl / Pr	303	8038.426	20925.31	42.53097

	323	7187.807		
	343	6337.187		
	363	5486.568		

The positive values of ΔG indicates that the removal of methyl orange dye using all prepared samples are a nonspontaneous process. The positive value of ΔH confirmed the endothermic nature of the sorption process and from the values of ΔH in the table, we find that the resulting heat of adsorption is small, close in value to the heat of physisorption, hence, in this case, the adsorption process may involve the formation of an adsorption layer with a thickness of several molecules. This is evidence of the existence of an adsorption process, in addition to the adsorption process, as the temperature increases, the material is adsorbed on the surface (adsorption) by spreads into the pores and the speed of its spread increases and this phenomenon is called Sorption. So that the adsorption of methyl orange dye is more efficient when the temperature is increased, because the increase in the degree of heat increases the kinetic energy of the particles, and then helps the methyl orange dye to bind to the sites. The typical range of ΔH value for physisorption is between 2.1-20.9 kJ/mol and for chemisorption involving complexation is between 20.9-418.4 kJ/mol. While, the positive values of ΔS indicates the methyl orange dye adsorption process on all surfaces was randomness of the system and this change is caused by several changes may be in the composition of the adsorbent surface and the dispersion of water molecules surrounding the methyl orange dye during the process of adsorption.

3.5. Adsorption Isotherm

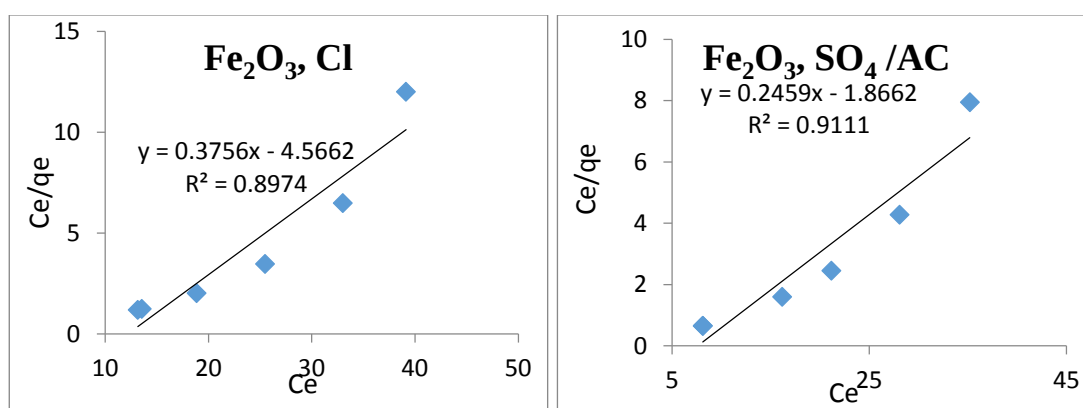
For the adsorption systems, the experimental data can be fitted with a good agreement using linear Langmuir isotherm:

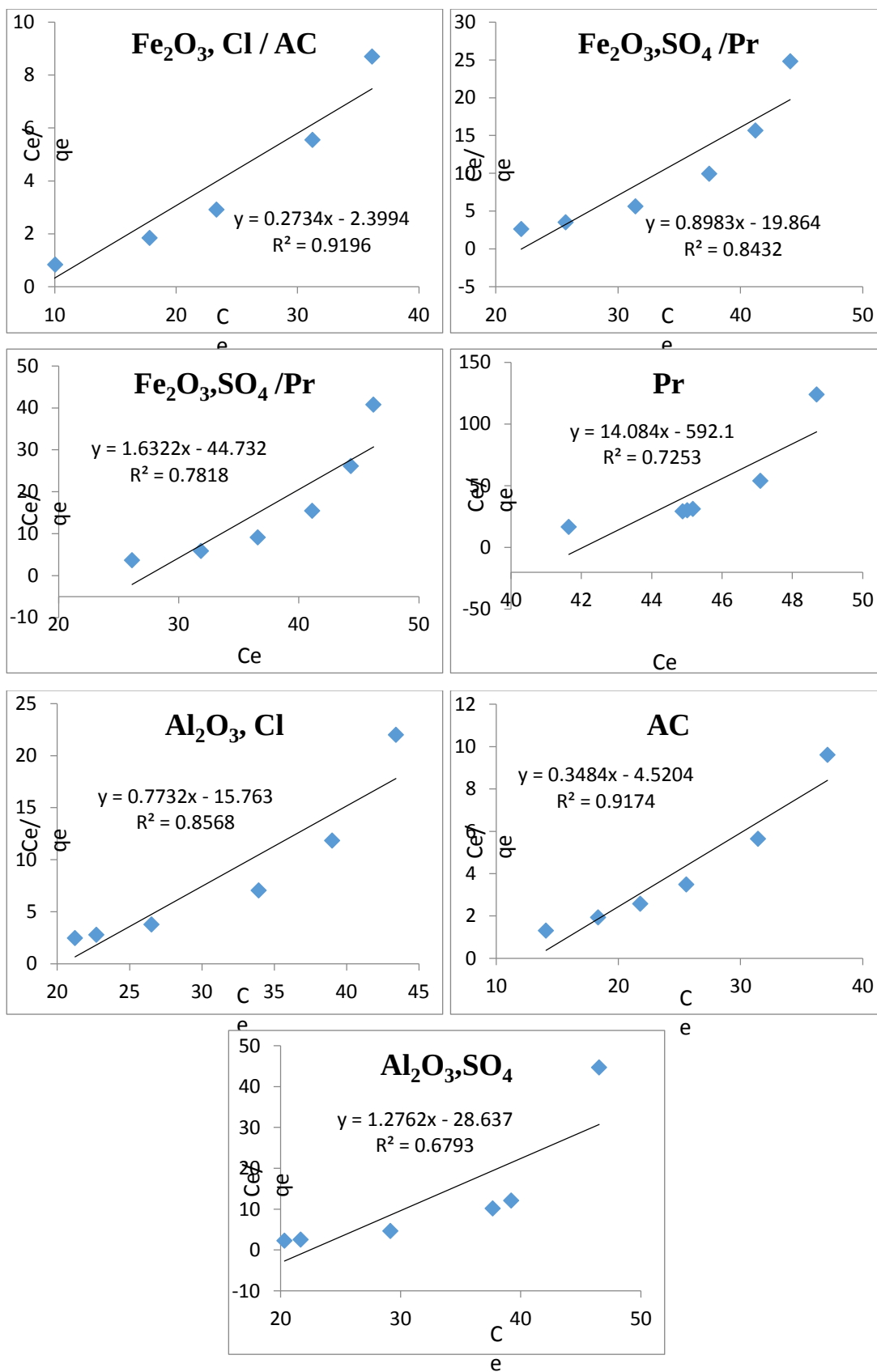
$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \left(\frac{1}{q_m}\right) C_e \dots (3-3)$$

where q_m is the maximum monolayer capacity of adsorbent (mg g^{-1}) and K_L , the Langmuir adsorption constant (L mg^{-1}), related to the adsorption free energy. The linear plot was derived between C_e/q_e versus C_e to calculate adsorption parameters. Moreover, the degree of suitability of adsorbent towards MO was estimated from the values of separation factor constant (R_L), which can be calculated from the following equation:

$$R_L = 1/(1 + K_L C_0) \dots (4-3)$$

where K_L is the Langmuir isotherm constant (L mg^{-1}), and C_0 is the initial dye concentration (mg L^{-1}). The value of R_L shows that the adsorption MO on all samples is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The values of q_{max} and K_L were computed from the slope and intercept of the Langmuir plot of C_e/q_e versus C_e . The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter.





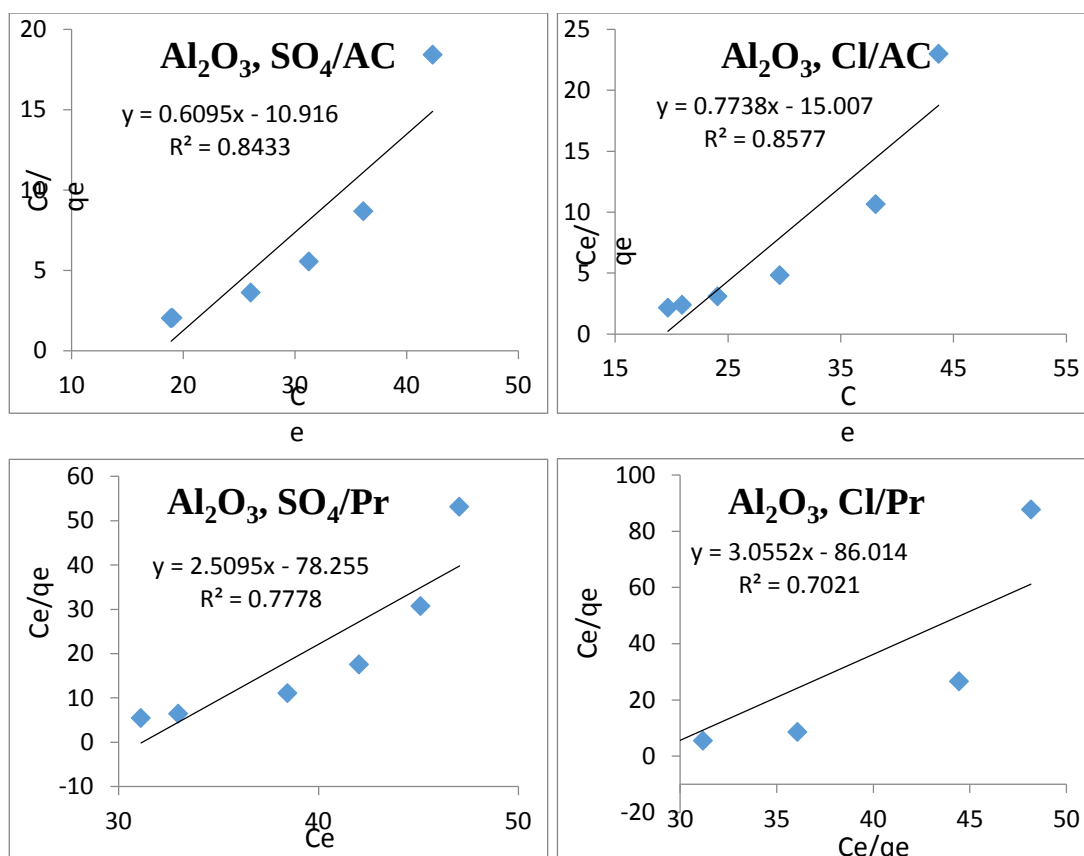
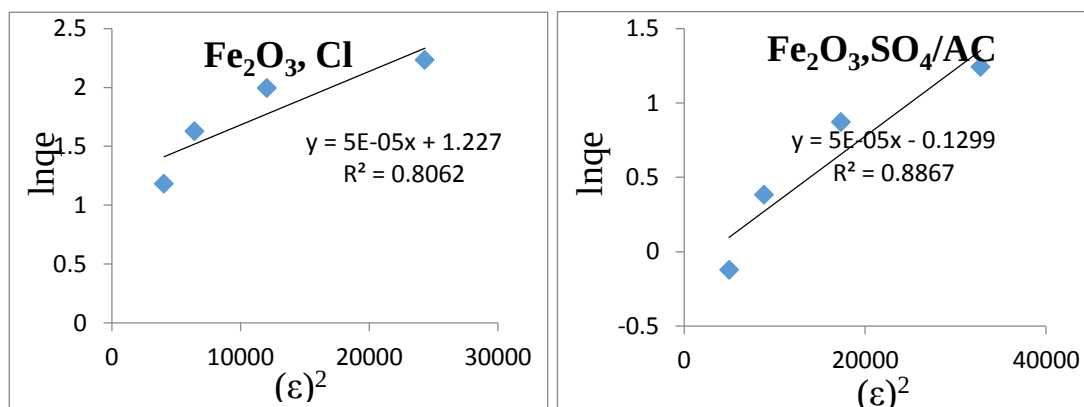
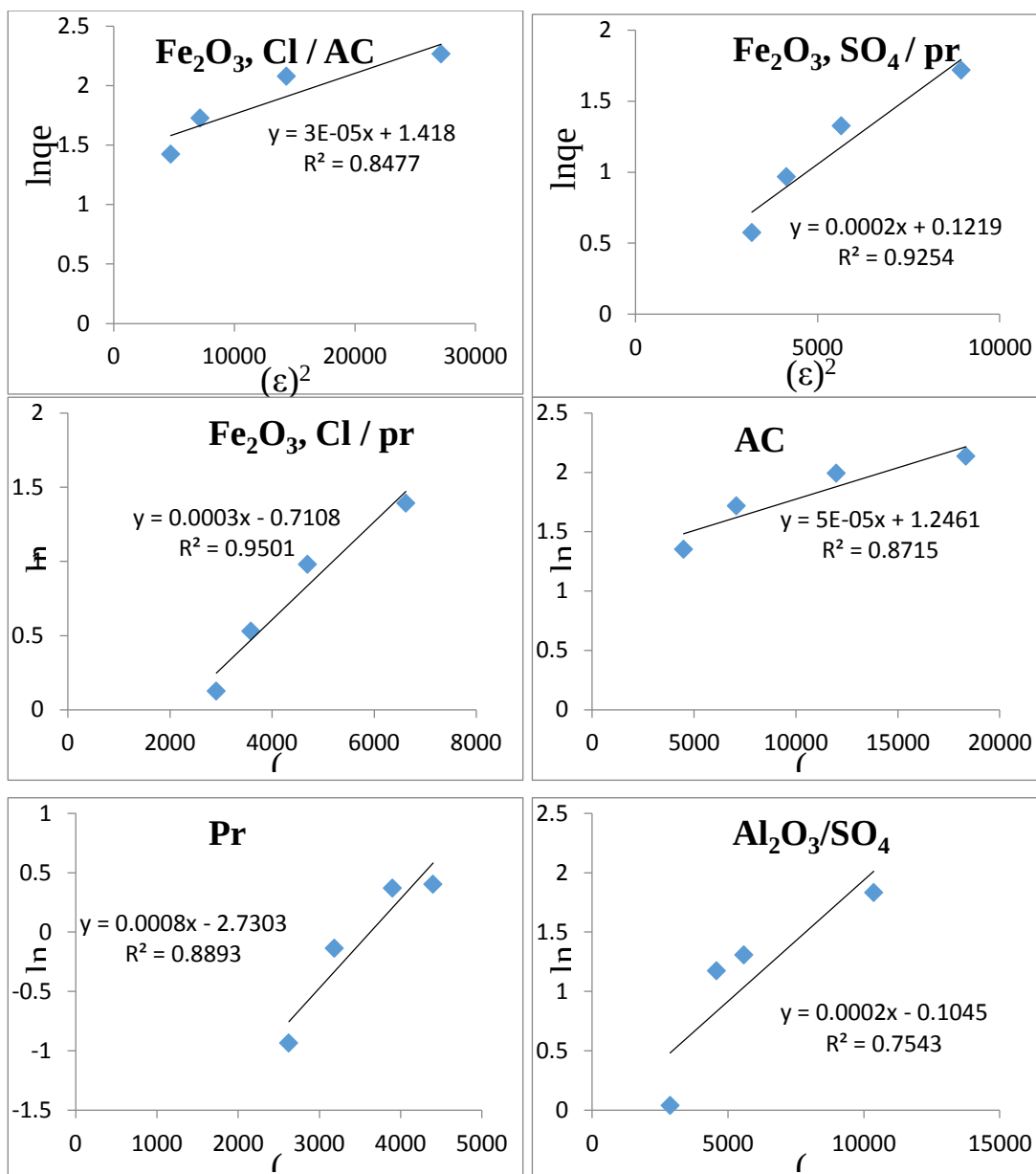


Figure 3.33. Langmuir isotherm model of MO removal by nanomaterials

Dubinin–Kaganer–Radushkevich (DKR) Model

Since the surface is heterogeneous, this isotherm is more significant according to Langmuir and Freundlich [101, 102]. The value of this isotherm is determine from equations (3-1) , (4-1) and (5-1).





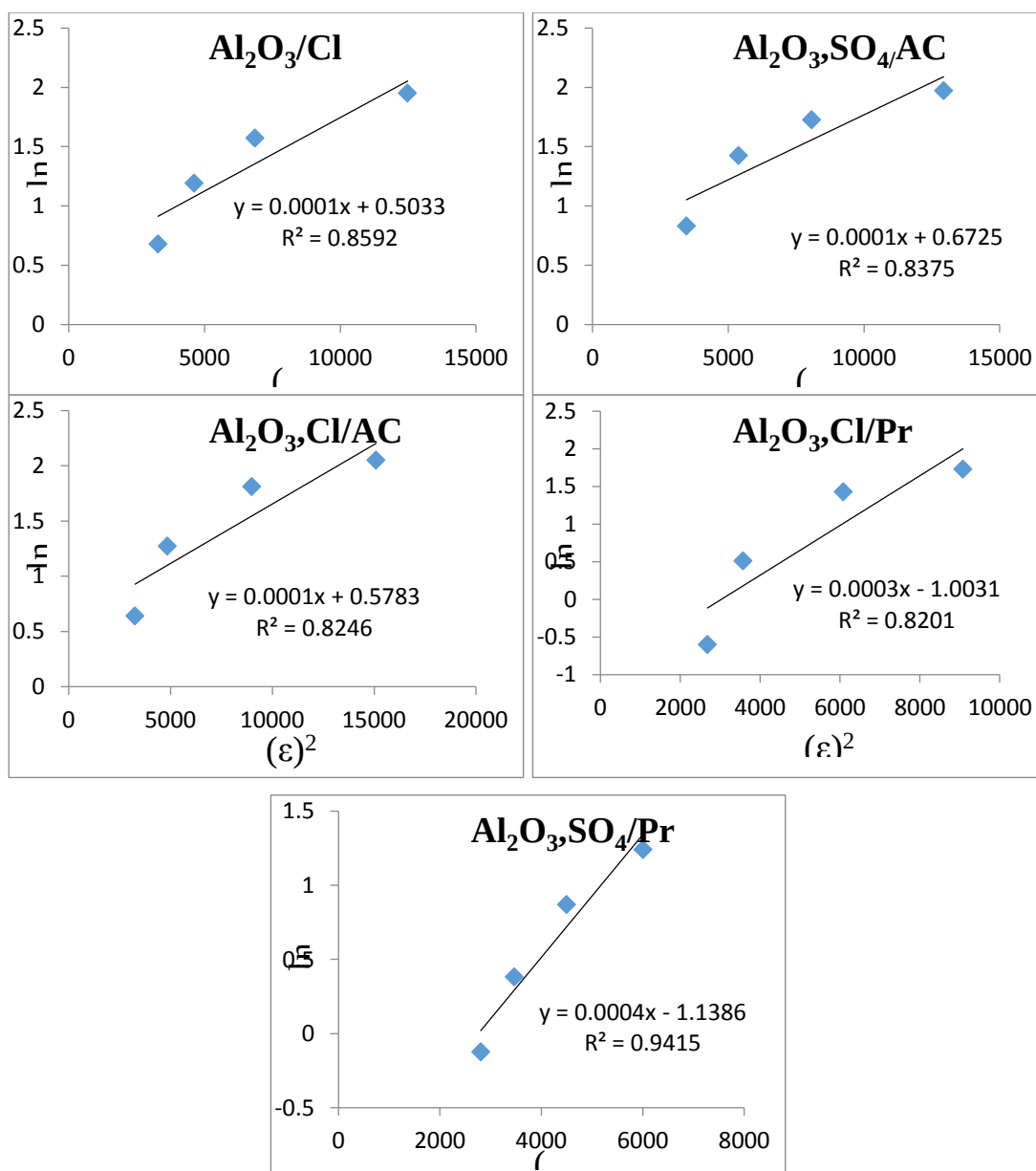


Figure 3.34. Dubinin–Kaganer–Radushkevich (DKR) isotherm model of M.O removal by nano materials

Table 3.8. Langmuir and DKR adsorption isothermal constants, correlation coefficients and the adsorption capacities of sample Adsorbents for MO

Adsorbents	Langmuir				DKR		
	K_L	R_L	R^2	β	E,J/mol	ϵ	R^2
Fe ₂ O ₃ ,SO ₄	0.465341	0.041208	0.87	7.39E-05	3382.95	82.23558	0.788
Fe ₂ O ₃ ,Cl	0.082263	0.195574	0.897	4.55E-05	5494.505	104.7905	0.806
Fe ₂ O ₃ ,SO ₄ /pr	0.045221	0.306651	0.843	0.000187	1336.898	1.37E+17	0.925
Fe ₂ O ₃ ,SO ₄ /AC	0.131767	0.131781	0.911	2.63E-05	9505.703	137.8503	0.911
Fe ₂ O ₃ ,Cl/pr	0.036489	0.354048	0.781	0.00033	757.5758	8.04E+15	0.9501
Fe ₂ O ₃ ,Cl/AC	0.113939	0.149322	0.919	3.42E-05	7309.942	120.8455	0.847
Al ₂ O ₃ ,SO ₄	0.044565	0.309765	0.679	0.000204	1225.49	8.82E+16	0.754
Al ₂ O ₃ ,Cl	0.049049	0.289648	0.856	0.000124	2016.129	1.06E+18	0.859
Al ₂ O ₃ ,SO ₄ /pr	0.032068	0.384114	0.777	0.000108	2314.815	2.16E+18	0.824
Al ₂ O ₃ ,SO ₄ /AC	0.055833	0.916081	0.843	0.00011	2272.727	1.98E+18	0.837
Al ₂ O ₃ ,Cl/pr	0.03552	0.360233	0.702	0.000331	755.287	7.87E+15	0.824
Al ₂ O ₃ ,Cl/AC	0.051559	0.279489	0.8577	0.000108	2314.815	2.16E+18	0.824
pr	0.023786	0.456769	0.725	0.000753	332.0053	1.29E+14	0.889
AC	0.077068	0.206041	0.917	5.28E-05	4734.848	7.58E+19	0.871

Comparative correlation coefficient (R^2) values of Langmuir and DKR models respectively indicate fitness of the adsorption data. However, higher value of correlation coefficient R^2 0.95 of DKR model in comparison to other studied models.

Conclusions

This study it is concluded that :

1. α -Fe₂O₃, Al₂O₃ Nanoparticles well prepared using eucalyptus leaves extract methods.
2. X-ray diffraction revealed that particle size obtained is about 48 nm, 37 nm for α -Fe₂O₃ and γ -Al₂O₃ respectively.
3. The percentage removal of methyl orange reach equilibrium in contact time (60) min, and at adsorbent weight (0.1) g. The highest percentage of removal for nano oxides and nanocomposites was for Fe₂O₃, SO₄ (75.22%), Fe₂O₃, Cl (73.68%), Fe₂O₃, SO₄/AC (83.76%), and Fe₂O₃, Cl/AC (80.84%). Fe₂O₃, SO₄/Pr (51.84 %), Fe₂O₃, Cl/Pr (47.76 %), Al₂O₃, SO₄ (59.34 %), Al₂O₃, Cl (57.54 %), Al₂O₃, SO₄/AC (62.22 %), Al₂O₃, Cl/AC (60.66 %), Al₂O₃, SO₄/Pr (37.78 %), Al₂O₃, Cl/Pr (46.86 %), AC (71.86%), and Pr (16%).
4. The kinetics results confirm best correlation of the experimental data of adsorption to Elovich model.
5. The Dubinin–Radushkevich model have a good linear relationship when applied to the metal oxides nanoparticles.
6. Calculated values of the thermodynamic functions (ΔG , ΔH , ΔS) of the adsorption declare that it is non-spontaneous, endothermic and randomness process on all samples prepared.

Future studies

- 1-Using prepared $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ Metal oxide nanoparticles by eucalyptus leaves extract methods to removal of various heavy metals
- 2- Preparation of $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ nanoparticles using another and different chemical met.
- 3- Preparation of other metal oxides nanoparticles using *Capparis* Leaves Extract and used them in removal of dyes .
- 4- Calculation of the percentage of removal of methyl orange using other temperature.
- 5-Using other models in adsorption isotherm such as Hill model.

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الخلاصة

تضمنت هذه الدراسة تحضير أكسيد الألومنيوم النانوي $\gamma\text{-Al}_2\text{O}_3$ ، وأكسيد الحديد النانوي $\alpha\text{-Fe}_2\text{O}_3$ ، وتحضير المتراكبات الثنائية $\gamma\text{-Al}_2\text{O}_3$ / paraffine و $\alpha\text{-Fe}_2\text{O}_3$ / paraffine و $\gamma\text{-Al}_2\text{O}_3$ / AC و $\alpha\text{-Fe}_2\text{O}_3$ / AC ، nanocomposites.

تم تحضير الأكاسيد النانوية بطريقة صديقة للبيئة (عن طريق المعاملة بمستخلصات نبات الكالبتوز) باستخدام مصادر مختلفة $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ و $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ كمصدر لأكسيد الحديد النانوي ، و $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ و $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ كمصدر لأكسيد الألومنيوم النانوي . وقد حصلنا على جزيئات $\text{Fe}(\text{OH})_2$ و $\text{Al}(\text{OH})_3$ النانوية عن طريق الإضافة البطيئة لمحلول هيدروكسيد الصوديوم . بعد ذلك للحصول على الجسيمات النانوية $\alpha\text{-Fe}_2\text{O}_3$ و $\gamma\text{-Al}_2\text{O}_3$ ، تم إجراء عملية الكلسنة للجسيمات النانوية $\text{Fe}(\text{OH})_2$ عند 550 درجة مئوية. تم تشخيص الجسيمات النانوية بواسطة تقنيات FTIR و XRD و FESEM و DLS. تم استخدام (Brunauer-Emmett-Teller (BET لتحديد مساحة سطح المواد النانوية. فحص حيود الأشعة السينية XRD بين أن حجم الجسيمات النانوية $\alpha\text{-Fe}_2\text{O}_3$ لأكسيد الحديد النانوي هو 48nm نانومتر الذي مصدره $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ و 37 nm لأكسيد الألومنيوم النانوي $\gamma\text{-Al}_2\text{O}_3$ الذي مصدره $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$.

استخدمت هذه الأكاسيد المتراكبات النانوية لدراسة امتزاز الميثيل صبغة البرتقالي MO من محاليلها المائية . تم دراسة تأثير كل من زمن الاتزان ، وزن السطح الماز ، ودرجة الحرارة على عملية الامتزاز. وبينت النتائج أن أفضل زمن اتزان هو (60 min) . و أفضل وزن اتزان هو (0.1 g) . تم دراسة البيانات التجريبية على النماذج الحركية التالية: المرتبة الأولى الكاذبة ، المرتبة الثانية الكاذبة ونموذج Elovich model وتبين من الدراسة الحركية أن نموذج Elovich model هو الأكثر ملائمة من النماذج الحركية الأخرى في امتزاز صبغة الميثيل البرتقالي . وكذلك تم دراسة الدوال الترموديناميكية للامتزاز وكانت قيم ΔH موجبة للمتراكبات النانوية الثلاثة أي أن عملية الامتزاز ماصة للحرارة بينما قيم ΔG الموجبة مؤشر على عملية الامتزاز غير تلقائية . بينما قيم ΔS الموجبة دليل على أن الجزيئات ليست مقيدة.

أخيرًا ، تم تطبيق ايزوثيرم Langmuir وايزوثيرم Dubinin–Radushkevich على النتائج المستحصلة للدراسة ووجد ان امتزاز صبغة المثل البرتقالي على جميع العينات يتبع ايزوثيرم Dubinin–Radushkevich .



وزارة التعليم العالي والبحث العلمي

جامعة ديالى

كلية التربية للعلوم الصرفة

قسم الكيمياء

تحضير وتشتيت جسيمات نانوية مختلفة (Al_2O_3 و Fe_2O_3) في مصفوفة بارافين كمواد امتزاز محسنة

رسالة مقدمة الى

مجلس كلية التربية للعلوم الصرفة / جامعة ديالى

وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

إعداد

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