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Removal of Chromium (VI) From Aqueous Solution Utilizing of Magnetic Nano Composite based on Sunflower

A Thesis

Submitted to the Physics Department, College of Science, University of Babylon in Partial Fulfillment of the Requirements for the Degree of Master of Science in Physics

By

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2022 A.D. **1444 A.H.**

بسم الله الرحمن الرحيم

(وَيَسْأَلونَكَ عَنِ الرُّوحِ قُلِ الرُّوحُ مِنْ

أَمْرِ رَبِي وَمَا أُوتِيتُمْ مِنَ الْعِلْمِ إِلَّا قَلِيلاً)

صدق الله العظيم

سورة الأسراء

الآية (٨٥)

Supervisor Certification

I certify that this thesis entitled (**Removal of Chromium (VI) From Aqueous Solution Utilizing of Magnetic Nano Composite Based Sunflower**) was prepared by (**Huda Hasan Nahar Jasim**) under my supervision at the Department of Physics, College of Science, University of Babylon, as a partial fulfillment of the requirements for the degree of master of science in physics

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Certication of the Head of the Department

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Date**:** \ \ **2022**

Dedication

To everyone who gave me hope and confidence to reach what I want…

To everyone who encouraged me to continue…

To everyone who repeated to me calls for success…

HUDA

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I thank my Almighty (Allah) for helping me in completing my thesis

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HUDA

Summary

Wastewater, heavy metal toxicity, and phytoremediation have been the main topics of this thesis. These topics depend on a variety of structural elements and the optical characteristics of modified nanocomposite materials. And isothermal adsorption, which looks at the relationship between the amount of adsorbent and the amount of dissolved adsorbate in the liquid at equilibrium. And discusses the thermal adsorption models to get the most out of adsorption.

Heavy metals, when in abundance, can be very toxic to the medium in which it is dissolved. Adsorption has been used as a suitable water treatment process to remove heavy metal. Many studies have been conducted to remove these Chromium (VI) by using different materials.

Sunflower (Helianthus annuus L.) stalks were used as the adsorbent to remove Cr (VI) from wastewater. The synthetic wastewater was produced in the laboratory to conduct the experiments. Were conducted the filtration process which is the most commonly used in treatment plants for wastewater. Batch tests were conducted to assess the performance of Cr (VI) removal adsorption under different process conditions. Samples has been characterizing by UV-visible spectrophotometer, X-Ray diffraction studies, Fourier transform infrared spectroscopy and magnetic hysteresis.

Study indicated that better adsorption is achieved at increased of the pH of the aqueous solution. The optimum removal of the Cr (VI) at pH=7 and 0.03 g of adsorbent dose and 25°C temperature, the applicability of Langmuir, Freundlich and Temkin isotherms was also tested at a range of temperatures (25,35 and 45)^{o}C .

It was shown that Langmuir isotherm was better able to fit the linearized data points than Freundlich and Temkin with Cr (VI). The results revealed that the hexavalent Cr (VI) is considerably adsorbed on sunflower stalks and it could be an economical method for the removal of hexavalent chromium from aqueous systems.

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List of Symbols

Symbol	*Definition*
Cr	**Chromium**
C_e	**Equilibrium concentration**
Q_m	**Capacity maximum**
Q_e	**Amount of metal ion**
K_F	**Freundich isotherm constants**
K_T	**Temkin isotherm constant**
A,B	**Temkin constant**
FWHM	**Full width at half maximum**
D	**crystallites size**
λ_{cu}	**the wavelength of light**
θ	**The Bragg angle of diffraction**
C_i, C_f	**Initial and final concentration**

Chapter One

General Introduction

1.1 Introduction

Industrial wastewater contains high levels of heavy metals that may pollute the water once it is discharged to the nature. These metals include arsenic, chromium, copper, zinc, aluminum, cadmium, lead, iron, nickel, mercury, and silver. Heavy metals are elements that have more than five times the specific gravity than that of water. They are one of the most toxic types of water pollutants. At least 20 metals are considered to be toxic, and approximately half of these metals are emitted to the environment in quantities that are hazardous to the environment and the human health [1].

Some of the treatment processes that have been used to remove heavy metals from wastewater include precipitation with coagulation and flocculation, ion exchange, complexation of dry biomass and adsorption. However, there are limitations: Precipitation produces large quantities of heavy metals rich waste sludge; ion exchange and biomass methods are costly and cannot be readily applied to large scale applications [2]. Adsorption is used for its inexpensive cost and large-scale application. Activated carbon adsorbs dissolved organic substances in water treatment, but it cannot treat highly soluble organics or high concentrations of organic and inorganic compounds. Operation costs are also substantial [3].

Other adsorbents that have been used include synthetic polymers and silica-based substances [4,5]. However, these materials are more costly compared to activated carbon. Hence, there is a perceived necessity and growing interest in finding adsorbents that are more cost-effective and produce fewer limitations including high temperatures and pressures. Therefore, finding suitable materials and operating conditions are essential to addressing the concerns of heavy metal pollution.

1.2 Heavy Metal Toxicity

A metal is classified as a heavy metal when its density is five times that of water. Such as metals, chromium, nickel, copper, cobalt, manganese, mercury, lead, zinc, cadmium, silver, arsenic, and barium are the most abundant found in wastewater. These metals originate from industrial wastewater that is emitted in the neighbouring water. However, because of their toxicity, it is important that they are removed from the wastewater before discharging to water. Of these heavy metals, the ones that was chosen for this research were Chromium mostly due to it abundance in the wastewater, and also due to it level of toxicity [6] Table 1. Shows the toxicological effect of some heavy metals on human health .

Table 1: Sources and toxicological effects of some heavy metals [7]:

Heavy Metal	Sources	Effects
Copper	Water pipes; Copper water heaters and canned greens using copper to produce a ultragreen color ,Alcoholic beverage ,equipment Instant gas hot water heaters Hormone pills; Pesticides insecticides fungicides Copper cooking pots	Mental disorders, Anaemia Arthritis/rheumatoid arthritis Hypertension, Nausea/vomiting Hyperactivity, Schizophrenia Insomnia, Autism, Inflammation and enlargement of liver, heart problem, Cysti fibrosis**.**

Heavy Metal	Sources	Effects
Chromium	Steel and textile industry	Skin rashes, respiratory problems haemolysis, acute renal failure weakened immune systems kidney and liver damage alteration of genetic material, lung cancer, Pulmonary fibrosis
Nickel	Effluents of silver refineries electroplating, zinc base casting and storage battery industries	Dermatitis, Myocarditis Encephalopathy, pulmonary fibrosis, cancer of lungs, nose and bone, headache, dizziness, nausea and vomiting, chest pain, rapid respiration
Lead	Industries such as mining, steel automobile, batteries and paints Pollutants arising from increasing industrialization	Nausea, Encephalopathy Headache and vomiting, Learning difficulties, Mental retardation Hyperactivity, Vertigo, kidney damage, Birth defects, Muscle weakness, Anorexia, Cirrhosis of the liver, Thyroid dysfunction Insomnia, Fatigue, Degeneration of motor.

Heavy Metal	Sources	Effects
Mercury	Industries like chloro-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizer, batteries, dental fillings adhesives, fabric softeners, drugs, thermometers fluorescent light tubes and high intensity street lamps, pesticides, Cosmetics and pharmaceuticals	Tremors, Birth defects, Kidney damage, Nausea, Loss of hearing or vision, Gingivitis, Chromosome damage,Mental retardation, Toothloss,Seizures, Cerebral palsy, Blindness and deafness, Hypertonia – muscle rigidity, Minamata disease.

1.2.1 Environmental Impact of Heavy Metals

Remove heavy metals from wastewater is one of the important tasks in wastewater treatment, especially in developing countries. The reason is due to the environmental impacts on plants, aquatic life, and ecology. Many heavy metals are even toxic to the human body because they can accumulate in the body and cause serious health problems .Generally, heavy metals may exist in soil, water, and air depending on their chemical and physical state. The heavy metals in the soil will be taken by the plant and then enter food chains that will have an impact on the ecosystem. The heavy metals in water have impacts on almost all organisms. The heavy metals in the air will mainly have impacts on human and animals health since it can be inhaled or cause skin problems [8].

1.3 Chromium (Cr)

Chromium is the most abundant of all the heavy metals that can be found in wastewater. It is discharged from the wastewater of the steel manufacturing industry, paints industry, leather tannery products, dye and textile industry, paper industry, electroplating, and chrome plated products [9,10]. Chromium exists in two forms: trivalent Cr (III) and hexavalent Cr (VI). Its abundance is harmful to the marine life, vegetation and plants, in addition to humans due to its toxicity. Cr (VI) is also a strong oxidizing agent, as well as a potential carcinogen. Other potential harmful effects on humans due to long term exposure to the metal include liver damage, kidney circulatory damage, nerve tissue damage and dermatitis. In general, chromium results in very grave harmful effects on human health [11].

Cr (III) is less toxic than Cr (VI) as it only affects plants, not humans. Thus, the total concentration of Chromium in the form of both Cr (VI), Cr (III), in addition to other forms, is regulated to a threshold of 2 mg/L. The reduction of chromium concentration is crucial in order to meet this threshold. Hence, the U.S. Environmental Protection Agency (EPA) regulates a threshold of maximum allowed concentration of the metal allowed to be discharged into water bodies without treatment to be 0.05 mg/L. The US EPA also set the maximum contamination level for chromium to be 0.1 mg/L in drinking water [6].

1.3.1 Sources of Chromium

Chromium in soils is inherited from parent rock and tends to be higher in soils derived from volcanic and mafic parent materials [12]. An elevated amount of natural Cr concentrations (1,700 -10,000 mg Cr/kg) was found by researchers in a 2009 study conducted on surface soils sampled from the Sierra Nevada and Coast Range geographic provinces in northern California, USA. Serpentine rocks that are rich in Fe and Mg silicate minerals dominate the geochemical processes and mineralogy of this particular area. The ultramafic serpentine comprises Cr-rich minerals, i.e., chrome magnetite ($Fe^{2+}(Fe^{3+},Cr)_2O_4$) and chromite ($FeCr_2O_4$) [13]. Soils on serpentines typically contain from 2.0-4.0 g/kg from Cr, which is much higher than the average worldwide surface soil content of 0.054 g/kg [12].

Through its presence in the soil, humans consume Cr in food and beverages, principally as Cr (III). The mean concentration of Cr ranged from 0.10 to 0.40 mg/L in canned beers sampled from Warri, Nigeria and included common brand names as Becks، Heineken, and Guinness Stout [14]. Food sources of Cr include broccoli، grape juice, mashed potatoes and turkey breast [15]. Trivalent Cr as an essential element and nutrient for plants, animals and humans is controversial and research results are contradictory, and will be addressed [16,17,18].

1.3.2 Health Effects and Regulation of Chromium

Data on workers exposed to air borne Cr (VI) over an extensive period of time showed an increased risk of developing lung cancer [19]. though the results were confounded by the high rate of smoking by such workers. Recent studies have shown Cr (VI) to cause cancer and certain mutagenic disorders via oral ingestion in drinking water over a lifetime. In July of 2008 the National Toxicology Program (a part of the NIH) released a report on the carcinogenic effects of sodium dichromate dehydrate ($Na_2Cr_2O_7 \cdot 2H_2O$), a common Cr (VI) containing-chemical. Dosages equivalent to 0, 5, 20 ، 60 and 180 mg Cr/L were given to 100 rats and dosages equivalent to 0, 5, 10, 30, and 90 mg Cr/L were given to 100, both in their drinking water. The conclusion of the two-year drinking water study was that exposure to Cr

(VI) caused cancer, based on increased incidences of tumors in the small intestine of mice (within the duodenum‹jejunum, and/or ileum) [20].
The researchers also saw a significant increase in the incidence of squamous cell carcinoma, a type of oral cancer, when experimenting with rats [20,21]. Besides being mutagenic, Cr (VI) is also corrosive and allergenic [22].

Due to its high solubility, Cr (VI) readily enters and damages cells. The disorders caused by Cr (VI) have been studied thoroughly and a principal, proposed mechanism is during reduction of Cr (VI) to Cr (III) in cells, a reactive carbon-based radical species is formed from the oxidation of a carbon-based reductant, such as ascorbic acid (Vitamin C), which is regularly found in the body. It has been suggested that this unidentified and yet to be discovered carbon-based radical causes DNA strand breakage and other types of chromosomal changes.
A second hypothesis suggests that a hydroxyl radical (OH), generated from Cr (III) and reactive intermediate species Cr (V) in the presence of elevated levels (mM) of H_2O_2, may also lead to oxidative DNA damage and strand breaks [23]. Another hypothesis is that Cr (V) and Cr (IV) are reactive intermediates that are toxic as potent oxidants [24]. The Institute of Medicine (IOM) advises a daily intake of 25 and 35 µg Cr (III) for females and males, [25]. Absorption of inorganic Cr (III) ranges from 0.4 to 2% of a daily intake of 40-240 µg, while organic Cr (III) is estimated to be greater than ten times more bioavailable [26,27].

1.4 Nanocomposites

The field of nanocomposites involves the study of multiphase material where at least one of the constituent phases has one dimension less than 100 nm. The promise of nanocomposites lies in their multifunctionality, the possibility of realizing unique combinations of properties unachievable with traditional materials. The homogeneous dispersion of nanoparticles is the primary condition of the preparation of nanocomposites with acceptable properties. Parallel alignment of there inforcement with the external load, as well as good adhesion are further conditions tobe met, if the particles are anisotropic (layered silicates, nanotubes) and the composite isused in load-bearing application. The constituent that is generally present in greater quantity is called the matrix. The constituent that is embedded into the matrix material in order to improve the mechanical properties of nanocomposites is called reinforcement (or nanomaterials). Reinforcement is generally in the form of nanosized filler materials.[28]. The properties of nanocomposites do not depend on the properties of individual components but also depends on the following parameters:

- Process used in nanocomposite fabrication.
- Types of filler materials and their orientations .
- Degree of mixing of two phases.
- Type of adhesion at the matrix interface.
- Volume fraction of nanoparticles.
- Nanoparticle characteristics.
- Nature of the interphase developed at the matrix interface.
- Size and shape of nanofiller materials and Morphology of the system.

In order to achieve enhanced properties of nanocomposites,the nanosized particles should be dispersed and distributed in the matrix material properly, otherwise there will be agglomeration of particles and the properties of nanocomposites will deteriorate. These aggregates will act as defects and limits the property enhancement of nanocomposite, therefore to achieve maximum property enhancement, the nanoparticles should be homogeneously dispersed in the matrix [29].

1.5 Literature Survey

This paragraph includes several studies , the most important of which are :

In (2010) **Attia. A *et al.*, [30]** activated carbon derived from olive stones was chemically activated with sulfuric acid (OS-S) and used as an adsorbent to remove Cr (VI) from an aqueous solution at concentrations ranging from 4 to 50 mg/L. The results show that biomass (OS-S)-activated carbon is a better sorbent than commercial active carbon that has been processed. The pH of the system was shown to be a major factor in the adsorption of Cr (VI), with pH 1.5 producing the best results. Low pH levels can cause a significant amount of Cr (VI) to be converted to Cr (III). When using lower amounts, chromium (VI) was readily absorbed.

In (2012) **Pal. A *et al.*, [31]** studied the low-cost biosorbents used, viz., Anabaena and Vetiveria. The biosorption phenomenon is more or less like a chemical reaction, and so several parameters are bound to affect the process. The results indicate that the adsorption of Cr (VI) by Vetiver root and the Cyanobacteria Anabaena proves to be a cost-effective adsorbent for the removal of Cr (VI) from plating effluent. Langmuir was found to be the best fit. Anabaena was found to adsorb a maximum of 87.03% of Cr (VI) at a low contact time of 60 minutes, compared to 84.32% by Vetiveria sp. at a low contact time of 60 minutes. Using the data from the experiments and modeling, an efficient treatment plant for Cr (VI)-rich effluent could be designed and built.

In (2013) **Palanisamy. K.L *et al.*, [32]** studied the removing a heavy metal, copper, nickel and chromium, from its aqueous solution by carrier oils mediated iron oxide nanoparticles filtration. The prepared nanoparticles were studied in terms of size morphology, magnetic behavior, structure, surface area including surface chemical structure and charges using different techniques such as XRD, FTIR and TEM. The results indicate that the electrostatic attraction was responsible for the metal removal in the case of magnetite nanoparticles. The obtained data represents only the preliminary result obtained for achieving a systematic study regarding the removal of heavy metals from wastewaters using as adsorbents the nanoparticles with high capacity of adsorption due theirs high surface area.

In (2013) **Barakat. M *et al*., [33]** studied the strong anion exchange resin (Spectra/Gel IE 1x8) can be used as adsorbent for the efficient removal of Cr (VI) ions from synthetic wastewater solutions. Batch experiments were conducted with initial Cr (VI) ions concentration ranging from 25-300 mg/L. Different parameters influencing Cr (VI) adsorption process such as; solution pH, Cr (VI) and adsorbent concentration and contact time were investigated. The results showed better fits with Langmuir isotherm than the Freundlich isotherm. The calculated isotherm parameters confirmed the favorable adsorption of Cr (VI) on the Spectra/Gel sorbent.

In (2014) **Liu. W *el at*., [34]** studied the one-step efficient simultaneous removal of Cr(VI) and Cr(III) with mixture of TiO_2 and titanate nanotubes (TNTs). Unlike the conventional two-step Cr removal with a first photocatalytic reduction of Cr(VI) and a subsequent adsorption of Cr(III), the proposed single process significantly reduced reaction time (over 50%). The synergetic mechanism was interpreted and indirectly confirmed with H_2O_2 variation during photocatalysis. indicating good synergy of photocatalysis and adsorption even at high ionic strength of electrolyte. Besides, the desorbed TNTs could be easily regenerated by remedying the damaged tubular structure and reused for Cr removal with excellent performance. The outstanding synergetic effects with essential explanation of the mechanism make this study not only fundamentally important but also potentially practical applicable .

In (2016) **Beheshti. H *el at.*, [35]** studied the chitosan/MWCNT/Fe_3O_4 composite nanofibrous adsorbent fabricated by electrospinning process and its application for the removal efficiency of Cr (VI) ions from aqueous solutions. The prepared nanofibers were characterized using XRD, FTIR, SEM and TEM analysis. The effects of sorption parameters such as contact time, initial concentration and temperature were evaluated in a batch system. The kinetic and equilibrium data were well described by pseudo-second-order kinetic and Langmuir isotherm models. The results showed the high potential of chitosan/MWCNTs/Fe_3O_4 nanofibers for the removal of Cr (VI) ions from water and wastewater.

In (2018) **Sobhanardakani. S *el at.*, [36]** studied the chitosan used for the removal of Cr (VI) ions from aqueous solution. The maximum removal of Cr (VI) by chitosan was found at pH 4.0. Moreover, increasing in the initial concentration of Cr (VI) ions in aqueous solution from 100 to 1000 mg L^{-1}, lead to reduction in adsorption percentage of Cr (VI) ions from 79% to 65% by chitosan. The Cr (VI) adsorption equilibrium was attained after 200 min and by increasing agitation speed, and adsorbent dose the amount removed was increased. Adsorption of Cr (VI) ions onto chitosan follows Freundlich model and kinetic of adsorption process follow pseudo-second-order model. The results revealed that chitosan could be used as an efficient adsorbent for the rapid removal of Cr (VI) ions from water samples.

In (2019) **Obaid. S.A ,[37]** studied the magnetic activated carbon Nano composite made by burning Gundelia tournefortii straw in a simple and inexpensive method. Effects of the magnetic activated carbon Nano composite on Chromium (VI) adsorption from water was measured in terms of various parameters. Of the FTIR analysis it observed that the hydroxyl and C-H groups near the cover of the adsorbent add to chromium adsorption. The results from FTIR analysis showed that all of the nanoparticles had the functional groups expected.

In (2021) **Ranieri. E *et al.*, [38]** studied the experimental tests to evaluate the effects of prolonged contamination by Cr on Moso Bamboo (MB) (Phyllostachys pubescens) and the adaptability of the MB to the Mediterranean climate. A preliminary test on the MB was developed in the laboratory, simulating irrigation under Mediterranean conditions (600 mm per year) and tropical conditions (1800 mm per year), to evaluate the rate of growth and the MB's capability for Cr phytoextraction from contaminated soil.

In (2021) **Karimi-Maleh. H *et al.*, [39]** studied the efficient removal of Cr (VI) before releasing into the environment became an essential issue from both biological and environmental perspectives. Currently, numerous techniques have been studied for Cr (VI) removal and its recycling from the wastewater. The results regarding the tolerance of the plant to Cr showed a good response of the plant to 100 mg Cr/L solution, utilized for irrigation of the pots. Plant growth during exposure to Cr was reduced to about 1 cm/week, as average. The Cr removal percentages were also noteworthy, showing that the rate of MB's removal of Cr from soil ranged from 49.2% to 61.7% as a function of the soil degree of contamination.

1.6 Aim of the Work

In this work, the principle aim is to remove the Cr (VI) from water using Sunflower : $FeCl_3$ Nano composite. During the work there will be some complementary measurements which leads to the following objectives:

1- Study the concentration effect upon chrome removal.
2- Study time effect upon chrome removal.
3- Study the absorbed dose effect upon ions of chrome.
4- Study of optical and structural properties.
5- Study the absorption of the thermal equilibrium and its relation with concentration.

Chapter Two

Theoretical part

2.1 Introduction

Many methods have been used by researchers to obtain the most optimal and cost effective method to remove soluble solids from wastewater. of these solids, metals have received a lot of attention due to their harmful and toxic effect when present in abundance. At least 20 metals are considered to be toxic, and approximately half of this number is emitted to the environment in quantities that are hazardous to the environment in addition to the human health [40]. The most abundant metal existing in wastewater is Chromium and is considered the most dangerous metal due to it being mutagenic and carcinogenic [41].

Other metals in high quantities include magnesium, calcium, copper, aluminum, nickel, zinc, and arsenic. Some of the methods employed, or studied, include precipitation, filtration, coagulation, ion-exchange, magnetic fields, fluidized bed reactor, ion flotation, flue gas purification, and adsorption [42]. These methods have their advantages; however, to choose the suitable method, the disadvantages need to be compared. Precipitation, for example, cannot be used when low concentrations of heavy metal ions are present in large volumes of water.

Flocculation or coagulation needs to accompany precipitation, which usually results in large volumes of sediments containing heavy metal ions forming. Also, small concentrations of the metals are still dissolved in the water after the process has been complete, hence, resulting in it as an unsuitable method for this research [43].

Other methods are either time consuming, expensive, or cannot be applied on large volumes of waste. however, adsorption is a cost effective, relatively quick method of removing heavy metals from water regardless of the concentration of the metals or the volume of water that it is dissolved in. Different materials may be used as adsorbents which collect, or adsorb, the heavy metals from the wastewater. of those investigated in prior research include cashew nut shells [44], olive cake [45], date pits and fruits [46,47], tea factory waste [40], maize cobs [48], and wood saw dust [49], to name a few. Waste products and other natural products are readily used as adsorbates, hence, allowing for an inexpensive and feasible method of removing solids from wastewater [49].

2.2 Adsorption

Adsorption is a process that collects, or adsorbs, dissolved substances in water to the surface of the materials being used, or adsorbent. Adsorption has not been readily used to treat wastewater, but as the demands for better water quality become more rigorous, extensive research have been conducted on the process of adsorption to provide better quality and reduced toxicity of water. Adsorption with activated carbon was the most sought-on process, where the carbon was used as a “polishing process” to remove a fraction of the existing dissolved substances in the water after treatment [50].

Adsorbents previously used usually require a chemical process for its production. This is usually accompanied by a complex or time-consuming process or one that results in a lot of waste or bi-products. Other adsorbents that have been used require organic materials such as nuts [51], leaves, shells [52], bark [53], pits [54,46], wood [49], etc, to be heated to high temperatures and undergo rigorous processes for them to form an activated carbon [50]. In the case of organic substances and activated carbon, interactions known as “specific adsorptions” occur between the surfaces of the adsorbent and the different functional groups of the adsorbate. An attraction occurs between the adsorbate and the adsorbent primarily due to one or more of the following phenomena:

1. exchange adsorption – electrical attraction.
2. physical/ideal adsorption – Van Der Waal force attraction.
3. chemical adsorption – chemical reactions.

Also, the solubility of the substance in water plays an important role in adsorption, since the more hydrophobic the substance is in water, the higher its ability to be adsorbed, and the more hydrophilic it is, the lower its ability. This is due to the effect the soluble substances have on the surface tension of the water: the more substances are dissolved and soluble in the liquid solution, the more the alterations to the surface tension of the liquid solution. Adsorbents that have active surfaces, such as activated carbon, will result in reduced surface tension upon the substances' movement to the surface. The movement results in a diminution of effort to increase surface area that is proportional to the amount of adsorbate at the surface. Moreover, hydrophobic impurities in the water reduce the tension at the surface of water [55].

2.2.1 Activated Carbon

Activated carbon has been used extensively by previous researchers due to its high capacity of removing heavy metals and other organics dissolved in water. Activated carbon is obtained by initially heating the material such as pits or barks at a high enough temperature to allow for water to evaporate completely. The material is then impregnated with an acid, and then carbonated in a furnace at very high temperatures of around 500 C to 900 C [54,56].

The reside is washed in hot distilled water to achieve the desired pH level, and finally the activated carbon is crushed and sieved to the required diameter. As it is known, the smaller the diameter of the carbon the better it is for adsorption as it allows for a greater surface area to volume ratio. The larger the ratio, the greater the ability of the carbon to attach the dissolved substances, such as heavy metals, in the water to it. Many previous studies and experiments on adsorption have been conducted using activated carbon. The activated carbon has been made from bark, date seed, food and agricultural waste, and other low cost waste materials. However, the problem with activated carbon is the extensive pretreatment required to produce it. In other words, a lot of energy and funding is spent on maintaining specific conditions to produce activated carbon. Very high temperatures are required, in addition to the use of acidic chemicals. Hence, what started off as a cheap waste material ends up as a costly adsorbent after a long process [50].

2.2.2 Low Cost Materials

Adsorption is a low-cost process as it uses relatively cheap materials. The method to obtain and prepare the materials is effortless and does not require the use of other resources, chemicals, or processes. Low cost material that only requires thorough washing and drying to remove moisture before being sieved is the latest research material being employed for successful adsorption [57]. Evaluation of tree leaves hazelnut shells , agricultural waste [58], date pits [47], cashew nut [44], barks [53], maize corn [48], saw dust [49] etc has been done to test adsorption capability on different metals at different conditions. Conditions that are tested for include obtaining optimal pH, contact time, agitation speeds, and initial concentrations of metals and dosage of adsorbent. Different conditions yield different results for different metals and adsorbents. Hence, what may apply for a certain combination of experimental conditions, metals, and adsorbents, may not apply for another [59].

2.3 Phytoremediation

Phytoremediation uses variety of plants to degrade, extract, contain, or remove contaminants from soil and water, including groundwater.These contaminants involve heavy metals and their compounds .

Phytoremediation mechanisms are phytoextraction, phytostabilization, phytostimulation,rhizofiltration, phytodegradation and phytovolatilisation [60-64].

- Phytoextraction/phytoaccumulation/phytoabsorption/phytosequestration: This technique, plant roots absorb the contaminants from soil then translocate to the shoots or some parts of the plants.
- Phytostimulatio /rhizodegradation:It uses plants to reduce the contaminated soil by their roots. This technology has some successes in treatment of organic chemicals, including petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), chlorinated solvents, pesticides, polychlorinated biphenyls (PCBs), benzene, toluene, ethylbenzene, and xylenes .
- Rhizofiltration: It uses plants to clean up communal wastewater or contaminated wetland, surface water. The contaminants involve heavy metals or other inorganic compounds, e.g. Pb, Cd, Cu, Ni, Cr and Zn. These are adsorbed or precipitated by plant‘s roots.
- Phytodegradation: This technique uses plants to degrade the organic pollutants from soil, sediment, or groundwater. It can also degrade the synthetic herbicides and insecticides. However, phytodegradation is limited to remove organic pollutants only. Therefore, it can not apply to remove heavy metals because heavy metals are non-biodegradable.
- Phytovolatilisation: This technique uses plants to absorb and transpire the contaminants or pollutants from the soil to the atmosphere by conversion them to volatile form. Phytovolatilisation is available for

removal of organic pollutants and some heavy metals such as Hg and Se.

2.3.1 Advantage and Disadvantage of Phytoremediation

Phytoremediation has been accepted for environmental treatment in a recently year. This technology is used for cleaning-up contaminated sites with metals, especially contaminated soil and water including groundwater. Additionally, it is the lower cost treatment than another technology. It is also the environmental friendly technology. Although the phytoremediation is the cleanest and cheapest technology, it still has limitation. This is caused by climatic and geologic conditions of the sites. The temperature, altitude, soil type and accessibility for agricultural equipment are considered as the limitation of phytoremediation .

Phytoremediation takes time longer than another technology to treat the contaminants. The contaminants can be accumulated in fuel wood. Moreover, the collected contaminants in leaves can be released again into the environment during litter fall. The formation of vegetation may be limited by extreme environment toxicity [65,66].

2.3.2 Metal Extraction from Plants: 'Phytoextraction' process

The most common methods used nowadays for the determination of heavy metals in environmental samples involve highly sensitive spectroscopic techniques, such as atomic absorption spectroscopy and inductively coupled plasma-optical emission and -mass spectrometry, the drawback of these techniques is that they first require the solid sample to be transformed into solution. Sample digestion is mainly carried out by a fusion or a wet procedure based on an acid digestion with a heated mixture of mineral acids.

There are different heating systems that can be used for digestion such as, sand-bath, heating plate, pressure digestion and aluminium blocks. The introduction of microwaves, with both open and closed pressurised systems, has allowed a considerable reduction in the total time of analyses as well as in the risk of sample contamination. Whereas the use of closed digestion systems is mandatory for total determination of volatile elements to avoid losses (for example As, Hg, Cr), use of open systems allows a higher sample intake and facilitates the acid evaporation to dryness, reducing in that way following analytical problems associated with high acid 79 concentration [67].

Microwave-assisted sample digestion is a widely used method in sample preparation, and several standard methods have been developed on the basis of this technique. To reduce contamination from the handling steps during sample preparation, Hoffman (1988) developed a one-pot method for sample digestion. In this method a quartz insert was placed inside a digestion vessel during the sample preparation stage. The sample was weighed, digested, diluted and measured in the same insert. As there are no sample transfer steps during this type of preparation, contamination was reduced considerably. Vapour-phase digestion has been used with conductive heating, and more recently with microwave heating. Vapour-phase digestion is primarily used to reduce contamination, because the reagents are vapourized during sample digestion and only the vapour from the reagents comes into contact with the sample [68].

2.3.3 Accumulation of Heavy Metals in Plants

Accumulation of a metal is a function of uptake capacity and intracellular binding sites. Waste water or water with multi-cellular organism has complexities in terms of the tissue and cell specific differences, intracellular transport concentration, affinities of chelating molecules, as well as the presence and selectivity of transport activities which can affect metal accumulation rates [69]. In addition to these factors, processes such as mobilization and uptake from the soil, compartmentalization and sequestration within the root, efficiency of xylem loading and transport, distribution between metal sinks in the aerial parts, sequestration and storage in leaf cell impact on the metal accumulation rate in the plants [70].

Many plants have shown the capability to extract and to process high concentrations of organic compounds with no significant toxic effects. Some plant species have developed the heavy metal tolerance capabilities which enable them to survive and to grow in the highly metal contaminated waters and soils [71,72].

By accumulation of heavy metals, xenobiotics and radinuclides through phytoremediaiton characteristics of plants, the cost effective treatment of wastewater, ground water and soil is possible. Once accumulated in the plants, these extracted heavy metals can be transformed rapidly to reduced toxicity metabolites. Also, these toxic metals can be translocated with the help of plants to surface shoots during phytoextraction, later which can be harvested, and the tissue processed by drying, ashing or composting.

A further application of these plants with extracted metals is to filter metals from water onto rootsystems that is called rhizofiltration or to stabilize hazardous metal containing sites which is called phytostabilization. With accumulation of heavy metals utilizing phytoremediation process, the volume of toxic waste produced is just a fraction of what other traditional methods of landfill and incineration typically generates [73].

2.3.2 Plant of Sunflower

The successful phytoremediation depends on the properties of selected plant species. Plants are able to be heavy metals hyperaccumulators, and also produce the high biomass productivity. Several common plants applying for phytoremediation are Typha latifolia [74]. Echhornia crassipe [75, 76]. Scirpus tabernaemontani [77]. paniculata Franch [78].

In recent years phytoextraction has been suggested by several authors as a green and low-cost technology to clean up metal polluted sites This technique uses the ability of certain plants to accumulate heavy metals in a high concentration in their aboveground parts. The success of a phytoextraction process depends on biomass production and metal concentration in plant shoots . Results of several studies under greenhouse or growth chamber conditions indicated that some crops and hyperaccumulating species have the potential to remove metals from polluted soils [79].
The sunflower (Helianthus annuus L.) is a member of the Asteraceae family. There are 65 distinct species in the genus Helianthus. The species trait that makes this family distinct is the plant features rough, hairy leaves, a wide, coarsely serrated stem, and round flowerheads. The heads are made up of several individual blooms that develop into seeds at the foot of a receptacle [80].

2.4 Filtration for Water Treatment

Filtration is a commonly used, physical, chemical, and in some instances, biological process of water treatment. The filtration process involves separation of suspended solids and impurities from water by passing it through porous media. The filtration process is a simple and an effective method of treating drinking water, and thus it is a suitable process to be use for treatment systems. The filtration process does not require any addition of chemicals and can be operated without a power supply. It is also easily adaptable to household-scale systems. These devices treat relatively small volumes of water typically only treat drinking and cooking water. There are numerous of point of use water treatment systems available for various purposes and efficacy. Filtration is the most commonly used treatment process for such systems [81].

2. 6 Batch Tests

Most of the research conducted on adsorption of metals using waste materials underwent batch tests to analysis how the adsorbate and adsorbent perform under various conditions. These conditions include pH levels, initial concentration of metal solution, concentration of adsorbent, temperature, agitation speed, and contact time. All of these conditions produce different results once changed; however, the magnitude and significance of change alters between the different conditions as each has a different effect on the adsorption process. As adsorption is a process which involves reactions between the adsorbate and adsorbent, varying the conditions may improve or exacerbate the rate and amount of adsorption. pH affects adsorption reactions through H^+ and OH- ions that are emitted into the solution. A more acidic pH releases more H^+ ions that may react with the adsorbent or adsorbate, it will be affected by results. Likewise, an alkaline pH solution releases OH^- which may also react with the adsorbent or adsorbate [82]. Hence, it is crucial when performing batch tests to evaluate the process at different pH levels. Unfortunately, a universal pH value cannot, be determined and set due to the different types of adsorbents used and their chemical constitutions.

Hence, tests need to be performed to determine the most efficient value of pH. Like pH, contact time is another crucial factor to consider when performing tests. This is also significant as the adsorbents used are organic materials, which may release additional organic materials in the system. Not allowing for enough contact time will not effectively complete the adsorption process, hence, results obtained will be incomprehensible and void. The greater the contact time, the greater the possibility that equilibrium has been reached, and hence, adsorption has reached its potential. Agitation speed is another important criterion to be test, as this either speeds up or slows down adsorption. Although, a higher excitation speed is not necessarily mean a higher rate of adsorption. Adsorption is highest at a certain speed that needs to be determined through experimentation.

Different initial concentrations of the metal solution evaluate the capacity of the adsorbent in its ability to adsorb and remove the metals from the solution. Usually, the lower the concentration of the metal, the better the adsorption, as there is less adsorbate for the adsorbent to remove. However, some adsorbents perform extremely well in high initial concentrations of adsorbate, and hence, have a higher adsorption capacity. These adsorbents are thus favorable due to their capacity. Also, to test the capacity of the adsorbent, the concentration dosage in the liquid solution needs to be evaluated. If only a small quantity is required to remove a large portion of the adsorbate, then the adsorbent is favorable. Likewise, the more the quantity that is required, the least favourable as its capacity is low. One way to reduce the quantity of adsorbent is to increase the surface area. This can be achieved by using very small diameters of the adsorbent. Larger surface areas are a lot more successful in adsorption, and hence, the same adsorbent may require smaller dosages once ground compared to its larger counterpart[59].

2.7 Adsorption Isotherm

Analysis of the isotherm data is necessary in order to develop an equation that can accurately represent the results and could be used for design purposes [75]. An adsorption isotherm describes the relationship between the amounts of adsorbants which is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium [83]. The parameter C_e corresponds to the remaining metal ion concentration in the solution and Q_e refers to the amount of metal ion adsorbed per unit weight of adsorbent [84].

- **The Langmuir isotherm** assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. the Langmuir isotherm models linear structure is as follows [85,86]:

$$C_e/Q_e = b\ Q_m + C_e/Q_m \quad \ldots\ldots\ldots\ldots\ldots(1)$$

where b is the constant of Langmuir proportional to adsorption energy and Q_m is the capacity maximum for adsorption (mg/g) .

-**The Freundlich isotherm** is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent. The linear form of Freundlich equation is expressed as [86, 87].

$$\log Q_e = \log K_F + 1/n \log C_e \quad \ldots\ldots\ldots..(2)$$

Where K_F and n are Freundlich isotherm constants related to adsorption capacity and adsorption intensity, respectively and C_e is the equilibrium concentration ppm. A value of n ~1 reduces equation 2 to the linear isotherm typically observed for the adsorption of dyes on to solid adsorbents [87].

-**The Temkin isotherm** model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent–adsorbate interactions. The linear form of Temkin isotherm model is given by the equation [86, 87].

$$\mathbf{Q_e = B \ln K_T + A \ln C_e \; \ldots\ldots\ldots\ldots (3)}$$

Where B: is the Temkin constant related to the heat of sorption (J/mol) and A: is the Temkin isotherm constant (L/g).

Chapter Three

Experimental Part

3.1 Introduction

This chapter includes a description of all tools and devices used in this work which are shown in Diagram (3.1).

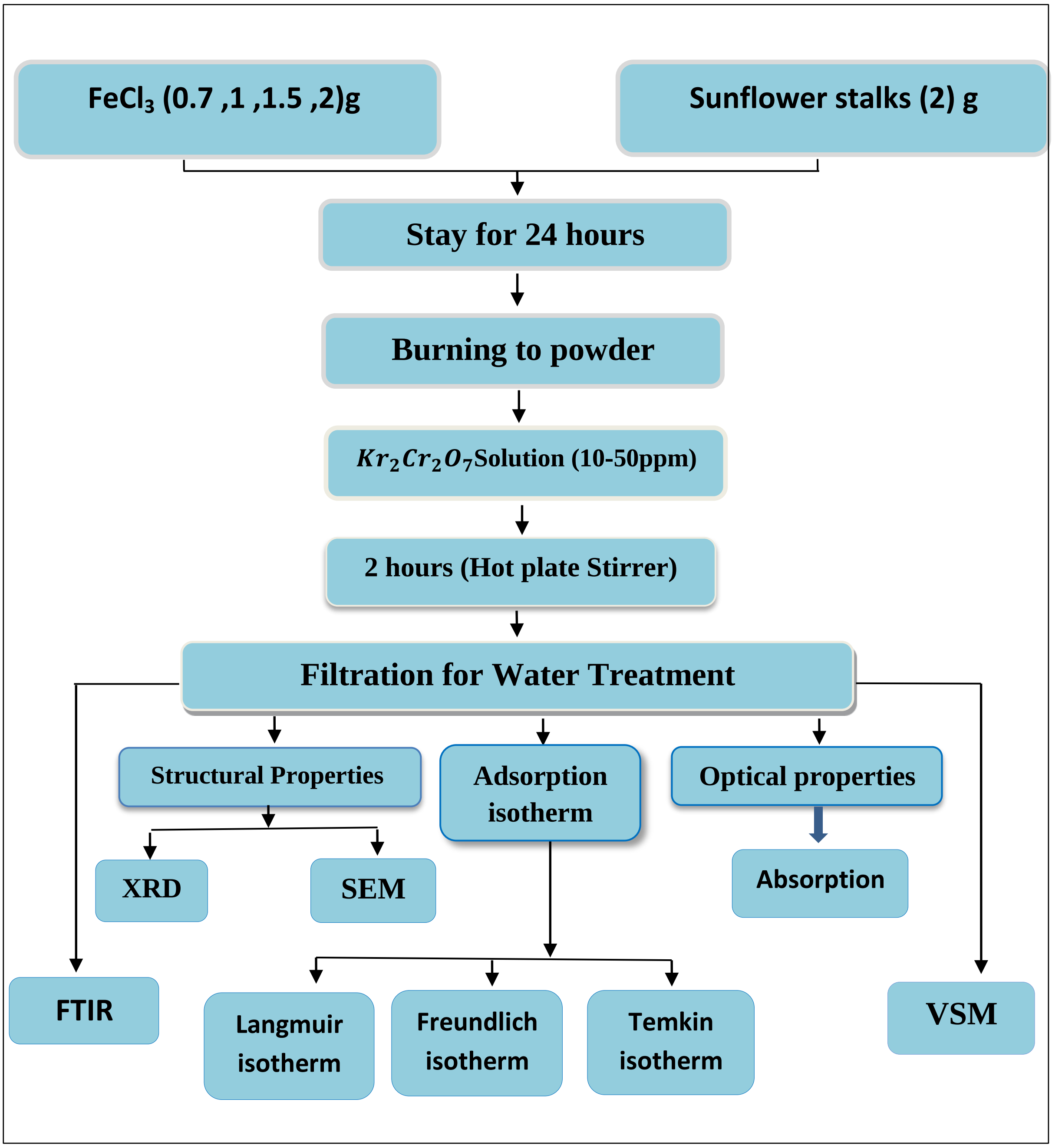

Figure (3.1): A schematic diagram of experimental the main steps for procedure.

3.2 Samples Preparation

3.2.1 Preparation of Sunflower (Helianthus annuus L.)

Sunflowers were gathered from fields in the city of Hilla, Iraq, washed in distilled water for 24 hours at 60 ºC in an oven, dried, and then put for 24 hours in a solution of 99% ethanol and FeCl3. To get the required concentration for the study. A small amount of straw was burned, becoming powder (nanocomposite).

3.2.2 Chromium Solution:

Different concentrations of soluble chromium using potassium dichromate ($K_2Cr_2O_7$) salt and distilled water was prepared. All experiments were conducted at room temperature, rotational speed of the stirrer at all stages 100 rpm.

3.3 Batch Adsorption Studies

The majority of trials were conducted in batches by melting and diluting a suitable amount of potassium dichromate ($K_2Cr_2O_7$), A stock solution containing 1000 mg/L Cr (VI) was made using deionized water. By diluting the stock solution with water repeatedly, the Cr (VI) concentrations in all experimental solutions were determined. Each of our equilibrium adsorption investigations was conducted in a thermostatic shaker rotating at a speed of 200 rotation per minute (rpm) while maintaining a constant temperature [88]. Experiments were conducted using a range of pH values, from 2 to 7, metal concentrations of 10, 20, 30, 40, and 50 ppm, and adsorbent dosages of 0.03- and 0.1 g/L respectively.

Batch adsorption studies were performed by mixing 1250 ppm $Kr_2Cr_2O_7$ was prepared by dissolving amount in the water 100 mL to become a standard solution. All experimental solutions of desired Cr (VI) concentrations were obtained by successive dilution of the stock solution.

Experiments on adsorption equilibrium were carried out in a thermostatic shaker with temperature control that rotated at a rate of two hundred revolutions per minute. The effects of pH on the elimination of Cr (VI) by the sunflower were investigated by changing the pH of the solution from 2.09 to 7. In addition, the pH of the solution was altered by adding either 0.1 M HCl or 0.1 M NaOH. Using an ultraviolet-visible spectrophotometer, one may determine the levels of chromium and iron by determining the absorbance of the sample at 540 nm (Shimadzu UV-1800, Japan). It was determined how to compute the percentage of chromium removal%R for each of the following expressions [89].

$$\mathbf{R\% = \left(\frac{C_i - C_f}{C_0}\right) \times 100 \quad \ldots\ldots\ldots\ldots(1)}$$

where C_i and C_f are the initial and final concentration of chromium in the solution. The adsorption capacity of an adsorbent which is obtained from the mass balance on the sorbate in a system with solution volume V is often used to acquire the experimental adsorption isotherms.

Adsorption tests were carried out at a pH of 2.09 and 20ml of adsorbent was utilized, using 100 mg/L Cr (VI) solutions with two concentrations (10-50 ppm of each main component). 20ml of adsorbent was utilized. The adsorbent was removed from the solution after the adsorption process had achieved an equilibrium. After that, the filtrate was examined for the presence of any residual Cr (VI). To test the Sunflower capacity for removing of Cr (VI) from real wastewater samples, a sample from the mining industry was used in batch mode. Sunflower extract was shown to be effective in the elimination and recovery of chromium in this investigation. Batch experiments done with varying amounts of chromium revealed that 5 minutes was sufficient to eliminate 90.18 percent of the chromium. Table (2) shows the effect of different adsorption parameters to removal of Cr (VI) .

Table (2) Effect of different adsorption parameters of Cr (VI) adsorption on sunflower.

parameters of the adsorption			
Contact time (min)	**pH**	**Dosage(g L^{-1})**	**Concentration of Cr (VI) ppm**
20	2.09	0.03	10
30	3.04	0.05	20
60	5.16	0.07	30
90	6.02	0.09	40
120	7	0.1	50

3.4 Adsorption Isotherms Studies

All of the chemical reagents employed were analytical grade and did not require any further purification. With concentrations of 10 -50 ppm and various sizes have been prepared and added 25 ml of distilled water after we added weight of 0.03 g of Chromium powder to each flask and put all of them on the flasks devices shaker (25 at room temperature, 35, 45) $^{\circ}$C for two hours and solutions had been nominated by filter paper, and examined using a spectroscopic method. As a result of the calibration curve's work, each substance has been assigned a maximum wavelength in the concentration range.

The absorption values were recorded to calculate the percentages of adsorption, and the solution concentration was designated when C_e ppm reached equilibrium. And using Langmuir, Freundlich and Temkin equation in chapter two.

3.5 Methodology

In this study, experimental procedures and measurement techniques used throughout this study were described. UV-Visible spectroscopy, X-ray diffraction (XRD) was used to acquire structural and morphological observations, and scanning electron microscopy (SEM) has been used to carry out experiments. Also Fourier transforms infrared spectra Magnetic hysteresis.

3.5.1 UV-Visible Absorption Spectrophotometer

UV-Visible absorption spectra have been recorded on Shimadzus (1800) UV-Visible spectrophotometer. The optical component of a spectrophotometer is made up of three parts: the source, the monochromator, and the detecting system in Fig. 3.2, these components are typically integrated into a unique framework to make spectrometers. The optical properties of solution at different parameters were investigated in the range of wavelengths (250-1050) nm. The spectrometer is powered by two light sources: deuterium and tungsten lamp, which operate at wavelengths of (190–390) nm and (390–1100) nm, respectively. The output data for wavelength, transmission, and absorption were utilized to calculate the optical energy band gap and basic optical edge using a computer algorithm.

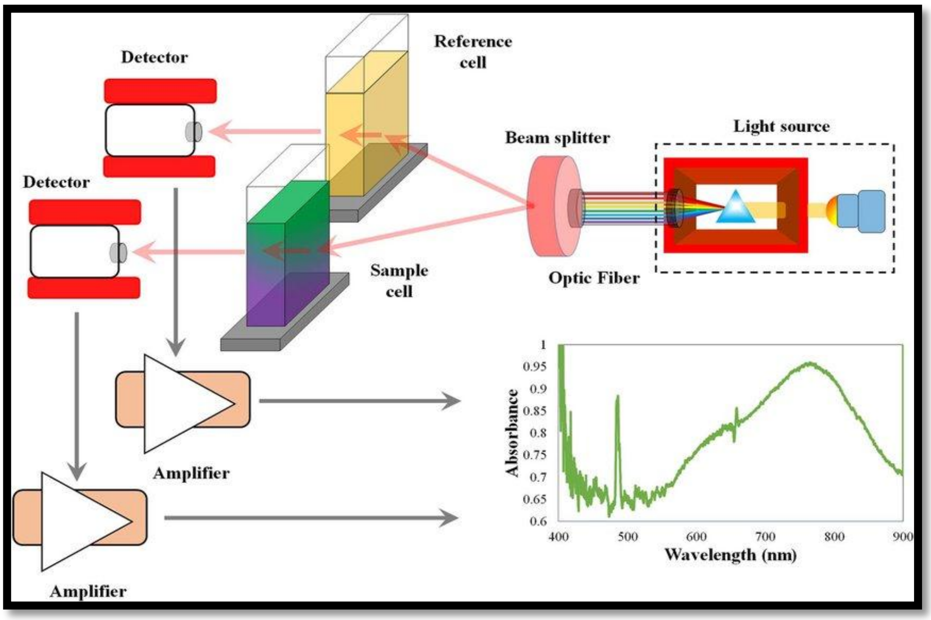

Figure (3.2): Schematic of UV spectrophotometer .

3.5.2 X-Ray Diffraction (XRD)

The main purpose of these measurements is to investigate the type of the structure of the prepared solution. X-ray diffraction is used to characterize of the materials, by which their orientation it is possible to determine the crystal structure and crystallites size. A typical X-ray wavelength that is equivalent to the interatomic distance in a crystal is used to communicate the characterization [90]. Samples were examined by sending the samples abroad (Islamic Republic of Iran). The solution was deposited on glass slides for carrying out these measurements.

3.5.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is one a type of electron microscope. The surface of a specimen to be examined is scanned with an electron beam, and the reflected (or back-scattered) beam of electrons is collected, and then displayed at the same scanning rate on a cathode ray tube (similar to a television screen). The image on the screen which may be photographed represents the surface features of the specimen.

Magnifications ranging from 10 to 100,000 times are possible. The surface morphology of the prepared samples was observed by sending the samples abroad (Islamic Republic of Iran). The solution was deposited on glass slides for carrying out these measurements.

3.5.4 Fourier Transform Infaraed Spectrometer (FT-IR)

Fourier Transform Infaraed Spectrometer is a wavelength and intensity measurement. Infrared spectra, bending, spinning, and vibrational movements of atoms in a molecule are all twisting. There are two sorts of molecular vibrations that may be used to characterize all of the movements. A stretch is one sort of vibration that results in a change in bond length. A stretch is a repetitive movement along the atom-to-atom line [91]. Infrared spectra of the solution prepared have been taken by sending the samples abroad (Islamic Republic of Iran).

3.5.5 Vibrating Sample Magnetometer

The magnetic properties of samples were examined using a sample magnetometer that vibrates (VSM, Magnetic Danesh Pajoh Co.) Magnetic characteristics were investigated at room temperature utilizing hysteresis curves and a magnetic field of up to 1 Tesla.

Chapter Four
Results and Discussion

4.1 Introduction

This chapter includes the results and the analysis of the experimental measurements of the solution with various concentration (10, 20, 30, 40 and 50) ppm and (0.03, 0.05 , 0.07 , 0.09 and 0.1) g of adsorbent dose and varying the solution pH from 2.09 to 7. In addition, we study the structural and optical properties of prepared solution.

4.2 UV-Visible Absorption Spectra

The preparation solution was measured by the optical properties and determined using UV-visible adsorbance at the (190 - 1100) nm, wavelength range and spectrofluorometer.

4.2.1 Absorption Analysis

Fig. (4.1) shows the UV-visible absorption spectra of the Cr (VI) solution. The reduction of the absorption peak intensity during exposure time indicates the reduction of Cr (VI) concentration in solution in contact to the nanocomposite. Results showed that after 5 min of exposure, over 30 % of chromate in the solution has been removed by nanocomposite powder. Considering the advantage of rapid removal process (lower exposure time), it can be concluded that one minute of exposure is enough to remove over than 90.18 % of Cr (VI). With increasing concentrations the peaks increase and this indicates the generation of new transitional levels.

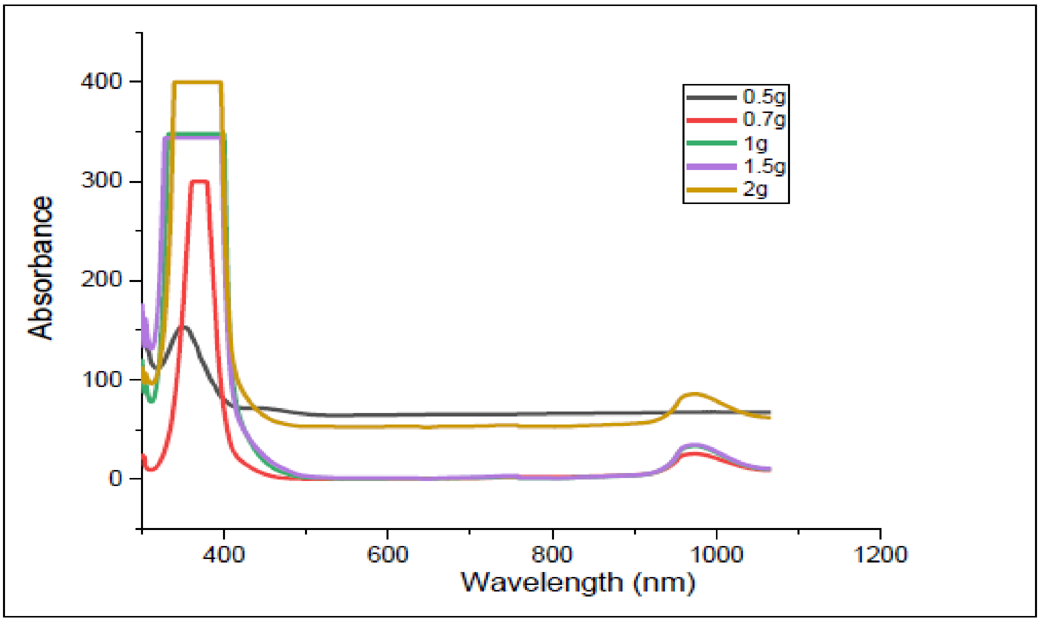

Figure 4.1 : Show of Absorbance with Concentration (20,30,40,50) ppm of Sunflower Nanocomposite.

4.2.2 X-Ray Diffraction Measurements (XRD)

X-ray diffraction is a versatile and non-destructive technique for classifying materials.crystalline phases seen in dense materials, as well as studying the structural properties of these states, such as stress, crystal size, phase structure, crystal orientation, and flaws are examples of such factors [92]. In the Fig. 4.2 (a ,b ,c and d) XRD analyses confirmed that the synthesized nanocomposite is magnetite (Fe_2Cl_3). The sharp diffraction peak at $2\theta = 40.331$ indicates good crystallinity of Fe_2O_3 nanoparticles and the crystallite size decrease with increasing of the concentration. This behavior can be explained the solution that has crystal defect and became good arrangements and more crystallized and to became nano scale. Structural analysis by XRD indicated that the high excess of Cl^- in the reacting mixture enabled the more favorable production of chloro-oxy-hydroxides In Fig. 4.2 (a, b, c and d) the multiple observed peaks were identified by variations in composition and crystallinity of the Cr (II) oxy-hydroxide with the formula $Cr_{21}Cl_{16}(OH)_{14}O_6$. The average crystallite dimension was calculated using the following equation [93 ,94].

$$D = K\, \lambda_{cu}\text{-}K_{\alpha} / \cos\theta\ \text{FWHM}$$

$$D = 0.89\, \lambda / \beta \cos\theta$$

Where;

D: crystallite dimension,

K: a coefficient (0.89).

λcu-Kα: wavelength of the emission from the diffraction tube.

FWHM: full width at half maximum of diffraction in the 2 θ scale (rad).

θ: The Bragg angle of diffraction.

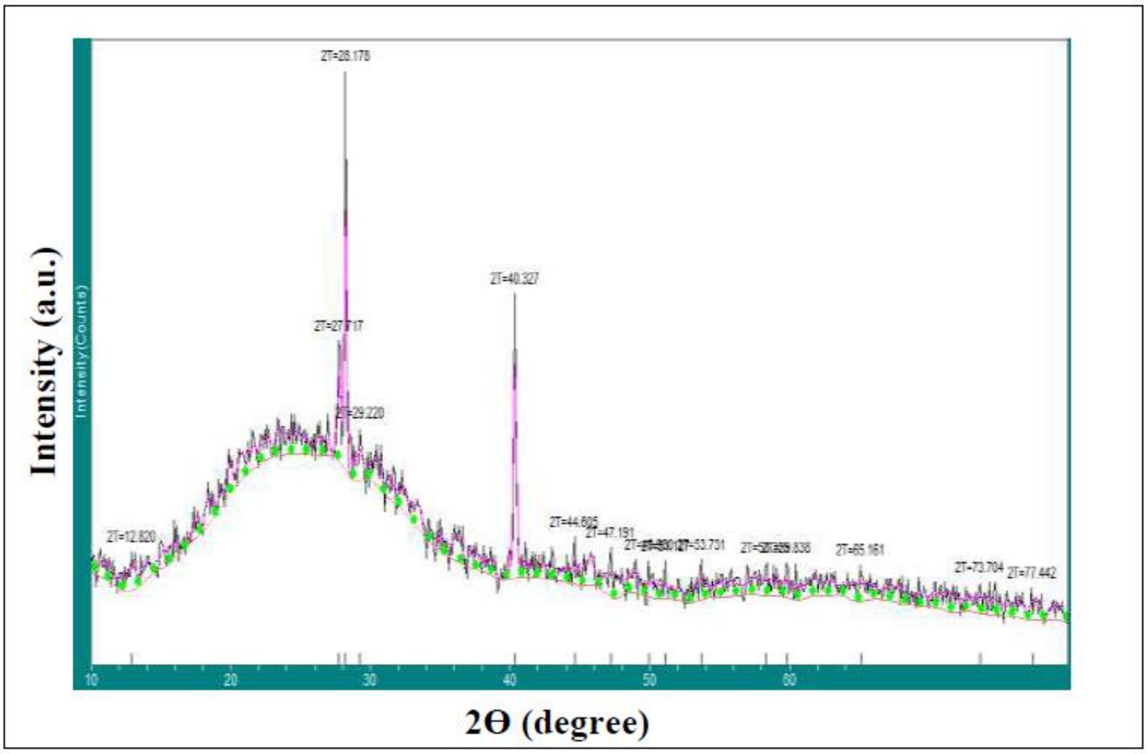

Figure 4.2 (a) : Show of XRD with concentration of (20) ppm for the Solution.

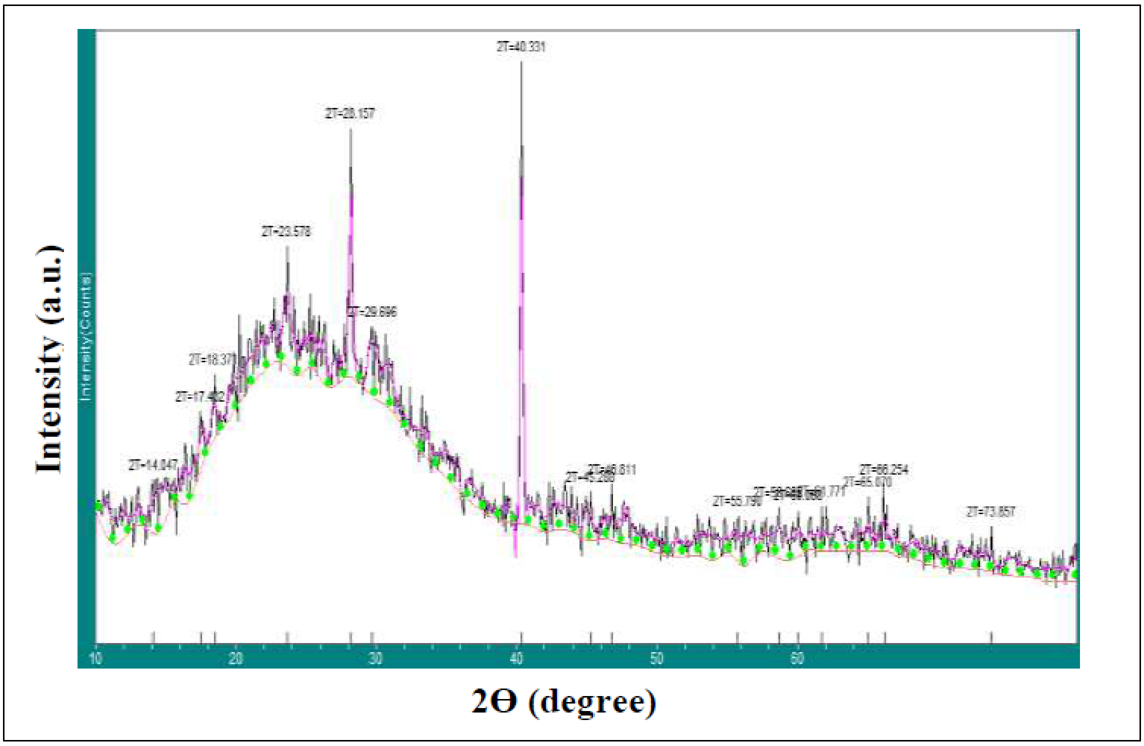

Figure 4.2 (b) : Show of XRD with concentration of (30) ppm for the Solution.

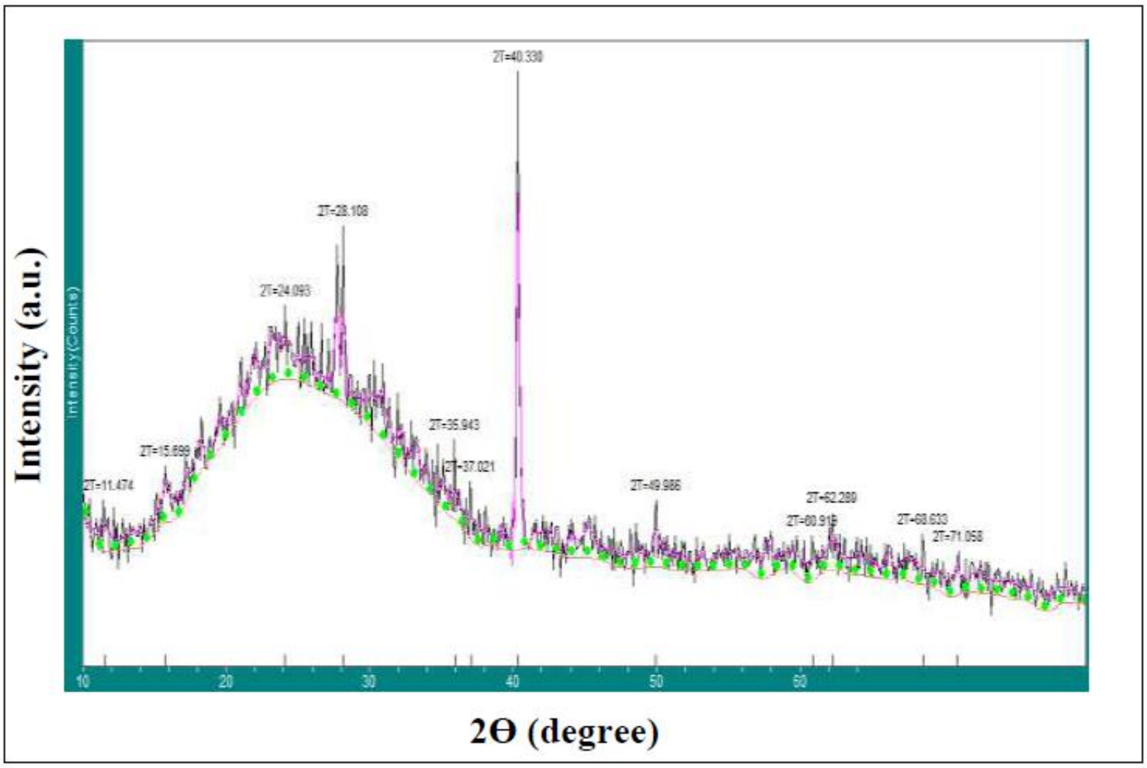

Figure 4.2 (c) : Show of XRD with concentration of (40) ppm for the Solution.

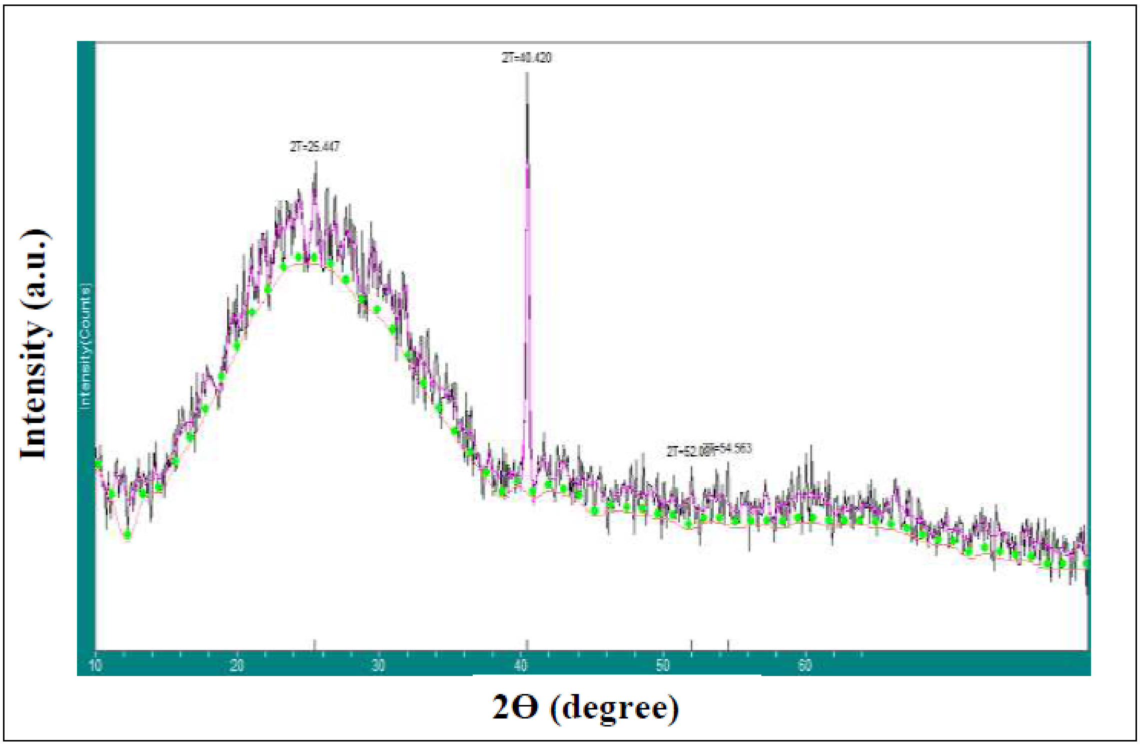

Figure 4.2 (d) : Show of XRD with concentration of (40) ppm for the Solution.

4.2.3 SEM Analysis

The scanning electron microscope may be used to directly observe the surface microstructures of adsorbents. The existence of new shiny bulky particles on the surface of metal-laden adsorbents that weren't there before the metal ions were loaded was clearly shown in Fig. 4.3. The adsorbent had a constant size and shape that resembled a semi-sphere. Due to a 300% increase in $FeCl_3$ concentration from 0.7 to 2 g the particle size has changed. The aggregation is assumed to be caused by the magnetic interaction between the iron particles [95].

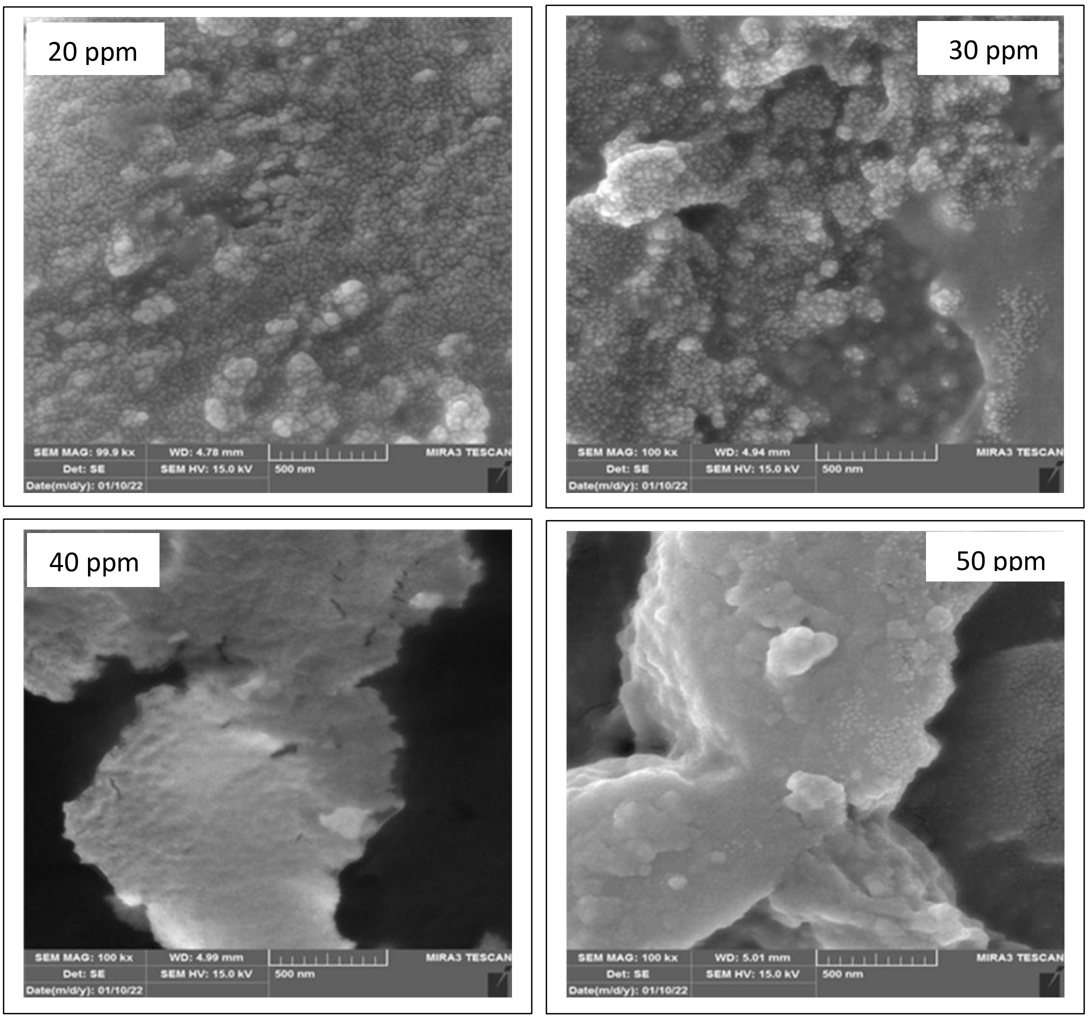

Figure 4.3: SEM images of solution at the concentration of (20, 30, 40, 50) ppm.

4.2.4 Fourier Transform Infrared Analysis (FT-IR)

Changes in the functional groups in the adsorbents. The spectra of the adsorbents was measured within the wave length range of 500-4000 cm^{-1}. The spectra were plotted using the same scale on the transmittance axis for all the adsorbents. The FT-IR spectra of the adsorbents display a number of absorption peaks indicating the complex nature of studied adsorbents. FT-IR spectra of both the adsorbents (native as well as chromium loaded) as shown in Fig. 4.4 (a, b, c and d) the broad absorption peak at 3276.75cm^{-1} is indicative of the existence of bonded hydroxyl group. It seems that this functional group participates in metal binding. The possible adsorption on these adsorbents may be due to physical adsorption, complexation with functional groups, ionic exchange, surface precipitations and chemical reaction with surface sites. The changes in FT-IR spectra confirm the complexation of Cr (VI) with functional groups present in the adsorbents .The intense bend at about region 2852.16–2933.13 for the precursor was attributed to the asymmetric and symmetric vibration modes of methyl and methylene group (C—H group) [96].

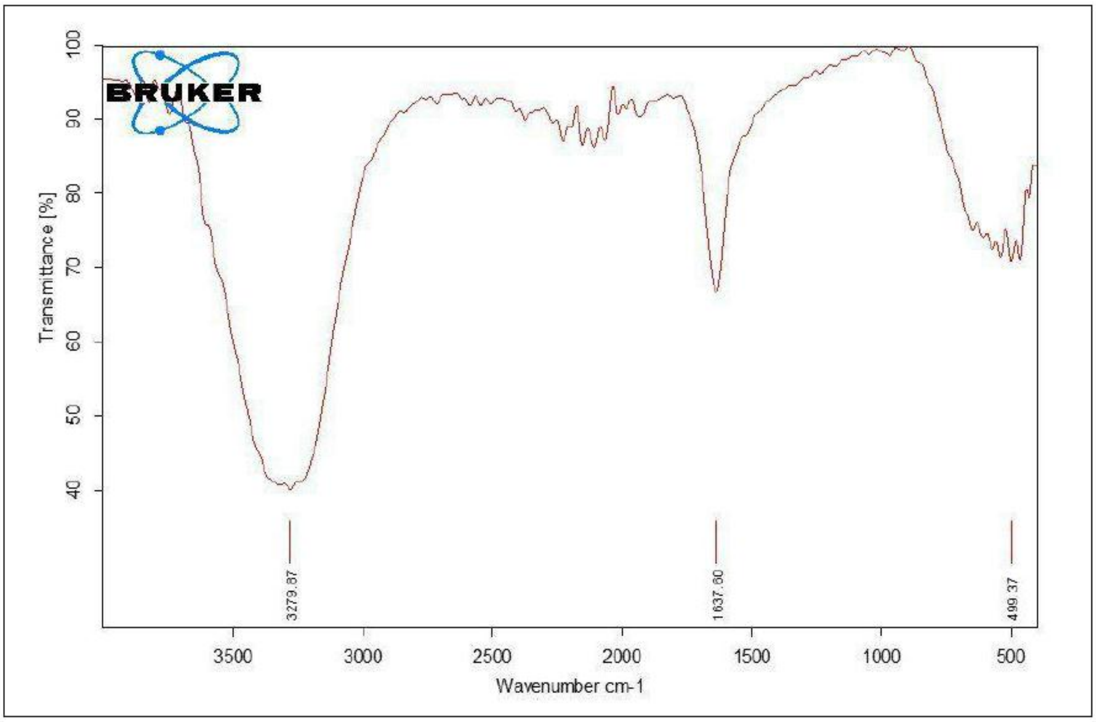

Figure 4.4 (a): FTIR Spectra of solution at the concentration of 20 ppm.

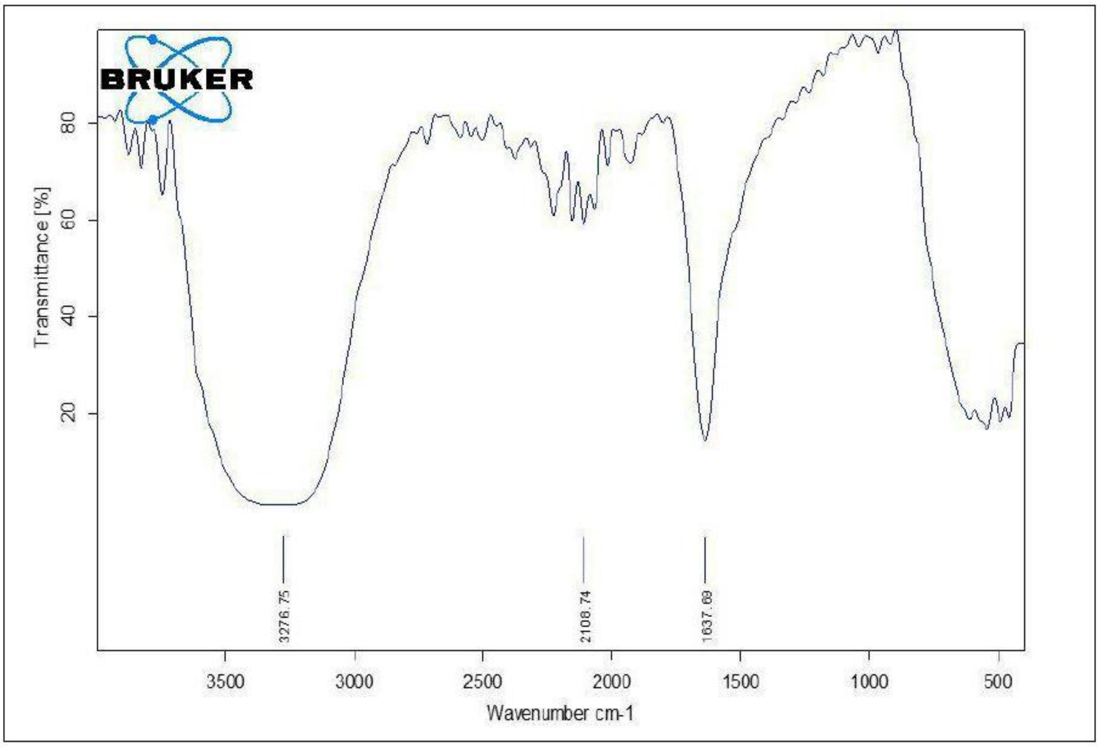

Figure 4.4 (b): FTIR Spectra of solution at the concentration of 30 ppm.

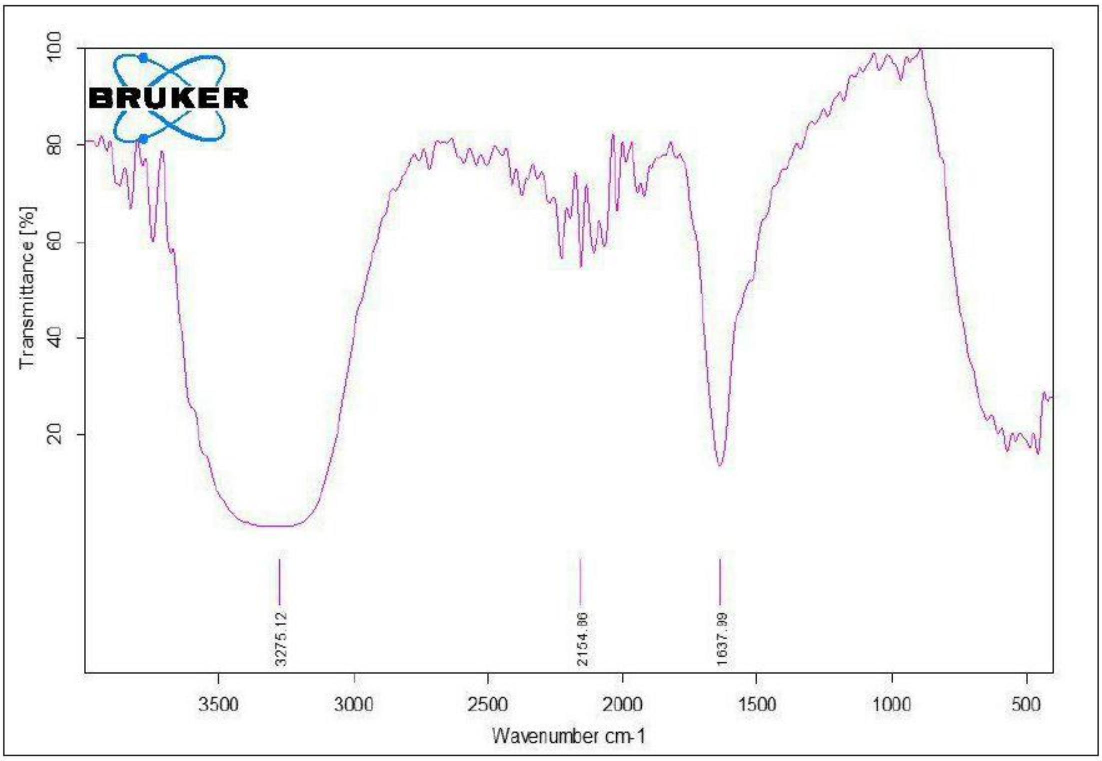

Figure 4.4 (c): FTIR Spectra of solution at the concentration of 40 ppm.

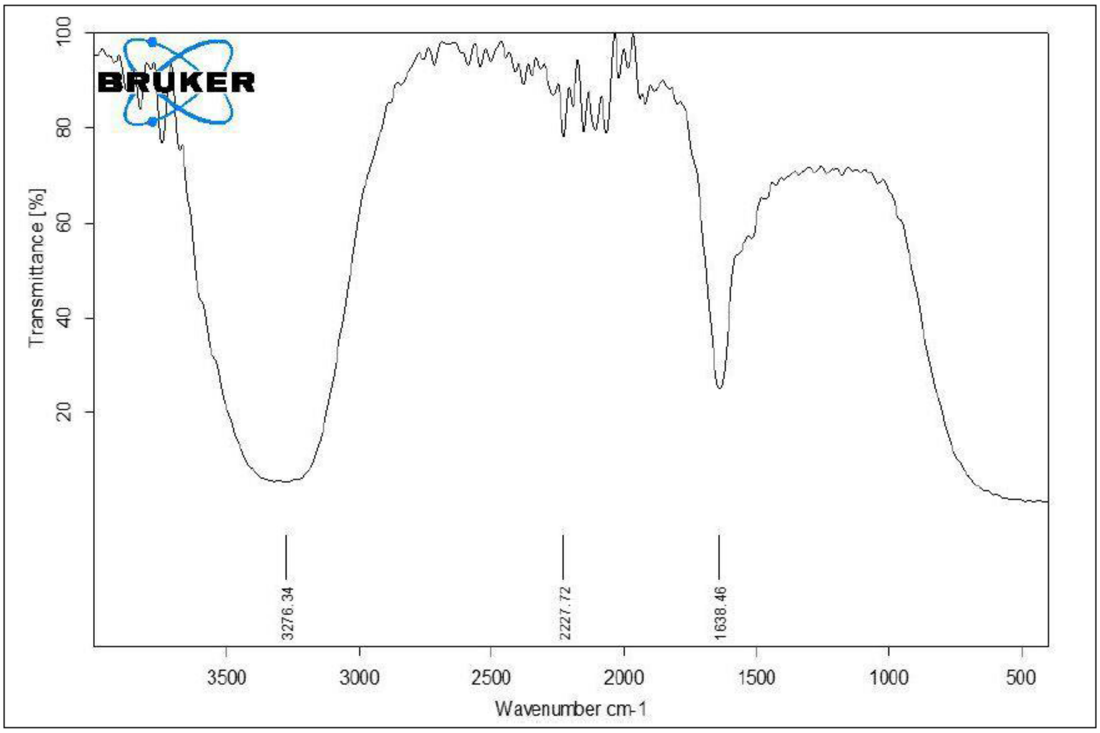

Figure 4.4 (c): FTIR Spectra of solution at the concentration of 50 ppm

4.2.5 Vibrating Sample Magnetometer Analysis

The magnetic properties of the magnetic composites were also measured after the treated with Cr (VI). As shown in Fig. 4.5 (a, b, c and d). the magnetic composite after treated with Cr (VI) were 46.74 and became 79.09 emu/g with increasing of the concentration.The coercivity (coercive force, H_c) is observed to be 0 O_e in both samples, and typical S curve indicating a super paramagnetic behavior. The magnetic composite after treated with Cr (VI) could still be attracted by a permanent magnet [97].

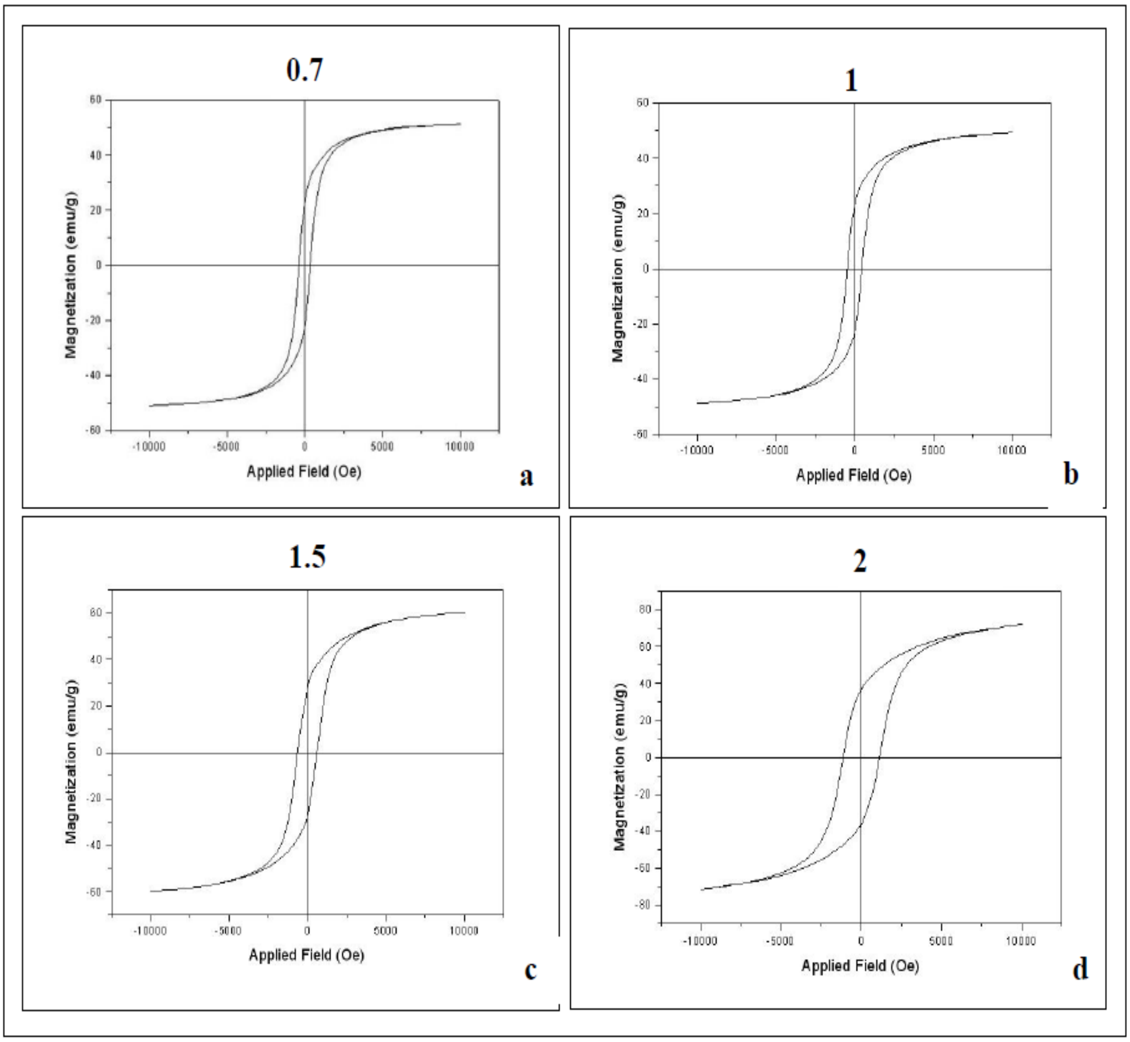

Figure 4.5 : Diagram of Activated Hysteresis Nanocomposites.

4.2.6 Effect Concentration of Chromium (VI)

The removal of Cr (VI) on to sunflower as a function of their concentrations was investigated at constant temperature (25˚C) by different the Cr (VI) concentration of 10 – 50 ppm while keeping all other parameters constant. The adsorption results of Cr (VI) by the sunflower are shown in Fig. 4.6 by increasing the concentration of Cr (VI) ions in aqueous solution, removal percentage was decreased, so that in the concentration of 10 ppm and constant contact time, the highest adsorption percentage was observed and with increasing in concentration amount of 10 - 50 ppm adsorption percentage decreased of 90% to 29 %. The decrease in the adsorption percentage is probably due to the saturation of the active sites on the sunflower surface at higher Cr (VI) concentrations. On the other hand, by increasing the Cr (VI) concentration the actual amount of Cr (VI) adsorbed per unit mass of the sunflower increased. The higher initial concentration of Cr (VI) provides an important driving force to overcome the mass transfer resistance for Cr (VI) transfer between the solution and the surface of the sunflower. This results is similar to the work of the researchers [98].

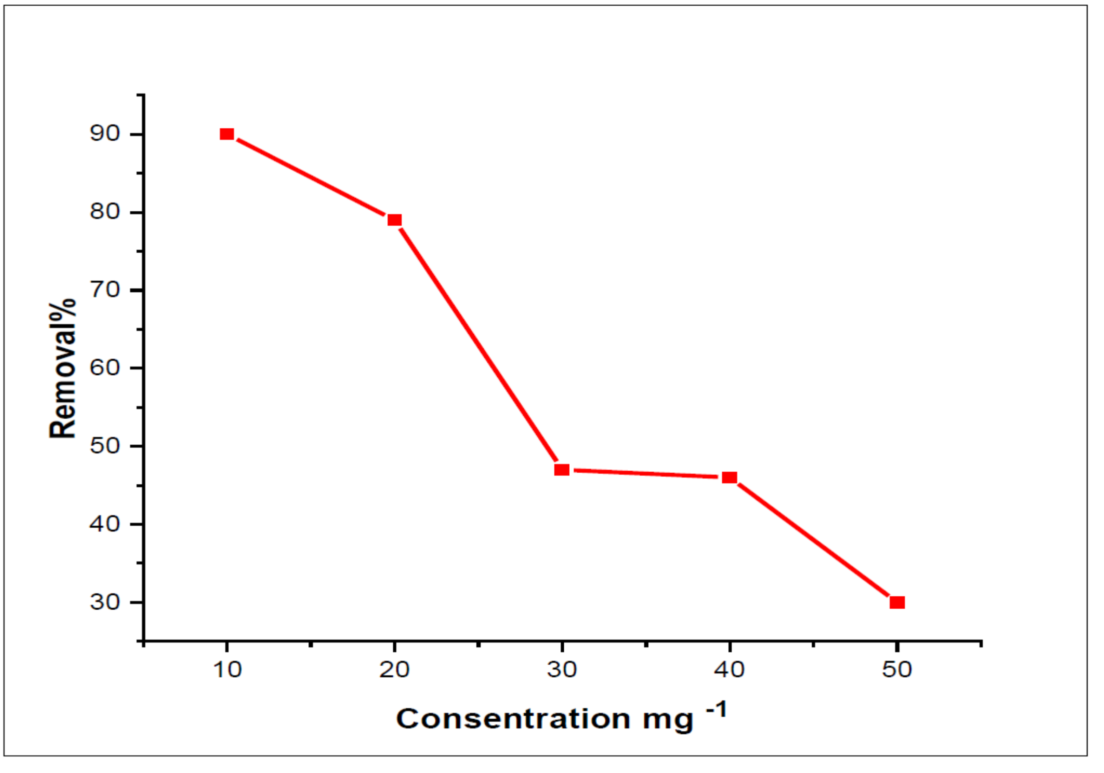

Figure 4.6: The effect of initial concentration on the percentage removal.

4.2.7 Effect pH on Adsorption of Chromium (VI)

The pH is one of the important parameters for adsorption process as it controls the adsorption capacity due to its influence on the adsorbent surface properties and ionic forms of metal ions in the solution. Adsorption experiments were carried out in the pH range of 2.09 –7.0 keeping all other parameters constant chromium concentration = 50 ppm adsorbent dose = 0.03 g, and stay to stirred for 2 hours. The best adsorption for solutions containing acidic pH 7-2. This suggests that at acidic pH or CrO^{4-} and $HCrO^{4-}$ ions there are often tends to absorption Fig. 4.7 Similar phenomenon also has been shown in the adsorption of Cr (VI) ion from water with Cu-Zn powders [99].

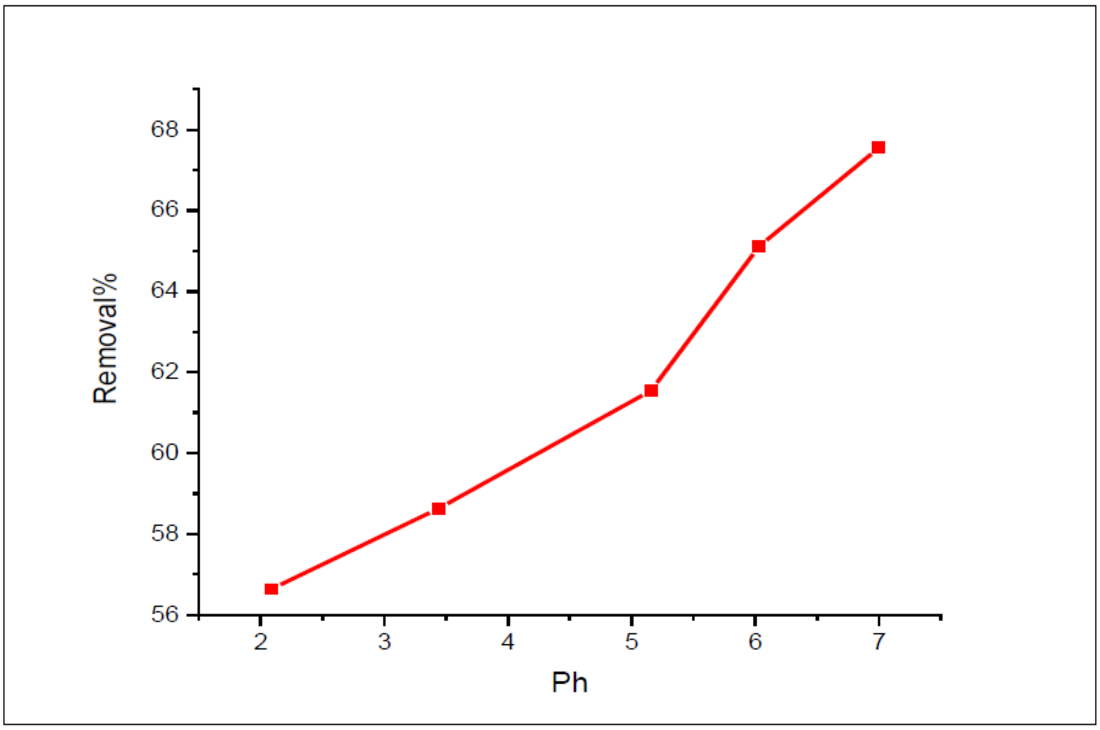

Figure 4.7 : Effect the PH on the percentage removal.

4.2.8 Effect of Contact Time

Equilibrium time between adsorbate and adsorbent is one of the most important parameters in the design of economical wastewater treatment systems Fig. 4.8 shows effect of contact time on removal percentage of Cr (VI) onto Sunflower from solution. Cr (VI) removal efficiency on to sunflower increased of 12% to 82% when contact time was increased of 20 to 120 min. A equilibrium adsorption is observed within 120 min for Cr (VI) ions, that due to the availability of large number of vacant sites. Subsequently, the less availability of the remained active sites and the decrease in the driving force lead to the slow adsorption process. Therefore optimum contact time for Sunflower adsorbent was 120 min for the 50 ppm concentration. This results are agree with the result of the researchers [100].

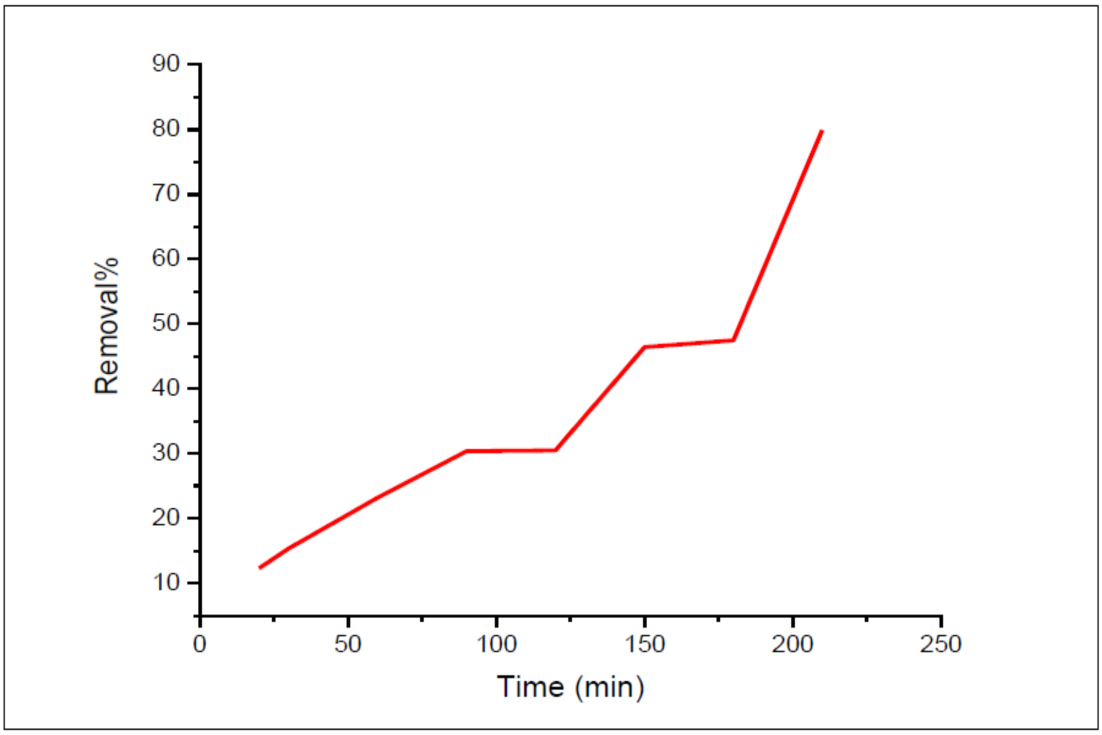

Figure 4.8 : Effect the time on the percentage removal.

4.2.9 Effect of Adsorbent Dosage

The effect of magnetic activated carbon adsorbent for the removal of Chromium using the values Sunflower consists of (0.03, 0.05, 0.07, 0.09, 0.1) g were investigated at this study .The specific adsorption rate and total volume level porous depends. At various stages of testing amounts to 25 ml of the solutions at constant concentration of chromium was added 30 ppm with adsorbent the solutions was stirred for 120 min.

The maximum absorbed at 0.03 g of the sunflower is adsorbent Fig. 4.9 Further adsorbent by increasing doses of 0.03 g to show to the adsorbent of composite nanoparticles glomerate, the resulting free surface available for adsorption decreases .So with absorbent increasing dose the adsorption rate is fixed and will not increase [37].

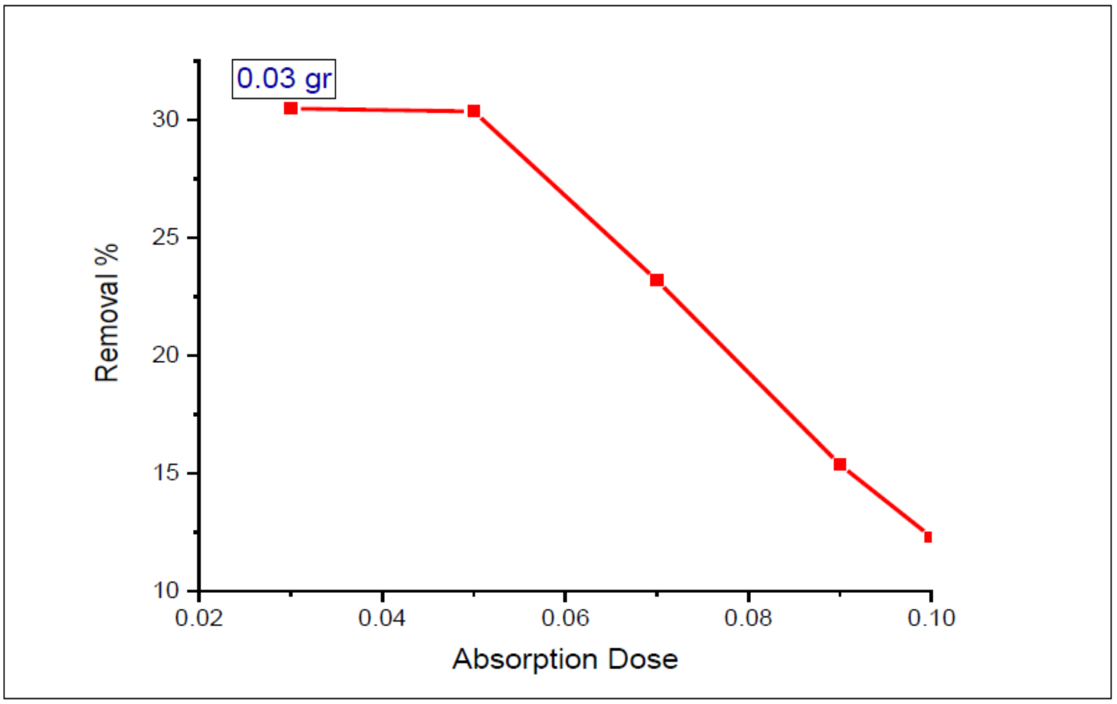

Figure 4.9 : Effect the dose adsorbent on the percentage removal.

4.2.10 Effect the Adsorption Isotherm Modals on Cr (VI)

The isotherms of sunflower are presented in Fig. 4.10 , 4.11 and 4.12. They are usually represented by Langmuir, Tamkin, and Freundlish models. The various models were able to find the best fits for the experiments. The results of the tests revealed that the surface coverage of Sunflower varied depending on the activation energy. The Langmuir isotherm model is commonly used for determining the Q_m of Sunflower adsorption capacity. It does so due to the various modifications that were involved in making the materials. The greater the association the coefficient for the Freundlich model shows that the Freundlich model suited the adsorption data better than any other model. The Langmuir model shows that a multilayer adsorption process has occurred on the surface of the object sunflower. For Cr (VI) ions, a value of n >1 suggests adsorption is diverse in nature and these results are a good approximation with the results of the researcher [101] and other parameters as shown Table 3.

Table (3). Isotherm parameters that found for the adsorption of Cr (VI) onto sunflower.

Langmuir isotherm			
Temperature (C^O)	**Q_m (mg/g)**	**b(L/mg)**	**R^2**
25	23.6	0.33	0.917
35	28.3	0.50	0.980
45	32.4	0.71	0.990
Freundlich isotherm			
Temperature (C^O)	**K_F (mg/g)(1/g)$^{I/n}$**	**1/n**	**R^2**
25	82.25	1.226	0.989
35	88.38	1.213	0.986
45	100.92	1.031	0.987
Temkin isotherm			
Temperature(C^O)	**A**	**B**	**R^2**
25	3.63	174.6	0.994
35	3.69	225.5	0.960
45	3.88	299.3	0.947

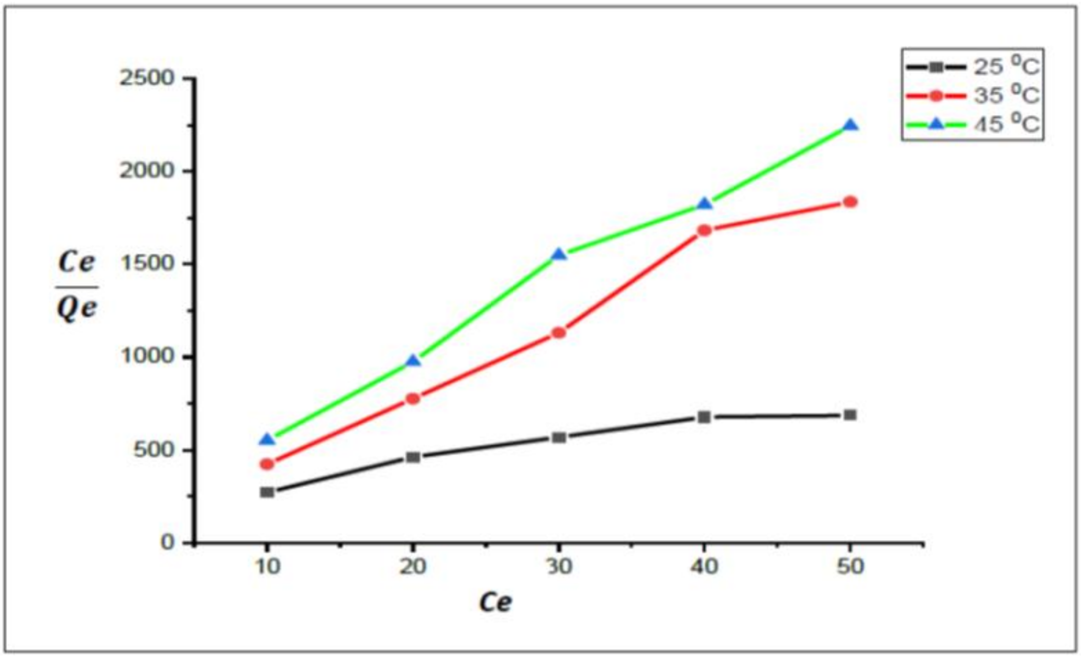

Figure 4.10: Langmuir model of Cr (VI) of the sunflower.

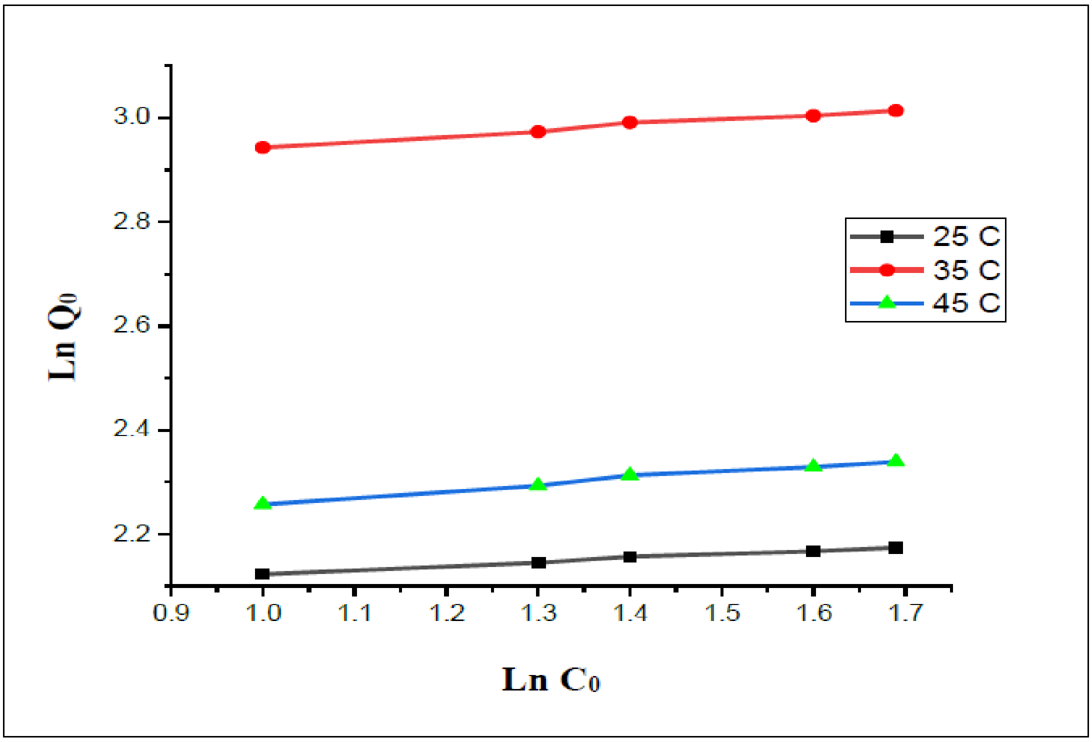

Figure 4.11: Freundlich model of Cr (VI) of the sunflower.

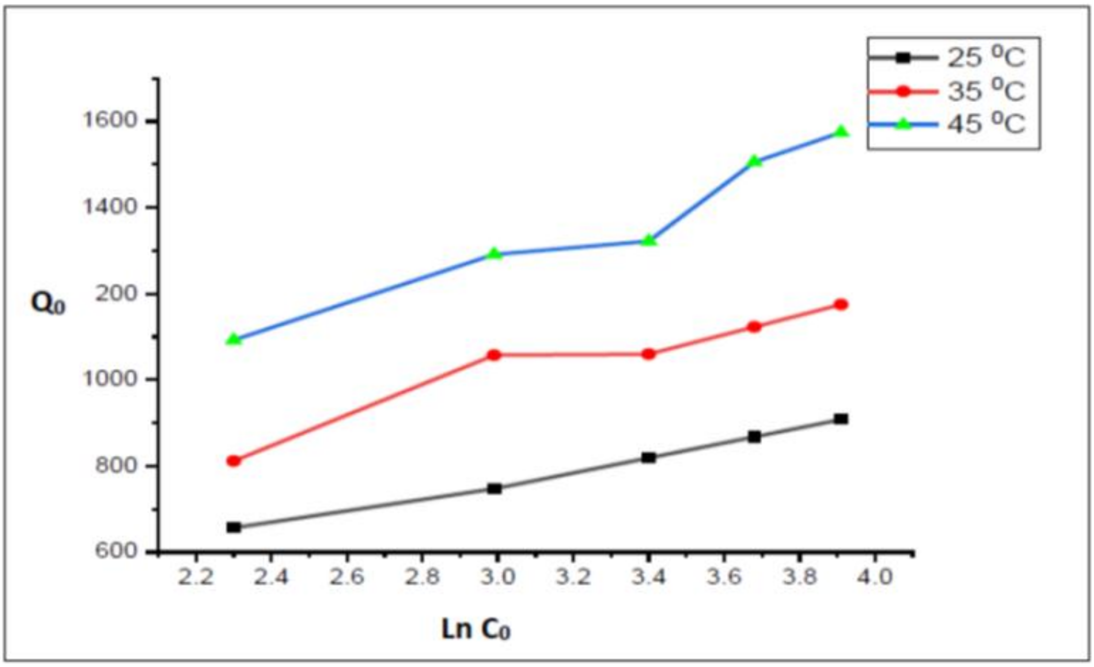

Figure 4.12 : Tamkin model of Cr(VI) of the sunflower.

4.3 Conclusions

In this section will show the main conclusions that we have obtained in our research. From overall measurement and observations , one can conclude the following :

1- X-ray diffraction studies confirmed that the synthesized nano-composite were magnetite (Fe_2Cl_3) by increasing in the intensity of diffraction peaks.

2- The results of the study of parameters affecting the rate of adsorption showed that the variables such as: contact time, pH of the solutions, their concentrations and the absorbed dose affect the capacity and efficiency of adsorption of sunflower plants. The greater effectiveness was at time T = 25 , pH = 7 and The absorbed dose = 0.03

3- The results showed that the sunflower plant has a high efficiency of removing hexavalent chromium from the aqueous solution, and this has a great economic value.

4- FT-IR spectra of Cr (VI) show a peak around (1600 - 1800) cm-1 is assigned to C=C stretching in the aromatic ring. The peak around (2650-3500) cm-1 is assigned to the compensation of carbon dioxide and water at the surface.The absorption peaks of the nanocoposite shifted towards higher wavelength, d to stronger interactions between C-O groups (500-1400) cm-1.

5- The results showed that the sunflower plant has a good efficacy to remove mainly chromium. Where the removal efficiency ranged between 90.18 %

6- The SEM images showed the homogeneously distributed throughout the solution Cr : sunflower with an obvious agglomeration of the Cr particles.

7- The results of the three models, under the conditions of thermal equilibrium adsorption, showed that the Langimure model represents the best among the two models due to the increase in the adsorption capacity.

4.4 Suggestion for Future Work

For future work it can be suggested the following:

1- Arsenic removal from aqueous solution using sunflower.
2- Studying the effect of adsorpation on coffee in removing some heavy metals from aqueous solutions .
3- Studying the effect of the bio-adsorption technique of chromium from the artichoke plant.
4- Application of nanomaterials to remove heavy metals using biological methods.

4.5 Build and solve a problem

In this work The Chromium (Vl) has been determined to study the extent of its ability to remove within the aqueous solution using the sunflower plant, and it was done within certain concentrations, as well as calculating the adsorption equilibrium for each of Lanqimur, Freundlich and Tamkin under temperatures (25, 35 and 45)^{0}C and it was concluded adsorption increases with increasing concentrations it was found that with increasing temperature the adsorption capacity increased. This has resulted in the development of new and more ecologically friendly purification methods.

References

REFERENCES

[1] Azza Khaled, Ola Abdelwahab, Amany El-Sikaily and Ahmed El Nemr. (2008)., "Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed,", Journal of Hazardous Materials, vol. 152, pp. 263-275.

[2] Metcalf and Eddy. (2004)., "Wastewater Engineering Treatment and Reuse,"New York, USA: McGraw-Hill.

[3] J.P. Pope. (1996)."Activated Carbon and some applications for the remediation of soil and groundwater pollution," Virginia Tech, Virginia.

[4] Lawrence L., Tavlarides Hyung-Jun Park., (2010). "Adsorption of Neodymium(III) from Aqueous Solutions Using a Phosphorus Functionalized Adsorbent," Ind. Eng. Chem. Res. , vol. 49, no. 24, pp. 12567–12575.

[5] Ki-Seok Yang, Dong-Ju Kim, Cheol Eui Lee and Jae-Woo Choi. (2009)., "Adsorption of zinc and toluene by alginate complex impregnated with zeolite and activated carbon," Current Applied Physics, vol. 9, pp. 694-697.

[6] Kaakani, M. (2012)., "Heavy Metal removal from Wastewater using novel Adsorbent, (Doctoral dissertation).

[7] Alluri, H.K., Ronda, S.R., Settalluri, V.S., Bondili, V.S., Suryanarayana, V.,Venkateshwar, P. (2007)., "Biosorption: An eco-friendly alternative for heavy metal removal". Afr. J. Biotechnol. **6**, 11,2924-2931.

[8] Wang, Y. (2021). Removing heavy metals from wastewater using graphene oxide.

[9] Yasar Nuhoglu, Murat Dundar and Emine Malkoc. (2006). "Adsorption of Chromium (VI) on pomace - An Olive Oil Industry: Batch and Column Studies," Journal of Hazardous Materials, vol. 138, pp. 142-151.

[10] Piero M. Armenante.(2006).,"Precipitation of Heavy Metals from Wastewater," New Jersey Institute of Technology, New Jersey, Lecture .

[11] ˙Ilk ¨un Orbak, Nilg ¨un Karatepe and Reha Yavuz. (2006)., "Factors Affecting the Adsorption of Chromium (VI) on Activated Carbon," Journal of Environmental Science and Health, vol. 41, pp. 1967-1980.

[12] Kabata-Pendias, A. and H. Pendias. (2001)., "Trace elements in soils and plants, " 3rd ed. CRC Press, Boca Raton, Fla.

[13] Morrison, J.M., M.B. Goldhaber, L. Lee, J.M. Holloway, R.B. Wanty, and R.E. Wolf. (2009)., "A regional-scale study of chromium and nickel in soils of northern California, " USA. Applied Geochemistry 24: 1500-1511.

[14] Iwegbue, C.M.A. (2010)., " Composition and daily intakes of some trace metals from canned beers in Nigeria, " Journal of the Institute of Brewing 116: 312-315.

[15] Anderson, R.A., N.A. Bryden and M.M. Polansky. (1992)., "Dietary chromium intake - freely chosen diets, institutional diets, and individual foods, "Biological Trace Element Research 32: 117-121.

[16] Anderson, R.A. (2000)., "Chromium in the prevention and control of diabetes, " Diabetes and Metabolism 26: 22-27.

[17] Vincent, J.B. (2010)., "Chromium celebrating 50 years as an essential element Dalton Trans, " 39: 3787-3794.

[18] Vincent, J.B., K.R. Di Bona, S. Love, N.R. Rhodes, D. McAdory, S.H. Sinha. (2011)., "Chromium is not an essential element for mammals effects of a low-chromium diet, " Faseb J. 25: 1.

[19] Langard, S. (1990)., "100 years of chromium and cancer - a review of epidemiological evidence and selected case-reports, " Am. J. Ind. Med. 17: 189-215.

[20] National Toxicology Program. (2008), "Toxicology and carcinogenesis studies of sodium dichromate dihydrate (Cas No. 7789-12-0) in F344/N rats and $B_6C_3F_1$ mice (drinking water studies), " National Toxicology Program technical report series, (546), 1-192.

[21] Stout, M.D., R.A. Herbert, G.E. Kissling, B.J. Collins, G.S. Travlos, K.L. Witt,. (2009), "Hexavalent chromium is carcinogenic to F_{344}/N rats and $B_6C_3F_1$ mice after chronic oral exposure, "Environ. Health Perspect. 117: 716-722.

[22] Burke, T., J. Fagliano, M. Goldoft, R.E. Hazen, R. Iglewicz and T. McKee. (1991), "Chromite ore processing residue in Hudson County, " New-Jersey. Environ. Health Perspect. 92: 131-137.

[23] O'Brien, T.J., S. Ceryak and S.R. Patierno. (2003), "Complexities of chromium carcinogenesis: role of cellular response, repair and recovery mechanisms. Mutation Research-Fundamental and Molecular Mechanisms of Mutagenesis, " 533: 3-36.

[24] Myers, C.R. (2012), "The effects of chromium(VI) on the thioredoxin system: Implications for redox regulation. Free Radic, " Biol. Med. 52: 2091-2107.

[25] Russell, R., Beard, J. L., Cousins, R. J., Dunn, J. T., Ferland, G., Hambidge, K., and Yates, A. A. (2001), "Dietary reference intakes for vitamin A, vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium, and zinc, " A report of the panel on micronutrients, subcommittees on upper reference levels of nutrients and of interpretation and uses of dietary reference intakes, and the standing committee on the scientific evaluation of dietary reference intakes food and nutrition board Institute of medicine, 797.

[26] Lyons, T.P. (1994), " Biotechnology in the feed industry: 1994 and beyond. In: K. A. J. P. Lyons, editor Proceedings of Alltechs 10th Annual Symposium, Biotechnology in the Feed Industry, " Nottingham University Press, UK. p. 1–50.

[27] Pechova, A. and L. Pavlata. (2007), " Chromium as an essential nutrient: a review, " Veterinarni Medicina 52: 1-18.

[28] Ajayan, P. M., Schadler, L. S., and Braun, P. V. (2006), " Nanocomposite science and technology, " John Wiley and Sons.

[29] Khan, W. S., Hamadneh, N. N., and Khan, W. A. (2016), " Polymer nanocomposites–synthesis techniques, classification and properties, " Science and applications of Tailored Nanostructures, 50-67.

[30] Attia, A. A., Khedr, S. A., and Elkholy, S. A. (2010), "Adsorption of chromium ion (VI) by acid activated carbon, " Brazilian Journal of Chemical Engineering, 27(1), 183-193.

[31] Pal, A., and Chaudhury, A. S. (2012), "Biosorption of chromium using Anabaena and Vetiveria, " International Journal of Pollution Abatement Technology, 1(1), 15-19.

[32] Palanisamy, K. L., Devabharathi, V., and Sundaram, N. M. (2013), "The utility of magnetic iron oxide nanoparticles stabilized by carrier oils in removal of heavy metals from waste water, " International Journal of Research in Applied, Natural and Social Sciences, 1(4), 15-22.

[33] Barakat, M., Rashid, J., and Alghamdi, M. (2013), "Removal of chromium (VI) from synthetic wastewater using spectra/gel ion-exchange resin, " In Proc. Seventeenth International Water Technology Conference, Istanbul.

[34] Liu, W., Ni, J., and Yin, X. (2014), "Synergy of photocatalysis and adsorption for simultaneous removal of Cr (VI) and Cr (III) with TiO_2 and titanate nanotubes, " Water research, 53, 12-25.

[35] Beheshti, H., Irani, M., Hosseini, L., Rahimi, A., and Aliabadi, M. (2016),"Removal of Cr (VI) from aqueous solutions using chitosan/MWCNT/Fe_3O_4 composite nanofibers-batch and column studies, " Chemical Engineering Journal, 284, 557-564.

[36] Sobhanardakani, S., Zandipak, R., Bonyadi, M., Parvizimosaed, H., Moslemi, M., Tahergorabi, M. T., and Hosseini, S. M. (2018), " Evaluation of removal efficiency of Cr (VI) ions from aqueous solution using chitosan, " Journal of Chemical Health Risks, 5(1).

[37] Obaid, S. A. (2019, July), "Removal chromium (VI) from water by magnetic carbon nano-composite made by burned straw," In Journal of Physics: Conference Series (Vol. 1234, No. 1, p. 012032). IOP Publishing.

[38] Ranieri, E., D'Onghia, G., Ranieri, F., Petrella, A., Spagnolo, V., and Ranieri, A. C. (2021), "Phytoextraction of Cr (VI)-Contaminated Soil by Phyllostachys pubescens, " A Case Study. Toxics, 9(11), 312.

[39] Karimi-Maleh, H., Ayati, A., Ghanbari, S., Orooji, Y., Tanhaei, B., Karimi, F., and Sillanpää, M. (2021), "Recent advances in removal techniques of Cr (VI) toxic ion from aqueous solution: a comprehensive review, " Journal of Molecular Liquids, 329, 115062.

[40] Mohammad Atif, B. Prasad, I.M. Mishra Kailas L. Wasewar. (2009). "Batch adsorption of zinc on tea factory waste," Desalination, vol. 244, pp. 66-71.

[41] Jing-song Wang, Yun-guo Liu, Xin Li, Guang-ming Zenga, Zheng-lei Bao, Xiao-xia Zenga, An-wei Chena, Fei Long and Xin-jiang Hu. (2011). "Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: Isotherms, kinetics and thermodynamics," Journal of Hazardous Materials, vol. 185, pp. 306-314.

[42] Lokman Uzun, Ali Kara, Adil Denizli, Serap Senel.(2008), "Heavy Metal Removal from Synthetic Solutions with Magnetic Beads Under Magnetic Field," Journal of Macromolecular Science, vol. 45, pp. 635-642.

[43] Z. Hubicki, P. Podkoscielny, E. Robens and A. Dabrowski. (2004). "Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method," Chemosphere, vol. 56, pp. 91-106.

[44] S. Ramalingamb, S. Dinesh Kiruphac, A. Murugesanc, T. Vidhyadevic, S. Sivanesanc, and P. Senthil Kumara. (2011). "Adsorption behavior of nickel(II) onto cashew nut shell: Equilibrium,thermodynamics, kinetics, mechanism and process design," Chemical Engineering Journal, pp. 122-131.

[45] Mohammed Abu Dayeh ,Matouq Zaid Ahmed Al-Anber. (2008), "Batch adsorption of cadmium ions from aqueous solution by means of olive cake," Journal of Hazardous Materials, vol. 151, pp. 194-201.

[46] A. A. M. Daifuallah, and M. M. S. Ali N. S. Awwad. (2008), "Removal of Pb^{2+}, Cd^{2+}, Fe^{3+}, and Sr^{2+} from Aqueous Solution by Selected Activated Carbons Derived from Date Pits," Solvent Extraction and Ion Exchange, vol. 26, pp. 764-782.

[47] Azza Khaled, Ola Abdelwahab, Amany El-Sikaily and Ahmed El Nemr.(2008), "Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed," Journal of Hazardous Materials, vol. 152, pp. 263-275.

[48] Mamdouh M. Nassar. (2006), "Adsorption of Fe^{+3} and Mn^{+2} from Ground Water onto Maize Cobs Using Batch Adsorber and Fixed Bed Column," Seperation Science and Technology, vol. 41, pp. 943-959.

[49] Bogdanka Radetic, Zarko Kevresan, Mile Klasnja Marina Sciban. (2007), "Adsorption of heavy metals from electroplating wastewater by wood sawdust," Bioresource Technology, vol. 98, pp. 402-409.

[50] Metcalf and Eddy. (2004). Wastewater Engineering, Treatment and Reuse. New York, USA: McGraw-Hill.

[51] S. Ramalingamb, S. Dinesh Kiruphac, A. Murugesanc, T. Vidhyadevic, S. Sivanesanc, and P. Senthil Kumara. (2011). "Adsorption behavior of nickel(II) onto cashew nut shell: Equilibrium,thermodynamics, kinetics, mechanism and process design," Chemical Engineering Journal, vol. 167, pp. 122-131.

[52] Mohamed Kheireddine Aroua, Wan Mohd Ashri and Wan Daud Mojdeh Owlad. (2010), "Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethyleneimine," Bioresource Technology, vol. 101, pp. 5098-5103.

[53] Apipreeya K, Prasert Pavasant and Phussadee Patnukao. (2008), "Batch studies of adsorption of copper and lead on activated carbon from Eucalyptus camaldulensis Dehn. bark," Journal of Environmental Sciences, vol. 20, pp. 1028-1034.

[54] Shaheen A. Al-Mutaseb.(2010), "Adsorption and Desorption Equilibria of Nitrogen, Methane, Ethane, and Ethylene on Date-Pit Activated Carbon," Journal of Chemical Engineering, vol. 55, pp. 313-319.

[55] R. T. Yang. (2003), "Adsorbents: fundamentals and applications, " New Jersey, USA: John Wiley & Sons, Inc.

[56] Krishna K, Chitra R, Vinod Kumar Garg Jyotsna Goel. (2005), "Removal of lead(II) by adsorption using treated granular activated carbon: Batch and column studies," Journal of Hazardous Materials, vol. B125, pp. 211–220.

[57] Salam, O. E. A., Reiad, N. A., and ElShafei, M. M. (2011), "A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents, " Journal of Advanced Research, 2(4), 297-303.

[58] Ahalya N, Ramachandra TV, and Kanamadi RD.(2006), "Biosorption of Heavy Metals by Low cost Adsorbents," Indian Institute of Science, Bangalore, Technical Report.

[59] Kaakani, M. (2012), "Heavy Metal removal from Wastewater using novel Adsorbent (Doctoral dissertation).

[60] Sharma, P., Pandey, S. (2014), "Status of Phytoremediation in World Scenario," International Journal of Environmental Bioremediation and Biodegradation, 2(4), 178-191.

[61] Ali, H., Khan, E., and Sajad, M.A. (2013), "Phytoremediation of heavy metals—Concepts and applications. *Chemosphere*, 91(7), 869-881.

[62] Pulford, I.D., Watson, C. (2003). Phytoremediation of heavy metal-contaminated land by trees—a review. *Environment International*, 29(4), 529-540.

[63] Singh, D., Tiwari, A., and Gupta, R. (2012), "Phytoremediation of lead from wastewater using aquatic plants," Agricultural Technology, 8(1), 1-11.

[64] Tangahu, B.V., Abdullah, S.R.S., Basri, H., Idris, M., Anuar, N., and Mukhlisin1, M. (2011), "A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation, " International Journal of Chemical Engineering, 1-32.

[65] Macek, T., Macková, M., and Káš, J. (2000), "Exploitation of plants for the removal of organics in environmental remediation," Biotechnology Advances, 18(1), 23-34.

[66] Schmöger, M.E.V., Oven, M., and Grill, E. (2000), "Detoxification of Arsenic by Phytochelatins in Plants," Plant Physiology, 122(3), 793-802.

[67] Al Akeel, K. (2013), "Empirical investigation of water pollution control through use of Phragmites australis," Brunel University School of Engineering and Design PhD Thesis.

[68] Eilola K and Perämäki P. (2009), "Microwave-assisted double insert vapour-phase digestion of organic samples," Analytica chimica acta . 634(2): 205-208.

[69] Clemens, S., Plamgren, M. G., and Kramer, U., (2002), "A long way ahead: understanding and engineering plant metal accumulation, " Trends, Plant Sci, 7, 309 – 315.

[70] Vymazal, J., Švehla, J., Kröpfelová, L., and Chrastný, V., (2007), "Trace metals in Phragmites australis and Phalaris arundinacea growing in constructed and natural wetlands, " Science of the Total Environment, 380, 154 – 162.

[71] Weis, J. S., Glover, T., Weis, P., (2004), "Interactions ofmetals affect their distribution in tissues of Phragmites australis," Environmental Pollution, 131, 409 – 415

[72] Wang, L. K., Chen, J. P., Hung, Y., Shammas, N. K. (2009), "Heavy metals in the environment, " Boca Raton: CRC Pres

[73] Gardea-Torresdey, J. L., (2003), " Phytoremediation: Where does it stand and where will it go, " Environmental Progress, 22, 1, A2 – A3 Editorial

[74] Sasmaz, A., Obek, E., and Hasar, H. (2008), " The accumulation of heavy metals in Typha latifolia L. grown in a stream carrying secondary effluent, " Ecological Engineering, 33(3–4), 278-284.

[75] Alvarado, S., Guédez, M., Lué-Merú, M.P., Nelson, G., Alvaro, A., Jesús, A.C., Gyula, Z. (2008), " Arsenic removal from waters by bioremediation with the aquatic plants Water Hyacinth (Eichhornia crassipes) and Lesser Duckweed (Lemna minor), " Bioresource Technology, 99(17), 8436-8440.

[76] NurZaida, Z., Piakong, M.T. (2011), "Removal of Heavy Metals by Indigenous Aquatic Plants from Simulated Wastewater," Proceedings of the CUTSE International Conference.

[77] Skinner, K., Wright, N., and Porter-Goff, E. (2007), "Mercury uptake and accumulation by four species of aquatic plants," Environmental Pollution, 145(1), 234-237.

[78] Tang, Y.-T., Qiu, R.-L., Zeng, X.-W., Ying, R.-R., Yu, F.-M., and Zhou, X. Y. (2009), "Lead, zinc, cadmium hyperaccumulation and growth stimulation in Arabis paniculata Franch, " Environmental and Experimental Botany, 66(1), 126-134.

[79] Solhi, M., and Hajabbasi, M. A. (2005), "Heavy metals extraction potential of sunflower (Helianthus annuus) and canola (Brassica napus), " Caspian Journal of Environmental Sciences, *3*(1), 35-42.

[80] Andrew, R. L., Kane, N. C., Baute, G. J., Grassa, C. J. and Rieseberg, L. H. (2013), " Recent nonhybrid origin of sunflower ecotypes in a novel habitat. Mol Ecol 22(3): 799-813.

[81] Sagara, J. (2000), "Study of filtration for point-of-use drinking water treatment,"Nepal (Doctoral dissertation, Massachusetts Institute of Technology).

[82] Walter J, and Weber Jr.(1974), "Adsorption Processes," The University of Michigan, Ann Arbor, Michigan, Techincal Paper.

[83] Roostaei N, and Tezel FH .(2004), "Removal of phenol from aqueous solutions by adsorption," Journal of Environmental Management. 1;70(2):157-64.

[84] Ugolini FC, and Dahlgren RA.(2022), "Soil development in volcanic ash, "GLOBAL environmental research-english edition-. 6(2):69-82.

[85] Tan G, and Xiao D.(2009), "Adsorption of cadmium ion from aqueous solution by ground wheat stems, " Journal of hazardous materials. 30;164(2-3):1359-63.

[86] Boparai HK, Joseph M, and O’Carroll DM. (2011),"Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles," Journal of hazardous materials. 15;186(1):458-65.

[87] Bhatt RR, and Shah BA. (2015), " Sorption studies of heavy metal ions by salicylic acid–formaldehyde–catechol terpolymeric resin: Isotherm, kinetic and thermodynamics, " Arabian Journal of Chemistry. 1;8(3):414-26.

[88] Bhaumik M, Choi H J Seopela M P , McCrindle R I and Maity A (2014), "Highly effective removal of toxic Cr (VI) from wastewater using sulfuric acid-modified avocado seed, " Industrial and Engineering Chemistry Research, 53(3), 1214-1224.

[89] Monika J , Garg V , and Kadirvelu K (2009), "Chromium (VI) removal from aqueous solution using sunflower stem waste, " J. Hazard. Mater, 162(1), 365-372.

[90] A. Piroth Fundamentals of the Physics of Solids, Vol. I, Structure and Dynamics, Translated p. 242-261.

[91] H. Meier. (1974), "Organic Semiconductors: Dark and Photo Conductivity of Organic Solids, " Verlag Chernie, Weirnheirn.

[92] Qiu, B., Xu, C., Sun, D., Wang, Q., Gu, H., Zhang, X., and Wei, S. (2015), "Polyaniline coating with various substrates for hexavalent chromium removal," Applied Surface Science, *334*, 7-14.

[93] Gan, M., Sun, S., Zheng, Z., Tang, H., Sheng, J., Zhu, J., and Liu, X. (2015), "Adsorption of Cr (VI) and Cu (II) by AlPO4 modified biosynthetic Schwertmannite, " Applied Surface Science, 356, 986-997.

[94] Zhao, Y., Yang, S., Ding, D., Chen, J., Yang, Y., Lei, Z., and Zhang, Z. (2013), "Effective adsorption of Cr (VI) from aqueous solution using natural Akadama clay," Journal of colloid and interface science, 395, 198-204.

[95] Villaescusa, I., Fiol, N., Martínez, M., Miralles, N., Poch, J., and Serarols, J. (2004), "Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. Water research, 38(4), 992-1002.

[96] Beheshti, H., Irani, M., Hosseini, L., Rahimi, A., and Aliabadi, M. (2016),"Removal of Cr (VI) from aqueous solutions using chitosan/MWCNT/Fe_3O_4 composite nanofibers-batch and column studies, " Chemical Engineering Journal, 284, 557-564.

[97] Nakanishi, K., and Solomon, P. H. (1977),"Infrared absorption spectroscopy, " Holden-day.

[98] Lv, G., Li, Z., Jiang, W. T., Ackley, C., Fenske, N., and Demarco, N. (2014), "Removal of Cr (VI) from water using Fe (II)-modified natural zeolite," Chemical Engineering Research and Design, 92(2), 384-390.

[99] Kaprara, E., Seridou, P., Tsiamili, V., Mitrakas, M., Vourlias, G., Tsiaoussis, I., and Simeonidis, K. (2013), "Cu-Zn powders as potential Cr (VI) adsorbents for drinking water, " Journal of hazardous materials, 262, 606-613.

[100] Chen, C., Hu, J., Shao, D., Li, J., and Wang, X. (2009), " Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni (II) and Sr (II) " Journal of hazardous materials, 164(2-3), 923-928.

[101] Mandel,K.(2013),"Synthesis and characterisation of superparamagnetic nanocomposite particles for water purification and resources recovery (Doctoral dissertation, Universität Würzburg).

الخلاصة

ركزنا في هذه الرسالة على مياه الصرف الصحي والمعالجة النباتية لسمية المعادن الثقيلة حيث اعتمدنا على العديد من العوامل الهيكلية والخصائص البصرية في تعديل المركبات النانوية. كما ذكرت الامتزاز على الأيزوثرم الذي يدرس العلاقة بين كميات الممتزات وتركيز الممتزات المذابة في السائل عند التوازن ومناقشة نماذج الامتزاز الحراري للحصول على أفضل امتصاص

عندما تكون المعادن الثقيلة وفيرة يمكن أن تكون شديدة السمية للوسط الذي تذوب فيه. تم استخدام الامتزاز كعملية معالجة مياه مناسبة لإزالة المعادن الثقيلة. حيث أجريت العديد من الدراسات لإزالة الكروم السداسي باستخدام مواد مختلفة.

استخدمنا سيقان عباد الشمس (Helianthus annuus L.) كمادة ماصة لإزالة الكروم (VI) من مياه الصرف الصحي. تم إنتاج مياه الصرف الصناعي في المختبر لإجراء التجارب. حيث إجريت عملية الترشيح وهي الأكثر استخدامًا في محطات معالجة مياه الصرف الصحي. و أجريت اختبارات الدُفعات لتقييم أداء امتصاص إزالة الكروم السداسي تحت ظروف عملية مختلفة. فحصت العينات بواسطة مقياس الطيف الضوئي المرئي فوق البنفسجي ، ودراسات حيود الأشعة السينية ، والتحليل الطيفي بالأشعة تحت الحمراء لتحويل فورييه والتباطؤ المغناطيسي.

أشارت الدراسة إلى أنه يتم تحقيق امتصاص أفضل عند زيادة الرقم الهيدروجيني للمحلول المائي. كانت الإزالة المثلى للكروم السداسي عند الأس الهيدروجيني = 7 و 0.03 جم من جرعة الممتزات ودرجة حرارة 25 درجة مئوية ، كما تم اختبار قابلية تطبيق Langmuir و Freundlich و Temkin في درجات حرارة مختلفة (25 ، 35 و 45) درجة مئوية.

تبين أن متساوي الحرارة Langmuir كان أكثر قدرة على ملائمة نقاط البيانات الخطية من Freundlich و Temkin مع الكروم السداسي . أظهرت النتائج أن الكروم سداسي التكافؤ يمتص بشكل كبير على سيقان عباد الشمس ويمكن أن يكون طريقة اقتصادية لإزالة الكروم سداسي التكافؤ من الأنظمة المائية

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة بابل / كلية العلوم

قسم الفيزياء

إزالة الكروم (VI) من محلول مائي باستخدام مركب نانوي مغناطيسي بالاعتماد على عباد الشمس

رسالة مقدمة الى

قسم الفيزياء /كلية العلوم /جامعة بابل

كجزء من متطلبات نيل درجة الماجستير في علوم الفيزياء

من قبل

هدى حسن نهر جاسم

بكالوريوس في علوم الفيزياء (٢٠١٧)

بأشراف

الاستاذ المساعد الدكتور

صبا عبد الزهرة عبيد الشياع

١٤٤٤هـ **٢٠٢٢ م**