

An-Najah National University

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Using Thiophene Supported on SiO₂ for Removal Cr(VI) from Water

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the Degree of Master of Environmental Science, Faculty of Graduate
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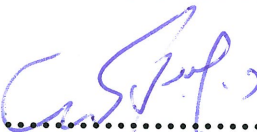
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Dedication

Any work needed to encourage and perseverance and strong will all who encouraged and helped me in completing this work. This work is dedicated to my dear wife and children. Also, I would like to thank my supervisors Prof. Shehdeh Jodeh and Dr. Ahmad Abu Obaid for helping me to finish this thesis. Many thanks also, go to the department of chemistry and their technicians for supplying me with chemicals and instrumentation to do the work.

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I offer my sincere thanks for all of you

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان

Using Thiophene Supported on SiO₂ for Removal Cr(VI) from Water

أقر بأن ما شملت عليه الرسالة هو نتاج جهدي الخاص, باستثناء ما تمت الإشارة إليه حيثما ورد,
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Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degrees or qualifications.

Student's Name:

اسم الطالب: احمد ذيب نمر نعيم

Signature

التوقيع: 

Date

التاريخ: 2016/8/22

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List of Abbreviations

Symbol	Abbreviations
C_o	Concentration of Cr(VI) in the sample solution before treatment (mg/L)
C_e	Concentration of Cr(VI) in the sample solution after treatment (mg/L) at equilibrium
C_i	Initial concentration of Cr(VI) in the sample solution (mg/L)
MSiTh	3-Glycidoxypopyl-functionalized silica
FT-IR	Fourier Transform Infrared
K_1	The Lagergren's first order rate constant
K_2	The pseudo second order rate constant
K_d	The distribution coefficient
K_F	Freundlich constant which is an approximate indicator of adsorption capacity of the sorbent (mg/g (L/mg) ^{1/n})
K_L	Langmuir isotherm constant (L/mg)
LD ₅₀	Lethal Dose which causes the death of 50% (one half) of a group of test
m _{sed}	Mass of adsorbent dose
n	Dimensionless Freundlich constant giving an indication of how favorable the adsorption process
Q_e	The amount of Cr(VI) adsorbed per gram of the adsorbent (mg/g)
Q_m	Maximum monolayer coverage capacity (mg/g)
Q_t	Amount of adsorbate per unit mass of adsorbent at time t (min)
R	The gas constant (8.314 J/mol. K)
R^2	Correlation coefficient (regression coefficient)
R_L	Dimensionless constant separation factor
SPE	Solid Phase Extraction
t	Time
T	The absolute temperature (°K)
TGA	Thermal Gravimetric Analysis
V	Volume of solution
ΔG°	Standard free Gibbs energy
ΔH°	Standard enthalpy
ΔS°	Standard entropy
R _f C	Reference Concentration
R _f D	Reference Dose
IARC	International Agency for Research on Cancer
ES	Epoxy Silica

DMF	dimethylformamide
BJH	Barrett-Joyner-Halenda
So	Free Silica
S _{BET}	A measure of surface area
IUPAC	International Union of Pure and Applied Chemistry
µg	microgram
NAA	Neutron activation analysis
UV	Ultraviolet-visible spectroscopy
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
rpm	revolutions per minute
ICP-MS	Inductively coupled plasma mass spectrometry
AAS	Atomic Absorption Spectroscopy

Using Thiophene Supported on SiO₂ for Removal Cr(VI) from Water**By****Ahmad Deeb Nemer Naem****Supervisor****Prof. Shehdeh Jodeh****Co- Supervisor****Dr. Ahmad Abu Obaid****Abstract**

Water pollution is a major environmental problem especially that produced from different industries, which produce large amounts of toxic heavy metals to the soil and wastewater; these heavy metals affect human health. This study was made to study the removal of one of these toxic heavy metals which is Cr(VI) by adsorption technique using silica gel compound 3-Glycidoxypopyl- functionalized silica.

The compound 3-Glycidoxypopyl- functionalized silica (MSiTh) was successfully prepared and characterized, studying the attachment of thiophene group to silica FTIR was used. Thermogravimetric analysis for MSiTh, and the average BJH pore diameter were made.

The adsorption experiments were applied for a range of pH (2-13), temperature, adsorbent dosage, initial concentration, and contact time. The results revealed that the percentage removal of Cr(VI) decreased with the increase of Cr(VI) concentration, pH and temperature, while the percentage removal increase with increase contact time and adsorbent dose.

The removal efficiency for Cr(VI) adsorption was more than 75% after 24 hour this achieved at pH around 6, and temperature 25°C, using 0.04g weight of dose, at initial concentration 10 ppm for 10 mL Cr(VI) solution.

The adsorption of Cr(VI) onto MSiTh was optimized under acidic conditions ($\text{pH} < 7$) at room temperature. According to pseudo second order the Cr(VI) sorption, the results achieved shows the MSiTh is able to remove Cr(VI) within 20 min with high removal efficiency.

The amount of Cr(VI) adsorbed per unit mass of MSiTh that obtained by Lagergren pseudo second order model, $q(\text{cal})$ has been agreed with experimental value of $q(\text{exp})$ indicates that exchange between the adsorbent and adsorbate .

The Langmuir maximum adsorption capacity Q_m is 10.672 mg/g, at 25°C, pH around 6, and 0.04g weight of adsorbent dose .the R_L value (0.2375 at 25°C) indicates the adsorption of Cr(VI) onto MSiTh is favorable.

From Freundlich isotherm model parameters, value of $1/n = 0.56$, while $n=1.786$, indicating that the sorption of Cr(VI) is favorable.

The negative ΔG° values (- 1.01443 – 0.92983 KJ/mol) indicate the adsorption is favorable and spontaneous at temperatures in the experiment. The negative value of ΔH° (- 1.62355 KJ/mol) shows an exothermic adsorption process and indicates the adsorption is favorable at 25°C. the positive value of $\Delta S^\circ = 2.115 \text{ J/mol.K}$ indicates some randomness at the solid/liquid interface in the adsorption system which increase the adsorption process.

Chapter One

Introduction

1.1 Overview

The main problem that affects our environment is pollution, because this processes making land, water, air and other parts of our environment unsafe and unsuitable to life. As the number of population increases over the world, the pollution increase and the industrial effluents are one of the main elements causes environmental pollution, toxic pollution is very dangerous to human life, its affects more than 200 million people worldwide according to Pure Earth [2 , 6, 24].

Babies in some of the world's worst polluted places are born with birth defects, due to toxic pollution life expectancy may be as low as 45 years because of cancers and other diseases caused by it, and children have lost 30 to 40 Intelligence Quotient because of pollution effects [2].

The exposure to heavy metals ions through ingestion or uptake of drinking water and foods can lead to its accumulation in animal's body and plants, as the human body exposure to high concentrations, some of these metals are very toxic to human's body. Lead, Mercury, Cadmium, Copper, Chromium and Zinc are considering the most hazardous [1].

Chromium is one of heavy metals that affect human body, it occurs in the environment in two states Cr(III) and Cr(VI), the toxicity of trivalent states Cr(III) is less toxic than hexavalent chromium Cr(VI). The exposure to

chromium come from natural as ground water or industrial sources of chromium, when chromium Cr(III) enter the body by respiratory tract it causes toxicity as chromium Cr(VI) at high concentrations, although chromium Cr(III) is an essential element to normal glucose, protein, and fat metabolism in human body, and our body can detoxify trace amount of chromium Cr(VI) to chromium Cr(III) [4,34].

Through inhalation exposure toxicity of Cr(VI) will increase and may cause shortness of breath, coughing and wheezing due to acute exposure to chromium Cr(VI), while chronic exposure to Cr(VI) cause perforations of the septum, bronchitis, decreased pulmonary function, pneumonia and other respiratory effects, several studies established on human body and explain that inhaled chromium Cr(VI) is carcinogen, causing an increased risk of lung cancer, but in animal studies chromium Cr(VI) effect cause lung tumors through inhalation exposure [5,37].

There are several uses of chromium; this metal is used mainly for making steel and in some other alloys. Chromium compounds that contains Cr (VI) or Cr(III) are used for manufactures of dyes and pigments, chrome plating, leather and wood preservation, and also in treatment of cooling tower water, while smaller amounts of chromium forms are used in drilling muds, toner for copying machines, and textiles [4,5,11].

Chromium is found in nature in animals, plants, rocks, soil, and in volcanic dust and gases, the main important industrial sources of chromium in the atmosphere are from the industries related to Ferro chrome production such as, chemical and refractory processing, cement-producing plants, ore

refining, leather tanneries, automobile brake lining and catalytic converters for automobiles, and pigments [30,31].

Exposure of population to chromium occurs by eating food, inhaling air which contains chemical, and drinking water that contain chromium. In studies that made the average daily intake from water, air, and food is estimated to be less than 0.2 to 0.4 μg . The Reference Concentration (RfC) for chromium (VI) (chromic acid mists and dissolved Cr(VI) aerosols) is 0.000008 mg/m^3 based on respiratory effects in humans, and the Reference Dose (RfD) for chromium(VI) is 0.003 $\text{mg}/\text{kg}/\text{d}$ based on the exposure at which no effects were noted in rats exposed to chromium in the drinking water, EPA has classified chromium (VI) as a Group A, known human carcinogen by the inhalation route of exposure [2,37, 43].

Chromium (VI) effects are to be a strong oxidizing agent, posing a high risk to humans and animals due to its carcinogenic and mutagenic properties, so it is necessary to determine the concentration of chromium in environmental and biological samples is of great interest [33,34].

Many techniques used for the determination of chromium such as neutron activation analysis (NAA) which is a nuclear process used for determining the concentrations of elements in a vast amount of materials. NAA allows discrete sampling of elements as it disregards the chemical form of a sample, and focuses solely on its nucleus. The method is based on neutron activation and therefore requires a source of neutrons, this method is expensive, UV-visible, ICP-MS and AAS, with high sensitivity which

needs complicated and expensive equipment, but these techniques are usually not available in most laboratories [44].

One of methods used for determination of chromium is kinetic catalytic method which is based on its effect on the oxidation of organic compounds with a suitable oxidant, most frequently hydrogen peroxide [3].

In order to remove toxic heavy metals from polluted water as a result of several industries that cause environmental problems abiotic processes are used but these processes expensive, and effectiveness. So scientists search about new active methods to remove toxic heavy metals as chromium(VI) that resulting from industrial dyes, pigments, galvanometric and electric, film and photography, metal cleaning, plating and electroplating, leather and mining . Hexavalent considered more hazardous to public health due to its effect as carcinogenic and mutagenic properties [4].

Many scientist use activated carbon for adsorption of heavy metal ion from wastewater, but this process is effectiveness for removal of heavy metal ions at trace quantities, and the high cost, for this reason the use of low cost materials as sorbent for removal of heavy metal ion from wastewater.

Great effort has been contributed for developing and improves adsorbents. Activated carbon, iron oxide coated sand, porous cellulose carrier modified with polyethylene mine and other processes have been used [5]. Biosorption technology has been used for the treatment of hexavalent chromium, and reaches its optimum treatment level at lower pH [4].

Chromium in the two oxidation states Cr(VI) and Cr(III) resulting from several industries have different biological, chemical and environmental

properties because the effect of this metal to human health due discharging to the environment, so chromium in discharged wastewater should be reduced as possible , several researches are utilized to remove it from wastewater, these methods include: reduction followed chemical precipitation, adsorption, solvent extraction, cementation, electrochemical precipitation, ion exchange, foam separation, evaporation, polymer based membrane separation, reverse osmosis, biosorption, and freeze separation[32,35].

For removing chromium adsorption method is effective and versatile, either it solve the problem of Cr(VI) if low cost adsorbent are used to remove Cr(VI) from water [5] .

1.2 Objectives of this work:

1.2.1: General Objectives

1. Using Thiophene Supported on SiO₂ for Removal Cr(VI) from water.
2. Identify the optimal conditions when Thiophene compound supported on SiO₂ used in the adsorption process.

1.2.2: Specific objectives

- 1) To explain if 3-Glycidoxypopyl-functionalized silica (MSiTh) can be used to clean up chromium (VI) contaminated wastewater.
- 2) To determine the extent that silica gel compound modified can tolerate and adsorb chromium (VI).

- 3) To study the adsorption behaviors of the new surface of (MSiTh) with chromium (VI).
- 4) To study the activity of (MSiTh) after the adsorption completed and reuse it several times.

1.2.3: Research question and identified problems

The main questions addressed in this thesis are:

- 1) Can (MSiTh) be used to remove Cr(VI) contaminated water?
- 2) To which extent that (MSiTh) can tolerate and adsorb Cr (VI)?
- 3) What are the optimal conditions of pH, temperature, amount of adsorbent, concentration, and contact time for (MSiTh) to adsorb Cr (VI) efficiently?

Chapter Two

Background and literature review

2.1 Chromium

Chromium ion is one of the heavy metal elements that occur in the environment in two valence states chromium (III), and chromium (VI), it is widely distributed in the earth's crust [6].

Chromium ion is a chemical element present in the environment in several different forms. The most common forms are chromium(0), chromium(III), and chromium(VI), and has atomic number 24. It is a steel-gray, lustrous, hard metal that takes a high polish and has a high melting point [31].

In Table 2.1 shows physicochemical properties of chromium as occurrence:

Table 2.1: physicochemical properties of chromium[7]

shape property	Cr	CrCl ₃	K ₂ CrO ₄	Cr ₂ O ₃	CrO ₃
Density (g/cm ³)	7.14	2.76	2.73	5.21	2.70 Major
Solubility (g/L)	Insoluble	Slightly soluble	790	Insoluble	624
Boiling point (°C)	2672	-	-	4000	-
Melting point (°C)	1857	1152	968.3	2266	196

Description of chromium [7].

Table 2.2: chromium in the periodic Table[7] :

property of chromium/unit	value for Cr
1st Ionization Energy Cr	653kJmol ⁻¹
2nd Ionization Energy Cr	1592kJmol ⁻¹
3rd Ionization Energy Cr	2987kJmol ⁻¹
4th Ionization Energy Cr	4740kJmol ⁻¹
5th Ionization Energy Cr	6690kJmol ⁻¹
Cr atomic radius	125pm
Cr ²⁺ ionic radius	84pm
Relative polarizing power Cr ²⁺ ion	2.4
Cr ³⁺ ionic radius	69pm
Relative polarizing power Cr ³⁺ ion	4.3
Cr ⁴⁺ ionic radius	56pm
Polarizing power M ⁴⁺ ion	7.1
Oxidation states of Cr, less common/stable	+2, +3, +6
Simple electron configuration of Cr	2,8,13,1
Outer electrons of Cr	[Ar]3d ⁵ 4s ¹
Electrode potential Cr(s)/Cr ²⁺ (aq)	-0.90V
Electrode potential Cr(s)/Cr ³⁺ (aq)	-0.74V
Electrode potential Cr ²⁺ (aq)/Cr ³⁺ (aq)	-0.42V
Electronegativity of Cr	1.66

2.1.1: Industrial uses of chromium

Chromium used in the industries related to Ferro chrome production such as, chemical and refractory processing, cement-producing plants, ore refining, leather tanneries, film and photography, plating and electroplating, industrial dyes, automobile brake lining and catalytic converters for automobiles, galvanometric and electric, metal cleaning, and pigments [2,4].

2.1.2: Medical uses of chromium

- Chromium helps to move glucose in blood from the bloodstream into the cells to be used as energy and to turn fats, carbohydrates, and proteins into energy, and in helping the body use carbohydrates.
- Using of chromium supplements as being helpful in building muscle and burning fat [43].
- Using of chromium to slow the loss of calcium, so it may help prevent bone loss in women during menopause [8].

2.1.3: Effect of chromium on human health

Chromium enter human body by eating food, inhaling air which contains chemical, and drinking water that contain chromium, when human body exposure to chromium(VI) it effects as to be a strong oxidizing agent, posing a high risk to humans and animals due to its carcinogenic and mutagenic properties[14,34].

Exposure to chromium (VI) by inhalation may results in complications during pregnancy and childbirth [9].

There is a study on 21 rat (age 5week) that exposed to 25 mg Cr (III)per liter as CrCl_3 in drinking water, equivalent to 2.5 mg of chromium(III) per kg of body weight per day, the results shows that tissues were not affected, but some accumulation of chromium in various tissues in the body.

In acute exposure to chromate by ingestion (1-5g) many effects such as gastrointestinal disorders, haemorrhagic diathesis, and convulsions, following cardiovascular shock may lead to death [3].

Chromium is considered one of the 14 most noxious heavy metals [18]. While Cr(III) in trace amount is considered as an essential nutrient [34]

In some studies, workers exposed to chromium (VI) compounds incidences of genotoxic effects such as chromosome aberrations.

While other studies explain, there is a relationship between mortality due to lung cancer and the exposure to Cr(VI) compounds. Epidemiological studies shows that the risk increase when human exposure to a mixture of different chromium (VI) compounds, International Agency for Research on Cancer (IARC) classified Cr(VI) in Group 1 as carcinogenic to humans [38]. Many studies recommend the value of chromium (VI) 0.05mg/L, if the values more than this value the toxicity increase [34].

Table 2.3 : Toxicity of Cr(VI) [9]:

Animal studies	Toxic doses	Risk
Rat	1-5g/week By ingestion	gastrointestinal disorders, haemorrhagic diathesis, and convulsions, following cardiovascular shock may lead to death
Human studies	1.2×10^{-2} ($\mu\text{g}/\text{m}^3$) by inhalation	developing cancer
	50 ppb by drinking water	carcinogenic effect

2.2 Adsorption

Adsorption is a phenomenon underlies a number of important process, it has a technological, biological, and environmental application, the importance of adsorption in solving environmental problems that this

technique is vital for purification of water, sewage, air, and soil from toxic substances that affect human health [24].

Different substances were used in the adsorption technique as activated carbon fibers and carbon molecular sieves, microporous glass and nonporous, and fullerenes. Another technology is used in adsorption which is a silica gel compounds, and this technique has been given a good results in adsorption [20].

2.2.1 Adsorption Phenomenon

Adsorption is a term linked with the surface of solid particles with mechanism for organic and inorganic pollutants removal, the principle based on the contact of absorbable solute with the solid particles with highly porous surface structure. An intermolecular force of attraction between adsorbent and adsorbate cause solute molecules in the solution to be concentrated at the solid surface, this process is called adsorption [22].

Adsorption also is mass transfer process by which the adsorbate substance transferred from liquid to the solid adsorbent surface by physical interactions [24].

The adsorption capacity depends on the surface area of the adsorbent and several factors, as the surface area of the adsorbent increase the adsorption capacity increase [25].

2.2.2 Adsorption Isotherms Models

Modeling of the experimental adsorption data is an essential for predicting the mechanisms of adsorption, several isotherm models employed in the

adsorption as Langmuir, Freundlich, Brunauer-Emmett-Teller, Redlich-Peterson, Dubinin-Radushkevich, Toth, Koble-Corrigan, Temkin, Sips, Khan, Flory-Huggins, Hill, and Radke-Prausnitz [26].

The adsorption models describe the adsorption process at constant temperature and pH [27].

In this study Langmuir and Freundlich were used because the Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface. Once a site is filled, no further sorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved [28,39].

The adsorption is achieved at equilibrium when the adsorbate comes into contact with the adsorbent with sufficient time to make a dynamic balance between the bulk solutions with the interface [28].

2.2.2.1 Langmuir Adsorption Isotherm Model

This model describes the formation of monolayer adsorbate on the outer surface of the adsorbent. For Cr (VI) adsorption onto MSiTh was favorable due to the value of dimensionless separation factor (R_L).

Langmuir represents the equilibrium distribution of Cr(VI) between solid and liquid phases, which indicates that the adsorption occurs on a homogeneous surface of the adsorbate by monolayer, and can be described

as chemisorption process with formation of covalent or ionic bonds between Cr(VI) and MSiTh [29].

Langmuir represented as equation 2.1:

$$\frac{C_e}{q_e} = \frac{1}{Q_o^b} + \frac{C_e}{Q_o} \quad 2.1$$

C_e : is the equilibrium concentration (mg/L)

q_e : is the amount of Cr(IV) adsorbed per gram at equilibrium (mg/g)

Q_o (mg / L) and b (adsorbent per mg of adsorbate) : are Langmuir constants related to the adsorption capacity and energy of adsorption , respectively.

Other form of linear form of Langmuir adsorption isotherm is represented in equation 2.2 :

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L} \quad 2.2$$

Where:

C_e = the concentration of the adsorbate at equilibrium (mg/L)

Q_e = the amount of Cr(VI) adsorbed per gram of adsorbent (mg/g)

Q_m = Maximum capacity of monolayer coverage (mg/g)

K_L = Langmuir isotherm constant (L/mg)

The term of dimensionless constant separation factor (R_L) can be estimated from equation 2.3 :

$$R_L = \frac{1}{(1+K_L C_o)} \quad 2.3$$

Where C_o is the highest initial concentration of adsorbate

If R_L value > 1 , the adsorption isotherm is unfavorable, either if ($R_L = 1$) means linear, and if ($0 < R_L < 1$) indicates the adsorption is favorable [27].

2.2.2.2 Freundlich Adsorption Isotherm model

This isotherm adsorption model is an empirical equation describes the heterogeneous system, linear form of Freundlich model expressed as in equation 2.4:

$$\log q_e = \log K_F + \frac{1}{n} \log C \quad 2.4$$

Where :

q_e : is the amount of Cr(IV) adsorbed per unit of mass of adsorbent (mg/g)

C_e : is the residual concentration of Cr (IV) in solution (mg/L)

K_F : is a constant which is a measure of adsorption capacity

$\frac{1}{n}$: is a measure of adsorption intensity

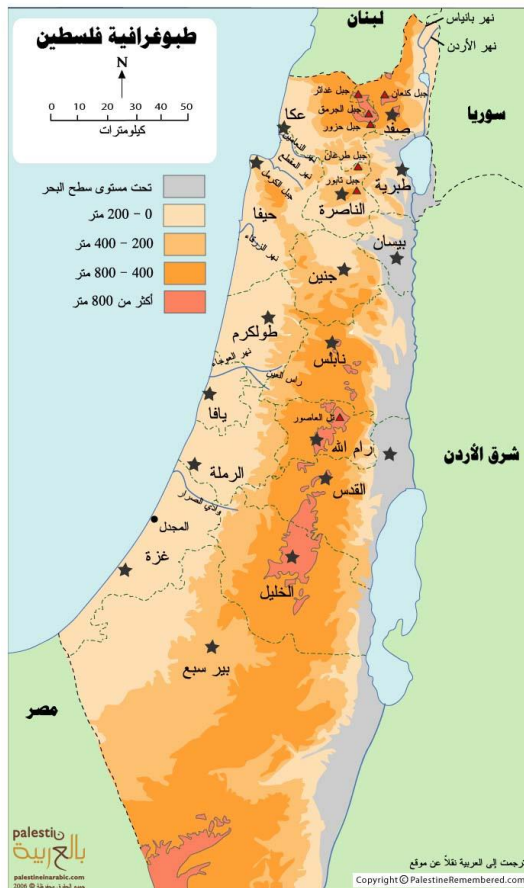
K_F and n are Freundlich constants, K_F indicate the adsorption capacity of the adsorbent, while n indicate the favorable way of the adsorption, and $\frac{1}{n}$ value shows the favorability of the adsorption process if $\frac{1}{n}$ value < 1 , this indicate a normal adsorption , if ($1 < \frac{1}{n} < 10$) indicates a favorable adsorption process.

The adsorption process is dependent temperature term as the temperature increase the values of (K and n) changes and high pressure is needed to saturate the surface of the adsorbate [27].

2.3 Industrial Wastewater in the Palestine

Palestinians are suffering from several private-related problems in the wastewater problems and also industrial wastewater that contain a high concentration of toxic heavy metals that kill in the lives of human beings, because some of these elements very seriously and directly affects the human has lead to death and there are heavy metals accumulate in the body during time caused him severe damage may lead to cancer [40].

It is the responsibility of the Palestinian Authority to control of industrial facilities that use heavy metals in plants such as leather tanning and dyeing garment factories and other produce heavy metals in waste water, we have to set limits and controls on these facilities and the introduction of new laws to control wastewater pollution by heavy metals [41].



There are necessary in Solid Waste Management Tool, there are no controls to determine the types of toxic waste in the Palestinian Authority areas, there are no controls to determine the types of toxic waste in the Palestinian Authority and there is no valid ways to get rid of all toxic solid waste [40].

There are 71 of the dye factory in the West Bank produce hazardous substances to wastewater containing heavy metal ions. These plants use large quantities of fresh water and produces wastewater containing toxic heavy metals in the form of ions dissolved contaminating groundwater and soil [23].

About 2500 million cubic meters of motor oil are disposed of each year, without the collection of these toxic substances in sanitary ways system.

The biggest threat to the Palestinian environment is an Israeli occupation, where there are many Settlements on the Palestinian territories, which contain many of the factories that produce large amounts of hazardous materials and heavy metals, which are disposed in the Palestinian territories areas, where the groundwater and soil polluted from the settlements and thereby exposed the lives of Palestinian citizens at risk.

Of the challenges faced by the Palestinians that there is no ways to reduce waste water contamination with heavy metals which pose a threat to human life and pursue ways to reduce the heavy metals in the waste water through the development of scientific researches to reduce heavy metals in waste water [42].

It is the responsibility of the Palestinian Water Authority in partnership with institutions and ministries of Environment Quality Authority and the Ministry of Local Government and the Ministry of Health and Standards Institution control over the Palestinian factories that produce heavy metals and set limits and controls the licenses required by these plants were treating wastewater produced prior to disposal in the wastewater network [21].

Chapter Three

Experimental Work

3.1 Chemicals and Materials

Solvents and chemicals were used without further treatment, and were of analytical scale, MSiTh, compound has a size particle 70-230 mesh, these particles have 60 Å in diameter, the activation of particles was made with temperature (160 °C), by heating to 24 hour, it was used without purification[1].

Analytical grade Potassium dichromate ($K_2Cr_2O_7$), which have molecular weight 294.2 g / mole, boiling point 398°C, specific gravity 2.676 and density 1.6g/cm³, was used as adsorbent [1,10]. Deionized water was used to prepare stock solution, HCl (0.1N), and NaOH (0.1N) were used for pH adjustment. HCl(6N) was used for sustainable of (MSiTh).

The required materials and apparatus are: Flame Atomic Absorption (ThermoScientific iCE3000, Type iCE3500AA System).

Glass Ware, pH meter (model: 3510, JENWAY), centrifuge (model : 1020DE,Centurion Scientific), scale apparatus, Shaking Water Bath(JLabtech, 20to250 rpm Digital Speed Control), hood.

3.2 3-Glycidoxypentyl-functionalized silica (MSiTh) as adsorbent

There are different techniques used for removing different heavy metals that polluted in water, some techniques are used such as adsorption the metal ions using zeolites, other compounds was used is activated carbon, either clays was used and some removing ions. But using these substances have different problems such as long equilibrium time, there were no

selectivity, the activity for removing is low, and mechanical and thermal stability. In the last years the researchers preparing new material silica-based adsorbents due to their regular pore structure, the properties of particles especially at well, and the particles surfaces properties were checked.

3.3 Synthesis of 3-Glycidoxypropyl-functionalized silica (MSiTh)

Synthesis of this silica gel compound MSiTh with functional group based on several steps: the first step after activation of silica gel compound with heating, the silica gel react with 3- glycidoxypropyltrimethoxysilane, a new compound was formed which is Epoxy-Silica (ES), then the ES act as to stop the activity of the compound that containing the donor atom, by this technique a condensation between the epoxide group of ES and compound containing a nucleophilic salt in reflux dimethylformamide “DMF”, the immobilization at the outside surface of the silica - gel compound that can occur by 2- thiophenmethanol was achieved.

The procedure that explain synthesis of (MSiTh) compound shown in Figure 3.1

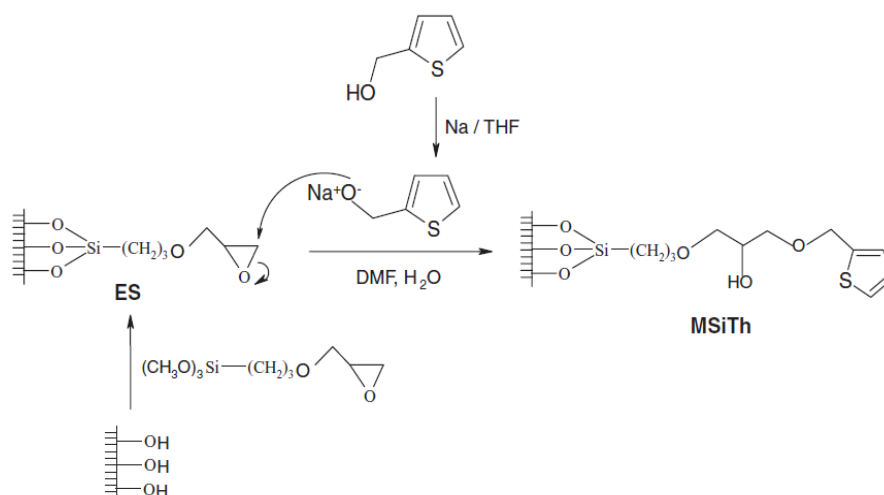


Figure 3.1: Steps of synthetic of silica - gel compound (MSiTh) [1].

The experimental procedure for synthesis of 3-Glycidoxypropyl-functionalized silica (MSiTh) as : First activated silica gel was added to 3-glycidoxypropyltrimethoxysilane to form epoxy – silica (ES), then 2-thiophenmethanol was added to sodium metal in tetrahydrofuran to form alkoxide derivative salt, this salt was added to Epoxy-Substituted silica with suspension, 1g was put in solution 30ml dimethylformamide “DMF”, the solution of the mixture that formed was mixed, and reflection with nitrogen for a period about 24 hour.

The solid compound that formed was separated by filtration, and about 150ml of each of the following solutions (DMF, toluene, deionized water, dichloromethane, and methanol) were used to wash the residue and then the solid residue was dried to give 3-Glycidoxypropyl-functionalized silica (MSiTh) , and was used in the adsorption process for chromium(VI) as adsorbent to obtain test results .

3.4 The experimental part for characterization of 3-Glycidoxypropyl-functionalized silica (MSiTh)

The characterization of MSiTh compound was made by using (FT-IR) on a Perkin- Elmer 1310, Brunauer–Emmett–Teller (BET) equation has been used to determine the specific area of modified silica MSiTh.

Perkin – Elmer PE-2400 analyzer was used for elemental analysis, Thermoquest Sorpsomatic 1990 analyzer used to obtain the nitrogen adsorption – desorption results, after that the silica compound had been put into a tube containing dry nitrogen, and the silica compound was prepared at temperature 35-60°C, time constant 5°C min⁻¹ for 12 h.

Another analysis is Barrett-Joyner-Halenda BJH was made branch at $P/P_0 = 0.3$ to 1 by standardization model was made for pore size distribution. TGA Q so V6.7 Build 203 instrument was used to determine the mass loss under 90% of oxygen and 10% of nitrogen at heating rate of $10^\circ\text{C min}^{-1}$. Spectra Varian A.A.400 spectrophotometer was used for absorption measurements.

3.5 Preparation of Chromium(VI) Solution

About 1.41g of potassium dichromate was taken in 500ml volumetric flask and diluted up to the mark by addition of deionized water, and then different concentrations (2.5ppm, 5ppm, 10ppm, 20ppm, 30ppm, and 50ppm) were prepared by dilution [11].

3.6 Calibration curve

The concentrations of Chromium (VI) (2.5ppm, 5ppm, 10ppm, 20ppm, 30ppm, and 50ppm) were analyzed by Flame Atomic Absorption (ThermoScientificiCE3000, Type iCE3500AA System), and the absorbance was determined as shown in Figure 3.1:

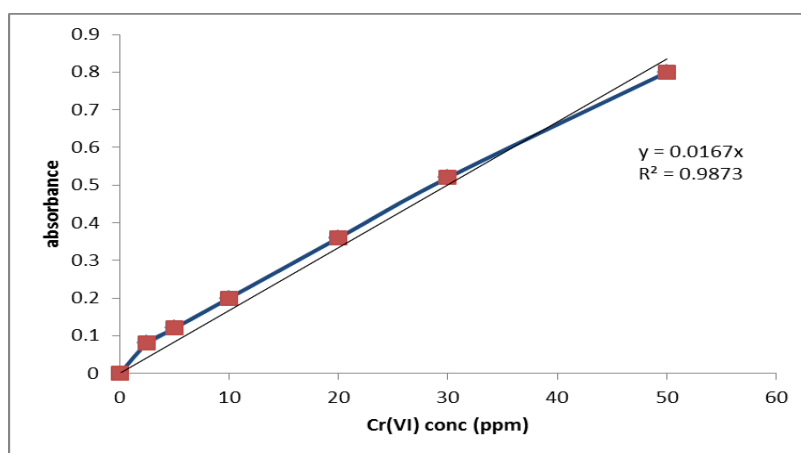


Figure 3.2: Linear calibration curve of absorbance versus concentration, Cr(VI) concentrations (2.5-50 ppm)

Maximum absorption of Cr(VI) at 357.9 nm wave length at the concentration below 20 ppm Cr (VI). Using Beer's Law, the absorbance of Cr(VI) at different concentrations was plotted to give a linear curve [12], as shown in Figure 3.2.

3.7 Experiments

The analysis and measurements were made at Wavelength $\lambda = 357.9$ nm to obtain the adsorption data, and at different concentrations for Cr(VI) in the solutions. the pH of solutions was adjusted using roughly concentrations of 0.1M HCL, and 0.1M NaOH.

3.7.1 The temperature effect

For studying the temperature effect on adsorption, 0.04 g adsorbent (MSiTh) samples were added to test tubes contain 10 mL of Cr (VI) solutions each has concentration of 10 mg/L at pH around 6. Each mixture was placed in Shaking Water Bath (JLabtech) at desired temperature (the range was 15-60°C) for 30 min. After each time period, the adsorbent was separated by centrifuging at 600 rpm and supernatant was tested by Flame Atomic Absorption for the residual concentration of Cr(VI), at 357.9 nm wavelength.

3.7.2 The effect of pH on Cr(VI) adsorption

The effect of initial pH at adsorption of Cr(VI) onto MSiTh was studied at the pH range from 1 to 13. The pH was adjusted using roughly concentrations of 0.1N HCL and 0.1N NaOH. 0.04 g adsorbent samples

were added to 10 ml volume of Cr(VI) solutions with concentration 10 ppm. The mixtures were placed in Shaking Water Bath at constant temperature (25°C) for 30 min. At the end of each time period, the adsorbent was separated by centrifuging at 600 rpm and supernatant was analyzed by Flame Atomic Absorption for the residual concentration of Cr(VI), at 357.9 nm wavelength. Also the same experiment was made with the same conditions but the interval was 24 hour.

3.7.3 The effect of concentration of Cr(VI) on adsorption

The following procedures were used to find out the optimum conditions, 0.04 g of (MSiTh) compound was added to a number of tubes contains 10 mL of different concentrations of Cr(VI) solution (2.5-30ppm), under optimized temperature (25°C) and pH 6 for 30 min, the absorbance of the solution above the solid residue was measured by Flame Atomic Absorption at 357.9 nm.

3.7.4 The effect of adsorbent (MSiTh) dose

The effect of adsorbent (MSiTh) dose on the adsorption of Cr(VI) onto MSiTh was studied. The condition to find out optimum adsorbent dose, 0.020, 0.100, 0.150, 0.200 and 0.250 g of adsorbent were added to five tubes contains 10 mL of 10mg/L Cr(VI)solution the pH =6 . The mixtures were placed in Shaking Water Bath at constant temperature (25°C) for 30 min. The absorbance of the solution above the solid residue was measured by Flame Atomic Absorption at 357.9 nm for the residual concentration of Cr(VI).

3.7.5 Optimization for contact time

Adsorption of Cr(VI) on the adsorbent was studied as a function of shaking time at 25°C. A sample of 50 mL of Cr(VI) (10 mg/L) solution at pH=6 was taken in a volumetric flask and shaken with 0.20g of adsorbent. Aliquots of the clear solution were drawn out by a small slim pipette at different time intervals until equilibrium was achieved. Each aliquot was taken and centrifuged for 5 minutes at 600 rpm. The supernatant was carefully removed by a thin plastic dropper and absorbance was measured by Flame Atomic Absorption at 357.9 nm wavelength.

Chapter Four

Results and Discussion

4.1 Characterization of (MSiTh)

In order to determine the amount of functional thiophene groups per gram of silica, the analysis of the elements sulfur and carbon was used, and it's found that (%S=1% and %C=2.12%). Another method which is thiosulfate method also was used and gives results of the amount of thiophene groups (3.12 μ mol/g) per gram of silica[1].

For studying the attachment of thiophene group to the silica the FTIR spectra was used, and the results obtained shown in Figure 4.1

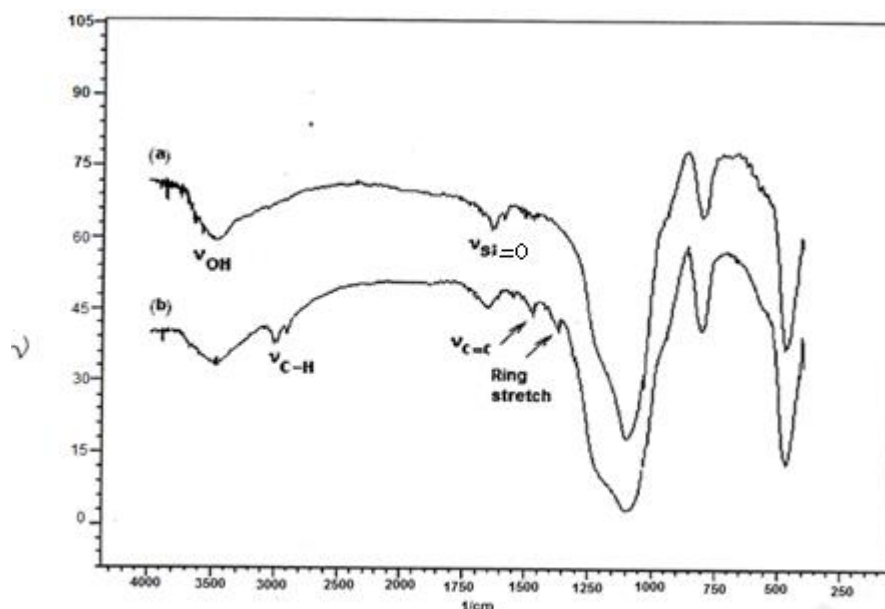


Figure 4.1 : Analysis of FT-IR spectra for silica-gel(So)(a) and thiophene- modified silica(b)[1].

Around 330 cm^{-1} , ν decreased strongly that explain adsorption of OH, and at 3000-2800 cm^{-1} weak band of ν for (C-H) was appeared, from this figure

at 1475 cm^{-1} there is (C=C) stretching and at 1410 cm^{-1} there is ring stretching, which means that thiophene group was successfully grafted to the silica.

By studying the thermogravimetric analysis, Figure 4.2 shows that at temperature between $275\text{--}800^\circ\text{C}$ there is a degradation which explain the good compound stability for 3-Glycidoxypopyl-functionalized silica “MSiTh”.

In mass loss of the three substances were studied Free-Silica (So), (ES), and the silica compound containing thiophene (MSiTh), and the results shown in figure 4.2.

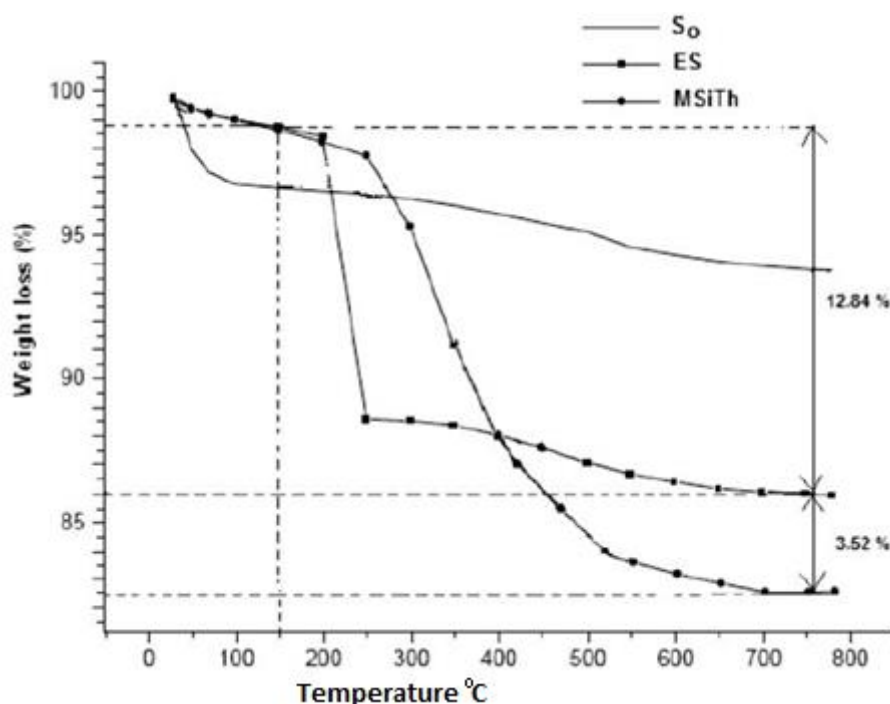


Figure 4.2: The analysis curve for Free-silica (So), epoxy-silica (ES), and silica compound containing thiophene (MSiTh).

For free silica, there are two stages of mass loss for free silica (So), the first stage (25°C to 150°C) corresponds to 3.30% shows the adsorption of water (150°C - 800°C) corresponds to 2.84% of mass loss. For epoxy silica

(ES) there is a mass loss in the range (150°C to 800°C) about 12.84%, in addition the mass loss increased of for (MSiTh) at the range (150°C to 800°C) corresponds to 3.52%, this mass loss related to the decomposition of thiophene groups at the surface of silica-gel compound, results obtained at 312 $\mu\text{mol/g}$.

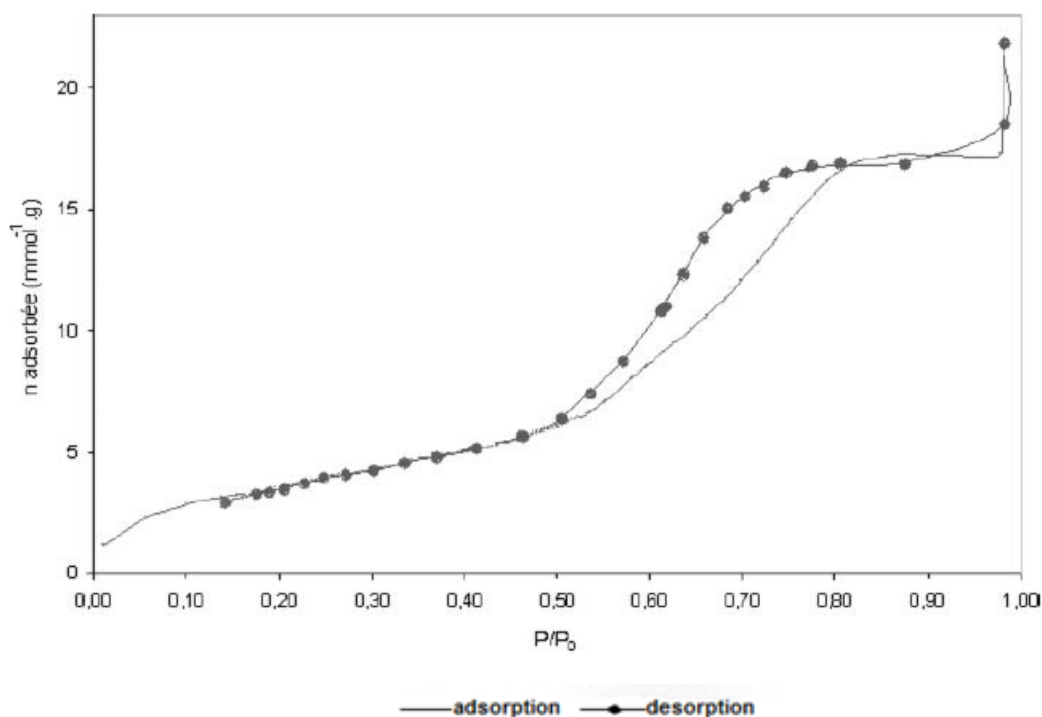


Figure 4.3: Isotherm for adsorption – desorption for MSiTh compound.

The results shows that before functionalization the porous Free-Silica give high value S_{BET} equal 550 m^2/g , while BJH diameter of pores equal 6 nm and the volume of pores equal 0.8 cm^3/g . After functionalization of silica, the pore volume decrease from 0.8 to 0.68 cm^3/g , the S_{BET} decreased from 550 m^2/g - 313 m^2/g .

The presence of thiophene groups at the surface of silica because it prevent the partially adsorption for nitrogen molecules, also by functionalization

the amount of nitrogen consumed to normalized the particle surface and adsorbed has little amount, which lead to reduce the particles size, this leads to give amount of $N_m = 71.967 \text{ cm}^3 / \text{g}$ for the layer of particles, while it give volume equal to $89.11 \text{ cm}^3 / \text{g}$ for the silica. Also from figure 4.4 there is slow motion for the particles due to pressure $0.4 \text{ cp} / \text{dp}_{oc1}$, which means there a regular distribution for the compound particles, and as the IUPAC classification, the hysteresis loops are type H₂, that means there is a uniform pore diameter distribution for , 3-Glycidoxypropyl-functionalized silica (MSiTh).

The average BJH pore diameter after functionalization decreased from 6nm to 2.866 nm. The pore size distribution of 2.866 nm also provides evidence for the uniform framework porosity of the MSiTh, the BET parameters are all within the range normally observed when the isotherm is adequately described by the BET equation as shown in figure 4.4.

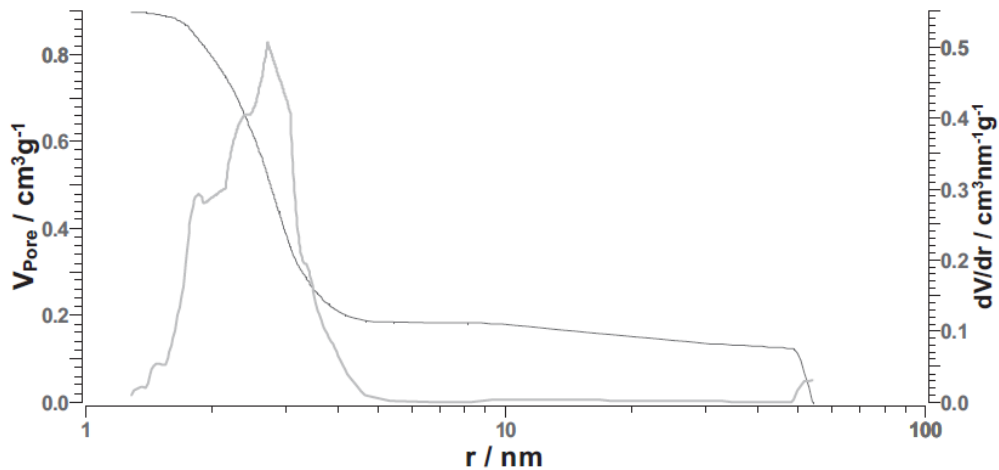


Figure 4.4 : The distribution of silica-gel (MSiTh) particles[1].

The functionalization of MSiTh gave large surface area and a uniform in pore size, the density of the particles surfaces and the distance between particles were calculated as density =0.60 molecule nm⁻² and distance =1.29 nm) from the following equations (4.1), (4.2) :

$$d = N_A \cdot l_o / S_{BET} \quad 4.1$$

$$I = (1/d)^{1/2} \quad 4.2$$

N_A : Avogadro's number.

l_o : the proportion of functional groups attached on the surface.

S_{BET} and l_o are BET parameters.

These obtained results can be explaining high surface area of 3-Glycidoxypopyl-functionalized silica (MSiTh).

4.2 Investigation of adsorption parameters

4.2.1 The effect of pH on Chromium (VI) adsorption on MSiTh

The study of initial pH for the chromium (VI) solution is an important factor that affect adsorption of chromium (VI), the adsorption capability of adsorbent depend on the pH value because activity of groups on the 3-Glycidoxypopyl-functionalized silica (MSiTh) may be protonated or deprotonated easily at different pH. At low pH the acidic solution (pH=1, 2, 3) the adsorption decrease due to the presence of high amount of hydrogen ions, that in turn neutralize the particle surface with negative charge [15].

Different solutions of Cr(VI) with different values of pH were used to study the activity of the adsorption by solution pH , the results represented in

Figure 4.5 , from the Figure there is an increase in chromium (VI) adsorption at pH=6.

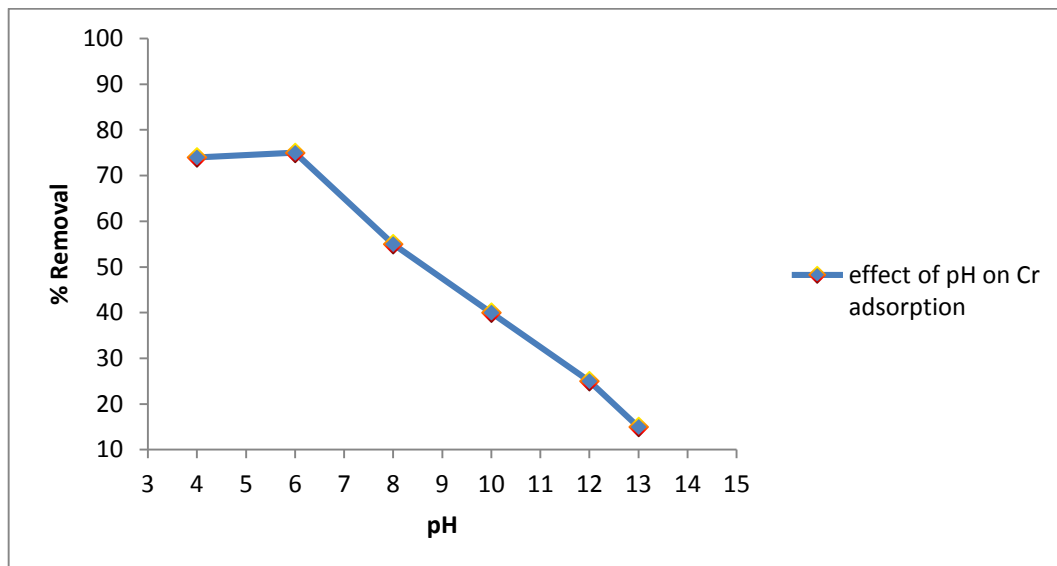


Figure 4.5: pH effect on Cr(VI) adsorption ($C_o=10\text{ppm}$, $T=25^\circ\text{C}$, adsorbent dose = 0.04g)

At high pH the adsorption of Cr(VI) ions decrease, it may be due to saturation of the particles sites by the negative ions like $\text{Cr}_2\text{O}_7^{2-}$ that retards the adsorption of these ions further to adsorbent surface. Also the attraction forces between the Cr(VI) ions and the adsorbent surface decreased.

4.2.2 The effect of temperature on Cr(VI) adsorption

Temperature effect on Cr(VI) adsorption was studied, at temperature (15°C - 60°C) the percent of removal and temperature results represented in Figure 4.6, the percent of removal of Cr(VI) decrease with increasing the temperature above the room temperature , at 25°C the maximum adsorption 78% was achieved at the surface of modified silica compound (MSiTh).

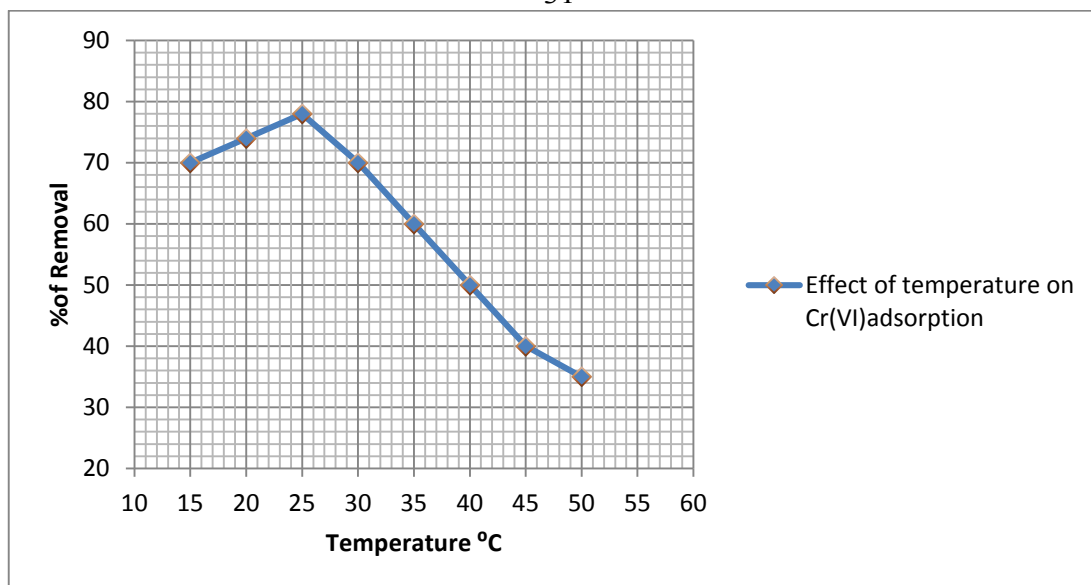


Figure 4.6: The effect of temperature on Cr(VI) adsorption ($C_o=10\text{ppm}$, time = 60min, adsorbent dose = 0.04 gm, solution volume = 50ml)

4.2.3 The effect of Cr(VI) concentration on adsorption

The study of initial concentration effect of Cr(IV) on the removal efficiency of (MSiTh) was determined over wide range of Cr(IV) concentration, the absorbance versus concentration represented in Figure 4.7:

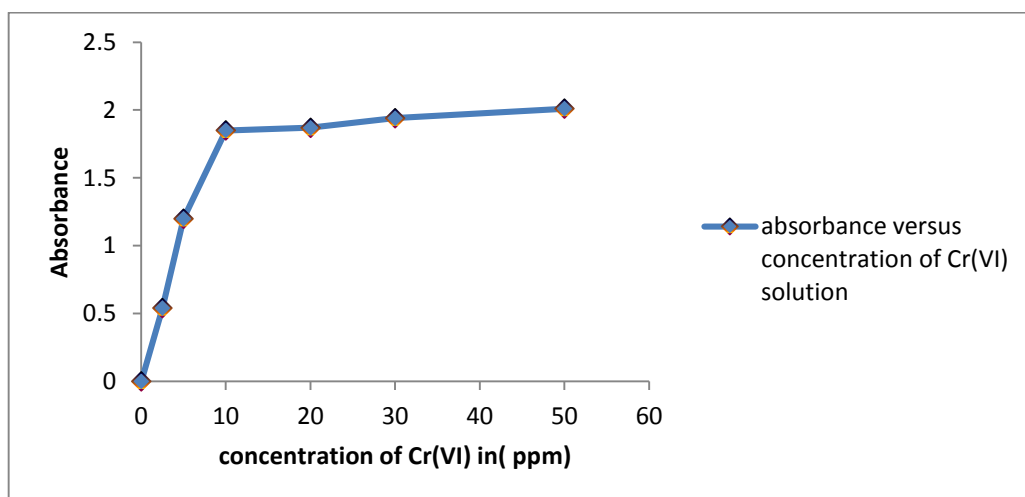


Figure 4.7: A representative plot of the absorbance and concentration of Cr(VI) solution.

At high concentrations of Cr(VI) above 20ppm, Beer's Lambert Law, the relation shows deviates from linearity and gives anon-linear relationship as in figure 4.6 , so our experimental work was focused at concentrations below 20ppm and restrict concentration up to 20 ppm, and there is another reason which is the amount of Cr(VI) in wastewater was found in the range (1.5 – 5ppm) [13].

While other conditions as volume of solution, adsorbent dose, and pH solution as constants, then the results obtained and represented as in figure 4.8:

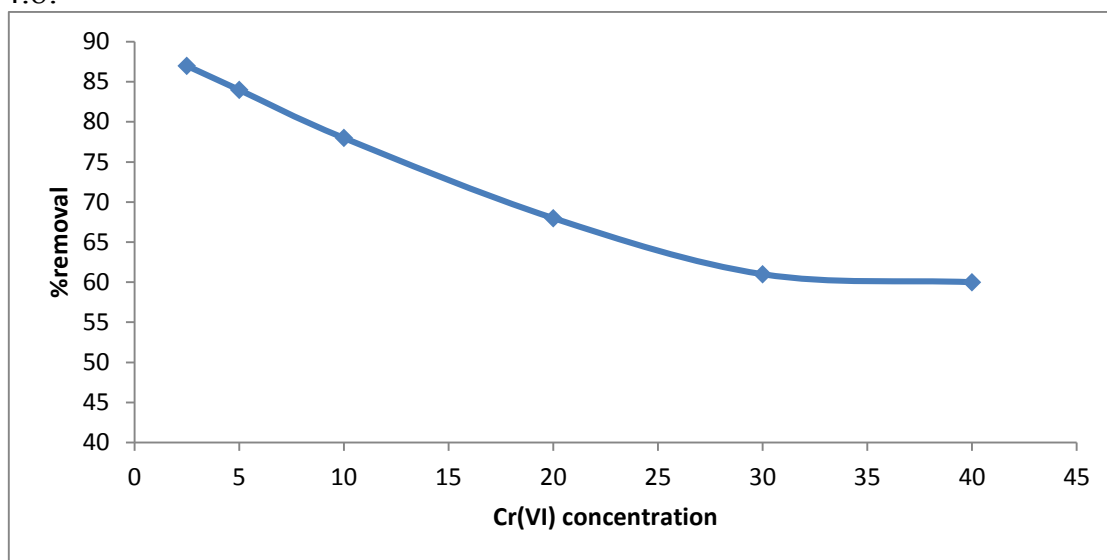


Figure 4.8: Effect of Cr(VI) concentration on adsorption (pH=6,Temp=25°C, Time=60min, solution volume=10ml, adsorbent dose=40mg)

This figure shows that at lower concentration (2.5 – 20 ppm) the adsorption of Cr(IV) was rapid, and as the concentration of Cr (VI) the adsorption of its ions was decreased . This decrease in adsorption may be related to the increase of Cr(IV) ions for affixed amount of (MSiTh). At the beginning the removal of Cr(IV) ions is high due to large surface area of

adsorbent and when the saturation point is reached, at equilibrium the capacity of the (MSiTh) to adsorb Cr(IV) ions is controlled and the ions goes from the out site to in sites of the (MSiTh) surface particles [16].

By increasing the Cr(IV) concentration from 2.5 ppm to 20 ppm all sites of the adsorbed occupied, then the adsorption becomes constant whatever the concentration increase in due to determine the effect of Cr(IV) concentration on the adsorption capacity, the distribution coefficient K_d was calculated from equation 4.3, [17]:

$$k_d = \frac{\text{amount of CrVI in adsorbent} * \text{volume of solution(ml)}}{\text{amount of CrVI in solution} * \text{mass of adsorbent dose(g)}} \quad 4.3$$

And K_d can be measured directly in the laboratory by equation 4.4:

$$K_d = \frac{V_w (C_0 - C_e)}{m_{sed} * C_e} \quad 4.4$$

These results can be represented in figure 4.9:

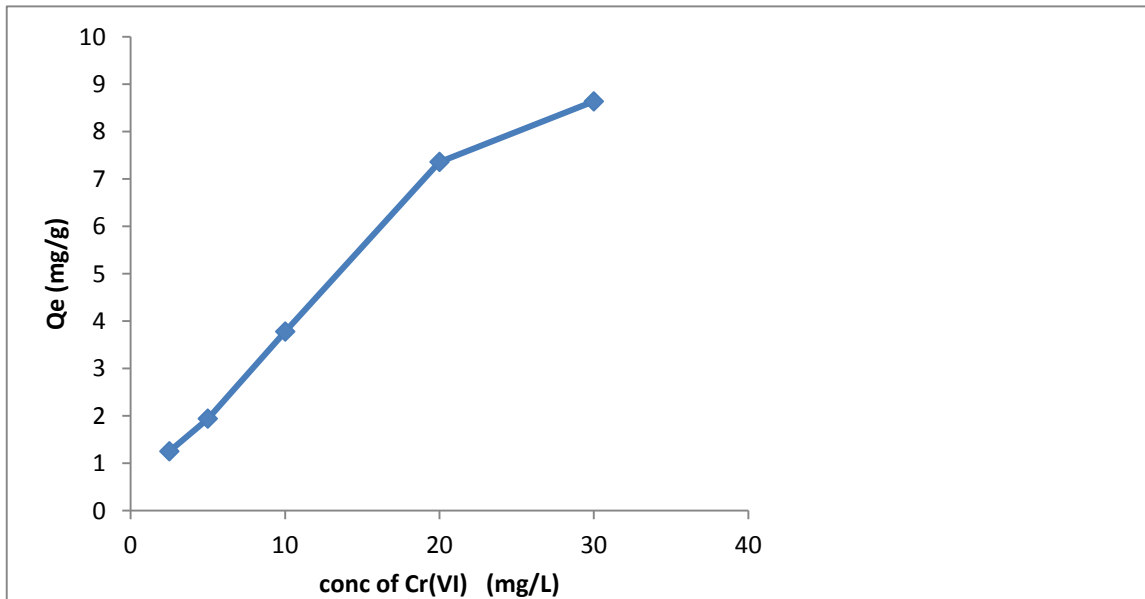


Figure 4.9: The effect of Cr(VI) conc. on adsorption capacity. (Temp= 25°C, time= 60 min., pH= 6, adsorbent dose= 0.04 g, sol. Volume= 10 mL).

When distribution ratio represented as a function of concentration as shown in Figure 4.10.

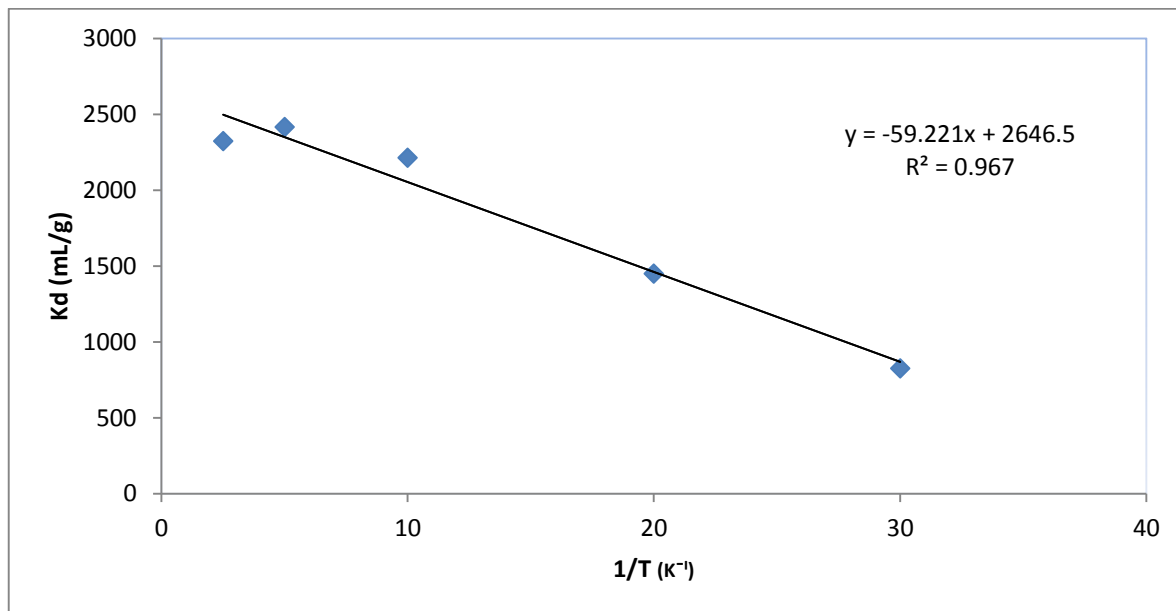


Figure 4.10: Effect of Cr(VI) on the Distribution Ratio K_d . (Temp.= 25°C, time= 60 min., pH= 6, adsorbent dose= 0.04 g, sol. Volume= 10 mL)

From this figure the distribution coefficient (K_d) values decrease with increase in Cr(IV) concentration.

4.2.4 The effect of contact time on Cr (VI) adsorption

The determination of the connection time of maximum adsorption for Cr (IV) on MSiTh was made and the results shown in Figure 4.11.

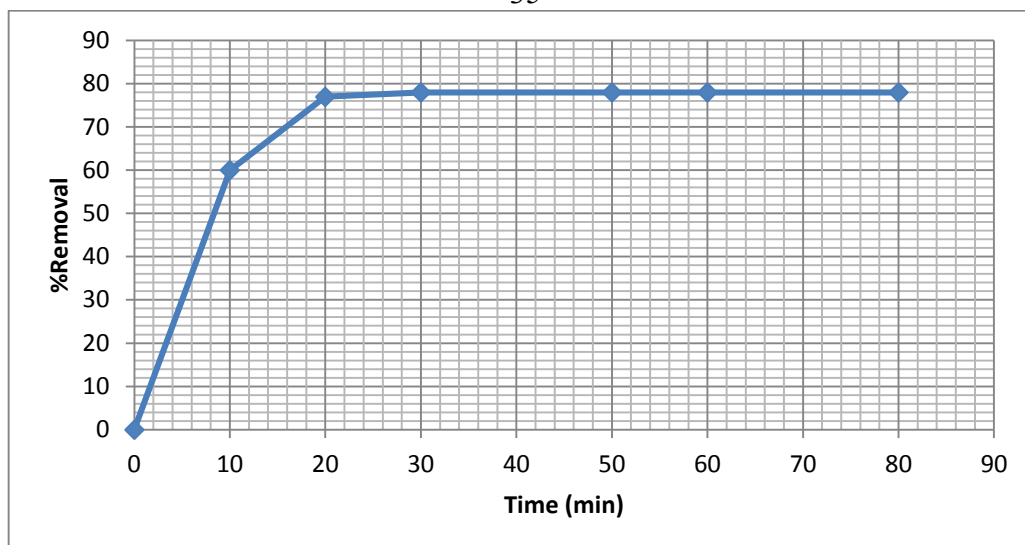


Figure 4.11: Effect of contact time to determine the time of maximum adsorption of Cr (VI). (Temp.= 25°C, pH= 6, conc. Of Cr(VI)= 10 mg/L, sol. Volume= 50 mL, adsorbent dose= 0.20g)

The adsorption process of Cr(IV) on MSiTh at the first 20 minutes was rapid and become insignificant after that, when contact time increased there is negligible effect on percentage removal of Cr(IV), it may be due rapid accumulation of chromium ions at the surface of MSiTh [16].

At the first few minutes the contact of Cr(IV) ions and solid particles of the adsorbent is high, and the transfer onto the MSiTh particle surface is faster, after 20 minutes the Cr(IV) ions take more time to transfer to the internal adsorption sites through the pores. So the optimum time for the adsorption of Cr(IV) on MSiTh is 20 minutes.

4.2.5 The effect of the adsorbent dose

The amount of the dosage of adsorbent MSiTh on the removal of Cr (IV) was studied. Various doses (20mg to 250mg) were mixed with metal ion solutions, while keeping the temperature 25°C, pH=6, initial volume=10ml, and Cr (VI) concentration= 10ppm for 24 hour on the shaker.

The results were represented as in Figure 4.12, the removal efficiency on Cr(IV) increases with the increase of weight of adsorbent dose MSiTh up to 150mg, then removal efficiency did not change significantly by increasing dose of adsorbent.

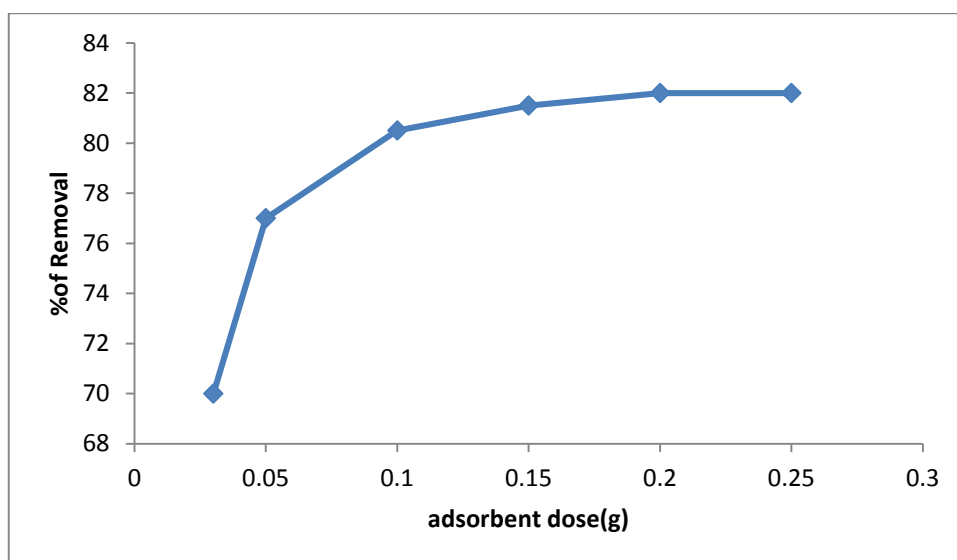


Figure 4.12: Effect of dosage of adsorbent on the removal of Cr (VI). (Temp.= 25°C, time= 30 min., pH= 6, concentration of Cr(VI) = 10 ppm, sol. Volume= 10 mL)

From the figure the removal efficiency at 30mg dose is high, this may be due to the great at the exchange of the sites of the adsorbent. The optimum value of adsorption at 10 ppm of Cr (IV) at pH=6, solution volume =10ml, is at 30 mg MSiTh.

4.3 Adsorption isotherm of Cr(IV)

The study of the adsorption at equilibrium gives adsorption characteristics of the adsorbent, and the capability to adsorb, specific values used to describe the adsorption isotherm such as a least square method to linearly transformed Freundlich and Langmuir.

4.3.1 Freundlich Adsorption Isotherm

The equation of Freundlich adsorption isotherm is:

$$\log q_e = \log K_F + \frac{1}{n} \log C \quad 4.5$$

Where :

q_e : represent mass of Cr(VI) adsorbed per unit of mass of adsorbent (mg/g)

C_e : is the concentration of Cr(IV) in solution (mg/L)

K_F : is a constant represent adsorption capacity

$\frac{1}{n}$: is the value of adsorption intensity

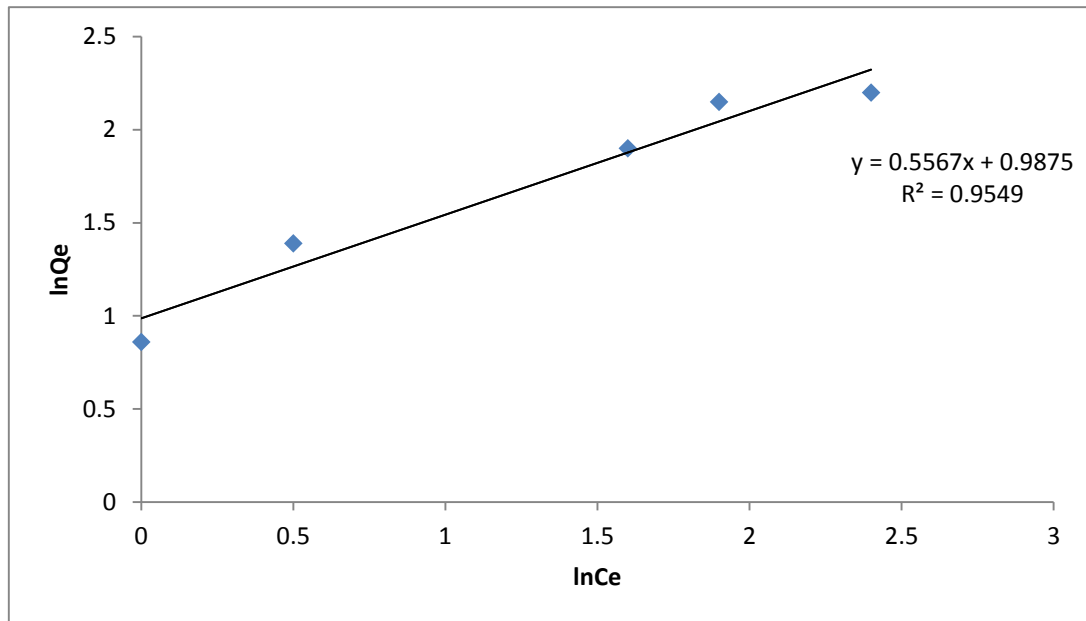


Figure 4.13: Freundlich plot for Cr (VI) adsorption on (MSiTh). (Temp= 25°C, pH= 6, time= 30 min., sol. Volume= 10 mL, adsorbent dose= 0.04 g)

Table 4.1: Parameters and correlation coefficient of Freundlich for adsorption of Cr(VI) onto MSiTh

Freundlich isotherm model Parameters				
Adsorbate	Parameters			
	$\frac{1}{n}$	n	K_F=(mg/g)	R²
MSiTh	0.56	1.786	2.15	0.9603

From table 4.1 the results given, $n=1.786$ and $1/n=0.56$, as Freundlich isotherm model these values indicate that, the sorption of Cr(VI) on MSiTh is favorable and the R^2 value is 0.9603.

4.3.2 Langmuir adsorption isotherm

The adsorption capacity of MSiTh was estimated by applying Langmuir model, the equation of Langmuir adsorption isotherm is represented in as in 4.6 :

$$\frac{C_e}{q_e} = \frac{1}{Q_0^b} + \frac{C_e}{Q_0} \quad 4.6$$

C_e : is the concentration (mg/L) at equilibrium

q_e : is the amount of Cr(IV) adsorbed per gram at equilibrium (mg/g)

Q_0 (mg / L) and b (adsorbent per mg of adsorbate): are Langmuir constants to get the adsorption capacity and energy of adsorption, respectively.

Other form of Langmuir adsorption isotherm is:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L} \quad 4.7$$

While:

C_e = the concentration value of the adsorbate at equilibrium (mg/L)

Q_e = the conc. value of Cr(VI) adsorbed per gram of adsorbent (mg/g)

Q_m = Max capacity of monolayer coverage (mg/g)

K_L = isotherm constant for Langmuir (L/mg)

The study of Langmuir adsorption was applied by using the results obtained from adsorption experiments at room temperature (25°C) as shown in figure 4.14

The values of Q_o and K_L were calculated from the slope and the y-intercept of the Langmuir plot of C_e/Q_e versus C_e

R_L value can be estimated by equation 4.8:

$$R_L = \frac{1}{(1 + K_L C_o)} \quad 4.8$$

While C_o is the highest concentration of adsorbate (mg/L).

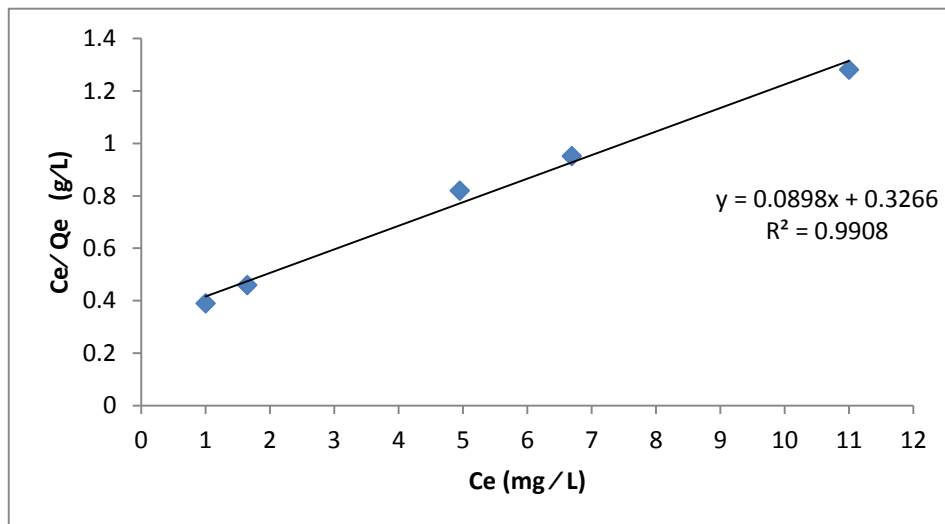


Figure 4.14: Langmuir plot for Cr(VI) adsorption on (MSiTh). (Temp= 25°C, pH= 6, time= 30 min., sol. Volume= 10 mL, adsorbent dose= 0.04 g)

Table 4.2: Parameters and correlation coefficient of Langmuir model for adsorption of Cr(VI) onto (MSiTh)

Langmuir isotherm model parameters				
Adsorbate	Parameters			
	Q_m(mg/g)	K_L=(L/mg)	R_L	R²
MSiTh	10.672	0.321	0.2375	0.9808

The R_L value is calculated and found to be equal to 0.2375 at 25°C, this value between 0 and 1, as this value the adsorption of Cr(VI) onto (MSiTh) is favorable.

4.4 Adsorption thermodynamics

Adsorption thermodynamics for Cr(VI) adsorption was studied, and determined by using Van't Hoff plot as shown in Figure 4.10, according to equation 4.9 :

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad 4.9$$

The enthalpy and entropy (ΔH and ΔS) of a reaction can be easily obtained using Van't Hoff plot, from plotting Ln K_d versus 1/T,

$$\Delta H = -R * \text{Slope}$$

And

$$\Delta S = R * \text{Intercept}$$

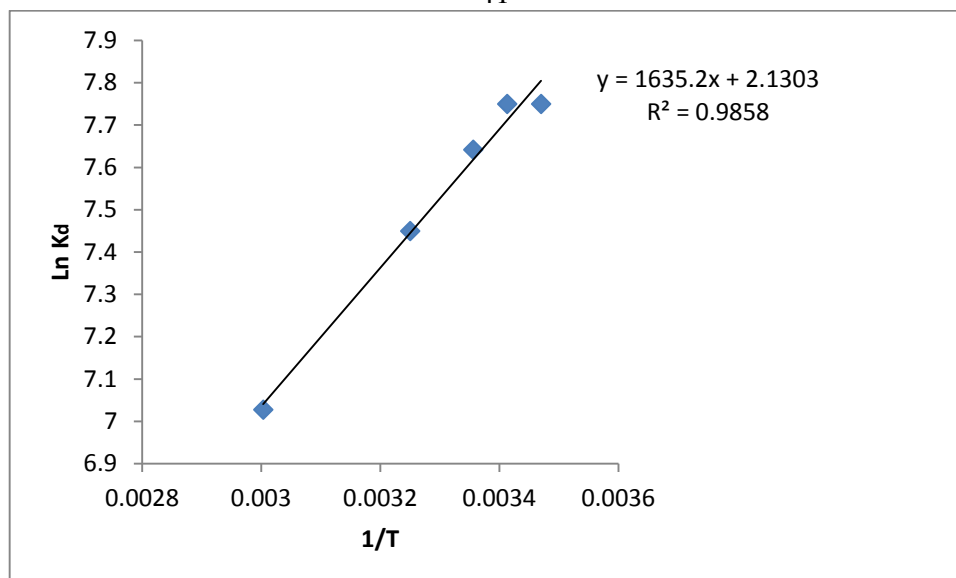


Figure 4.15: Van't Hoff plot. graph of $\ln K_d$ vs. $1/T$ for Cr(VI) adsorption onto (MSiTh).

(Temp.= 25°C, pH= 6, time= 60 min., adsorbent dose= 0.04 g, sol. Volume= 10 mL)

From Figure 4.15 , the results obtained the ΔH value = - 1.62355 KJ.mol⁻¹ and ΔS value = 2.1152 J. mol⁻¹. K⁻¹

Gibbs free energy ΔG was calculated at different temperatures by using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad 4.10$$

The results that evaluated are represented in Table 4.3.

Table 4.3: The values of the thermodynamic of Cr(VI) adsorption at various temperatures.

Adsorbent	ΔH° (KJ/mol)	ΔS° (J/mol.K)	ΔG° (KJ/mol)				
			288K	298K	308K	318K	328K
MSiTh	- 1.62355	2.115	- 1.0144	- 0.9933	- 0.972	- 0.951	- 0.928

The negative ΔG° values (- 1.0144 to - 0928 KJ/mol) indicate the adsorption is favorable and spontaneous at temperatures in the experiment. The negative value of ΔH° (- 1.62355 KJ/mol) shows an exothermic adsorption process and indicates the adsorption is favorable at 25°C. the

positive value of ΔS° (2.115 J/mol.K) indicates some randomness at the solid/liquid interface in the adsorption system which increase the adsorption process.

4.5 Adsorption kinetics of Cr(VI)adsorption onto MSiTh

Pseudo first- order equation was applied for evaluation the adsorption kinetics for Cr(VI) onto MSiTh, the rate constant for the adsorption K_1 was evaluated.

The pseudo first- order equation expressed as equation 4.11:

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - \frac{K_1}{2.303} \cdot t \quad 4.11$$

While:

q_e and q_t give the adsorption capacity at time(t) at equilibrium.

K_1 : constant of pseudo first- order adsorption ($\text{L} \cdot \text{min}^{-1}$) [19].

Plotting of $\text{Log}(q_e - q_t)$ versus time (t) was made as a linear graph to obtain the pseudo first- order rate constant K_1 as shown in Figure 4.16.

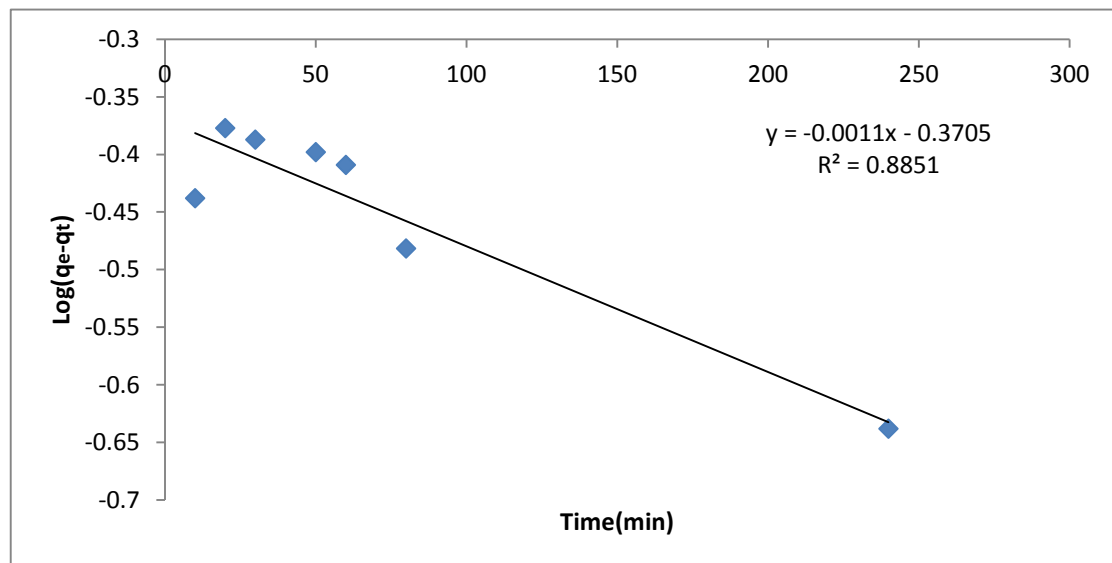


Figure 4.16: Pseudo first- order adsorption kinetics of Cr(VI) onto (MSiTh). (Temp.= 25°C, pH= 6, solution volume = 10 mL, adsorbent dose= 0.04 g)

From figure 4.16, the R^2 value shows that the adsorption process of Cr(VI) onto MSiTh does not obey the pseudo first- order kinetics, and the pseudo first- order model is not appropriate for the adsorption.

The Lagergren pseudo first- order rate constant (K_1) and (q_e) values are represented in Table 4.4.

Table 4.4: Pseudo first- order parameters for Cr(VI) adsorption onto MSiTh at 25°C.

Adsorbent	$q_e(\text{exp})$ (mg/g)	pseudo first- order		
		$K_1 \text{ min}^{-1}$	$q_e \text{ (calculated) (mg/g)}$	R^2
MSiTh	2.24	20.7×10^{-3}	0.426	0.8851

Pseudo second - order adsorption model for Cr(VI) adsorption onto MSiTh was applied and the rate constant for the adsorption K_2 was evaluated as shown in Figure 4.17 .

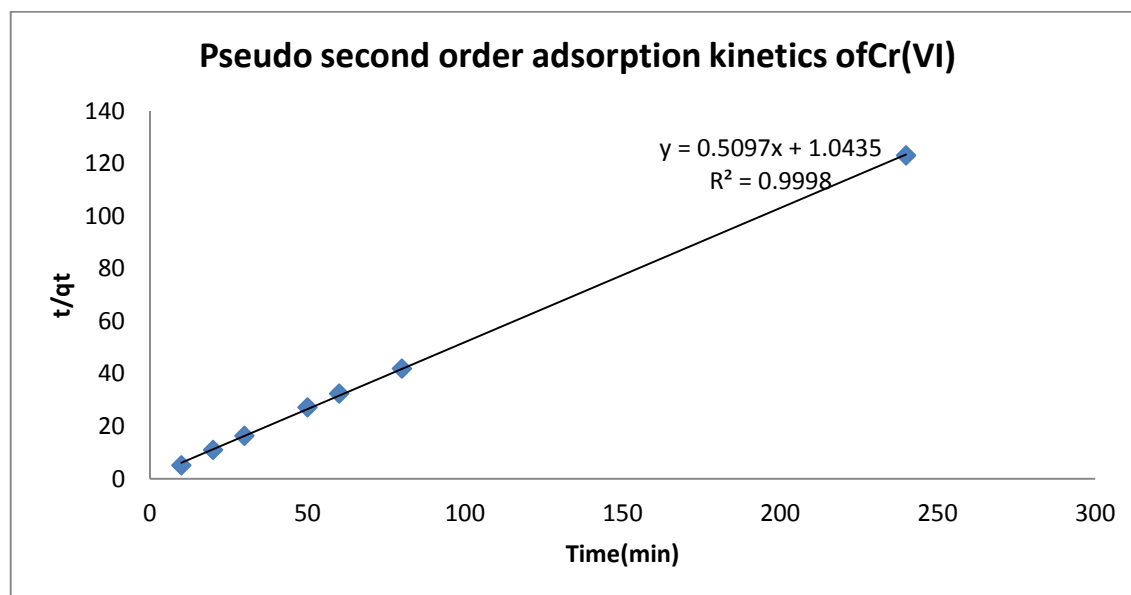


Figure 4.17: Pseudo model for second order adsorption kinetics of Cr(VI) onto (MSiTh). (Temp.= 25°C, pH= 6, sol. Volume= 50 mL, adsorbent dose= 0.04 g)

The results obtained shows that the value of linear regression coefficient R^2 is 0.9998, the values of q_e experimental, K_2 , R^2 and q_e calculated were listed in Table 4.5.

Table 4.5: Pseudo second - order parameters for Cr(VI) adsorption onto MSiTh at 25°C.

Adsorbent	q_e (exp) (mg/g)	pseudo second – order		
		$K_2 \text{ min}^{-1}$	q_e (calculated)(mg/g)	R^2
MSiTh	2.24	249.4×10^{-3}	1.96	0.9998

The results shows that the Pseudo second – order kinetic model perfect fit with experimental data and the value of $R^2 = 0.9998$, by comparing (q_e) experimental and (q_e) calculated values from Table 4.5, there is agreement between experimental value and calculated value for pseudo second order model, and K_2 value greater than K_1 value, so the pseudo second order model is favorable model for Cr(VI) adsorption onto MSiTh.

4.6 Reusability of MSiTh

Reusability of MSiTh compound was made by filtration, and washing with portions of 6N HCL at 25°C, then the adsorbent (MSiTh compound) washed in deionized water for three to four times, and allowed to dry at room temperature for two to three days.

The reusability of MSiTh compound was made for two times, and the adsorption capability of regenerated MSiTh was tested under the same conditions in the first use.

0.04g of recovered MSiTh was added to 10 mL of 10 ppm Cr(VI) solution at pH= 6. The results obtained were compared with the first experiment before recovering.

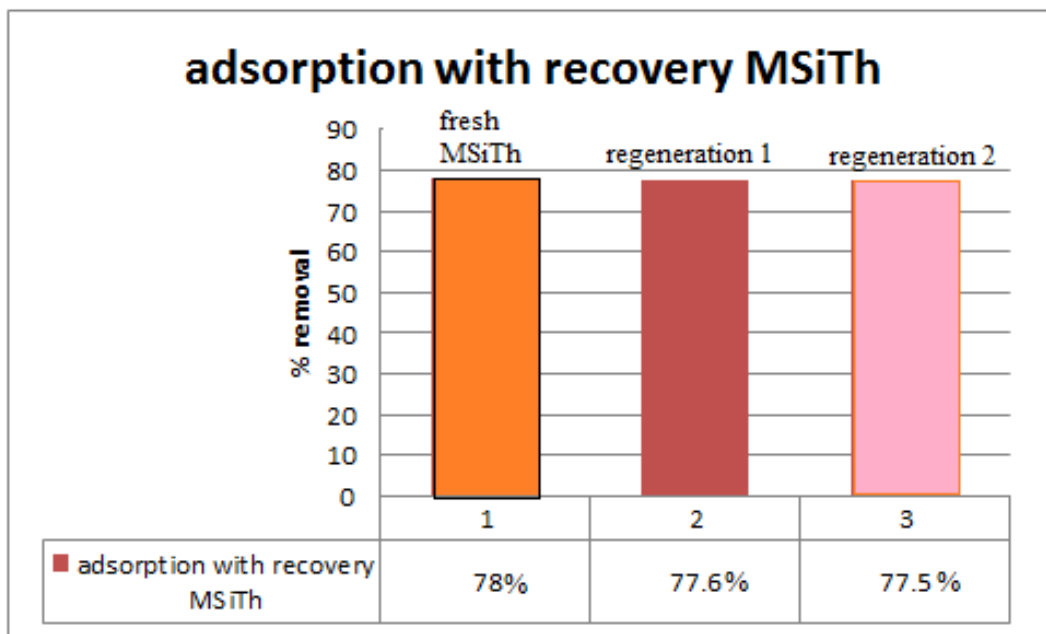


Figure 4.18: Percentage of Cr(VI) removal by the regenerated adsorbent compared with a fresh one at (Temp.= 25°C, pH= 6, adsorbent dose= 0.04 g, sol. Volume = 10 mL, contact time = 30 min)

This compound has been able to remove Cr(VI) several times with high efficiency.

Conclusions:

- The adsorption of Cr(VI) onto MSiTh was successfully for removing Cr(VI) from the aqueous solution .
- The results shows that MSiTh compound was able to remove Cr(VI) within 20 min at pH around 6, temperature 25°C , with adsorbent dose =0.04g in 10ml Cr(VI) solution and the initial concentration 10ppm, the removal efficiency of Cr(VI) was 78%, also this efficiency was achieved at 24 hour with the same conditions.
- The adsorption isotherm of Cr(VI) onto MSiTh was studied and the values of Langmuir maximum adsorption capacity $Q_m=10.672\text{mg/g}$, and $R_L =0.2375$, indicate that the adsorption of Cr(VI) onto MSiTh is favorable . Also Freundlich model parameters value $1/n$ and n , showing that the adsorption of Cr(VI) onto MSiTh is favorable .
- Lagergren pseudo second order model has been applied to obtain the amount of Cr(VI) adsorbed per unit mass of MSiTh, the $q_e(\text{cal})$ was found in agreement with the experimental value $q_e(\text{exp})$, which explain the exchange between adsorbent and adsorbate .
- The results obtained with negative values for ΔG° , explain that the adsorption is favorable and spontaneous at these temperatures, also the negative value for ΔH° explain that this adsorption is an exothermic and it favorable at low temperature.
- The small positive value of ΔS° indicates there are some structural changes take place on the adsorbent and entropy increases through the adsorption process.

- MSiTh silica gel compound has been used and has high efficiency to remove Cr(VI) from water, this efficiency is lower than other adsorbents that were used in other researches for removal of Cr(VI) at high pH, but it can be more effective at lower pH near water pH
- at 25°C .

Suggestions for the future

- more studies is needed to explain the adsorption of toxic heavy metals onto silica gel compounds
- Further studies of antimicrobial activity of this silica gel compound (MSiTh) is needed

Recommendations:

- Using this new silica gel compound (MSiTh) with its activity can be used in the adsorption process for heavy metals exist in the industrial wastewater at the end of pipe for most of factories that produce heavy metal ions in the wastewater before disposed in wastewater stream .
- More studies about the economic feasibility for using silica gel compounds in removing toxic heavy metals from wastewater.

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جامعة النجاح الوطنية

كلية الدراسات العليا

استخدام الثيوفين المثبت على السيلكا في استخلاص الكروم السداسي من المياه

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اشراف

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د . احمد ابو عبيد

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في العلوم البيئية من
كلية الدراسات العليا في جامعة النجاح الوطنية، نابلس، فلسطين

2016

ب

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الملخص

تلوث المياه مشكلة بيئية رئيسية وخاصة التي تنتج من الصناعات المختلفة، والتي تنتج كميات كبيرة من المعادن الثقيلة السامة للتربة ومياه الصرف الصحي، هذه المعادن الثقيلة تؤثر على صحة الإنسان. والهدف من هذه الدراسة هو التركيز على احد المعادن الثقيلة السامة وهو الكروم السداسي وازالته من المياه وخاصة التي تنتج عن المصانع باستخدام تقنية الامتزاز على مركب جديد وهو الثيوفين المركب من السيلكا التي تحتوي على الكبريت المانح (MSiTh).

لقد تم تحضير مركب الثيوفين المركب من السيلكا التي تحتوي على الكبريت المانح (MSiTh)، واجراء فحص التحليل الوزني FTIR وتمت دراسة ارتباط مجموعة الثيوفين بالسيلكا باستخدام جهاز الوزن الحراري لهذا المركب وفحص قطر الحبيبات.

في هذا البحث تم فحص امتزاز الكروم السداسي على مركب (MSiTh) على نطاق واسع مع تاثير كل من درجة الحموضة ، درجة الحرارة، كمية المادة المازة، التركيز البدائي للكروم وفترة الاتصال بين المادة المازة والمادة الممتزة على عملية الامتزاز.

اشارت النتائج الى ان فعالية الازالة للكروم السداسي وصلت الى اكثر من 75% بعد 24 ساعة على درجة الحموضة تقريبا 6 ودرجة حرارة الغرفة 25°س، وكانت كمية المادة المازة تساوي 0.04غم والحجم يساوي 10 مل وتركيز المحلول يساوي 10ppm.

كانت الظروف المثلى لعملية الامتزاز للكروم السداسي عند درجة حموضة اقل من 7 على درجة حرارة الغرفة (25°س) وبعد 20 دقيقة، بعد حساب كمية الكروم السداسي التي تم امتزازها باستخدام نموذج Largergren للتفاعلات من الدرجة الثانية، من خلال Qexp التجريبية التي

ج

قيمتها = 2.24 mg/g , وقيمة Qcal المحسوبة = 1.96 mg/g , تبين وجود تقارب بين القيمتين مما يدل على عملية امتزاز محبذة , وان هناك تبادل الكتروني بين المادة المازة والممتزة .
تم حساب السعة القصوى للامتزاز Q_m حسب نموذج Langmuir وكانت القيمة ($Q_m=10.672\text{mg/g}$) على درجة حرارة 25°س ودرجة حموضة تساوي 6 وكتلة المادة المازة = 0.04 غرام , حيث كانت قيمة $R_L=0.2375$, هذه النتائج تشير الى ان عملية الامتزاز للكروم السداسي على مركب الثيوفين المركب من السيلكا التي تحتوي على الكبريت المانح هي عملية ايجابية وفاعلة .

حسب نموذج Freundlich كانت قيمة ($n=0.56/1$) وقيمة ($n=1.786$) , مما يشير الى ان امتزاز الكروم على هذا المركب محبذ.

اشارت الدراسة حسب قيم ΔG (-1.01443KJ/mol to -0.92983) السالبة الى ان عملية الامتزاز تناسبت مع درجات الحرارة في التجربة كما ان قيمة $\Delta H^\circ = -1.62355\text{ KJ/mol}$, تبين ان عملية الامتزاز طاردة للحرارة وانها محبذة على درجة حرارة الغرفة 25°س, ان قيمة ΔS° هي ($\Delta S^\circ=2.115\text{KJ/mol}$) تشير الى حالة من الفوضى على سطح المازة مما يؤدي الى زيادة في عملية الامتزاز .